

CHAPTER-

Five

In this chapter, the method for the synthesis of PBNPs mediated through PEI is further explored for the synthesis of nanocrystalline mixed metal analogues especially copper-iron hexacyanoferrates and nickel-iron hexacyanoferrates. As synthesized mixed metal hexacyanoferrates was used for the electrochemical detection of dopamine and hydrazine. As mixed metal analogues also shows the peroxidase mimetic behaviour so the both the nanoparticles were also used for detection of H₂O₂ as peroxidase mimetic activity.

*Polyethylenimine mediated synthesis
of copper-Iron and nickel-iron
hexacyanoferrate nanoparticles and
their analytical applications*

1 PEI mediated synthesis of Cu-Fe HCFs and Ni-Fe HCFs nanoparticles and their analytical applications

1.1 Introduction

Transition metal hexacyanoferrates are the important class of coordination compounds. Among these, Prussian blue and its metal analogues have shown significant attention to the scientific community due to its unique physical, optical, magnetic, ion sensing, chemical and electrochemical properties. Mixed metal hexacyanoferrates have shown different properties depending upon the combination of transition metal ions like Ni-Fe, Co-Fe, Cu-Fe, Cu-Co, Ni-Pd, Mn-Fe, or Ni-Co [(Kulesza *et al.* 1999; Pandey and Pandey 2013d; Safavi *et al.* 2011; Yu *et al.* 2013)]. As far as electrochemical properties of mixed metal hexacyanoferrates are concerned, the mixed metal hexacyanoferrate shows unique and different electrochemical behaviour as a function of transition metal ions present into the crystal lattice of Prussian blue. The presence of other transition metal ions altered the properties and have been exploited in the electrochemical energy storage, electrochemical sensing of hydrazine, dopamine, and NADH and many more [(Cai *et al.* 1995a, b; Ghasemi *et al.* 2015; Pandey and Pandey 2013d; Salimi and Abdi 2004)].

Although many reports on the synthesis of Prussian are available in literature however the controlled nucleation of these materials have been one of the challenging tasks. In addition to that uncontrolled nucleation allows the formation of metal hexacyanoferrate which are not processable for practical applications. Normally the use of double precursor during Prussian blue formation leads uncontrolled nucleation whereas the use of singly precursor allow control over the nucleation process and may leads the formation of processable metal hexacyanoferrate [(Ding *et al.* 2009; Jia and Sun 2007; Ming *et al.* 2012; Pandey and Panday 2016b; Pandey and Pandey 2013c, 2014a; Wu *et al.* 2006)]. Recently, we have demonstrated controlled conversion of Prussian blue and it mixed metal analogues involving the participation of organic reducing agent that precisely control the nucleation process and lead the formation of stabilized Prussian blue

nanoparticles [(Pandey and Panday 2016a; Pandey and Panday 2016b; Pandey and Pandey 2013a, b, c, d, 2014a)]. The use of 3-aminopropyltrimethoxysilane (3-APTMS) and cyclohexanone allow controlled formation of Prussian blue nanoparticles (PBNPs) having electrochemistry with electron transfer rate constant to the order of 32.1 s^{-1} [(Pandey and Pandey 2013a, c)]. Similar process allows controlled synthesis of super peroxidase mimetic mixed metal hexacyanoferrate [(Pandey and Pandey 2013a, d)]. The use 3-APTMS introduced inherent disadvantage of alkoxide functionality that ultimately undergo the formation of –Si-O-Si- linkage through auto-hydrolysis and condensation of 3-APTMS as a function of time. To overcome this problem, another organic reagent tetrahydrofuran-hydroperoxide (THF-HP) justified the synthesis of stable, processable PBNPs [(Pandey and Pandey 2014a)]. THF-HP enables the conversion of potassium hexacyanoferrate into PBNPs at room temperature in 12 hours. THF-HP is also capable of reducing noble metal cations into respective nanoparticles in the presence of 3-APTMS [(Pandey and Pandey 2014b; Pandey *et al.* 2014b)] whereas $\text{K}_3[\text{Fe}(\text{CN})_6]$ undergo controlled conversion into PBNPs even in absence of 3-APTMS. However, poor commercial availability of THF-HP directed us to investigate whether such conversion may be accompanied with easily available organic reducing agents like tetrahydrofuran and hydrogen peroxide [(Pandey and Panday 2016b)] and indeed interesting finding on the synthesis of Prussian blue and its Ni-FeHCF has been recorded [(Pandey and Panday 2016b)]. It was found that $\text{K}_3[\text{Fe}(\text{CN})_6]$ undergo controlled conversion in to well disperse PBNPs in the presence of tetrahydrofuran (THF), hydrogen peroxide (H_2O_2) at $60 \text{ }^\circ\text{C}$ in 20 minutes. The same method efficiently enabled the synthesis of Ni-Fe hexacyanoferrate [(Pandey and Panday 2016a)]. Although such process allowed several advantages however, suffered from the following problems: (i) poor crystallinity of as made Prussian blue and its mixed metal analogues, (ii) limited to Ni-Fe hexacyanoferrate formation and was unable to precisely control the formation of Cu-Fe HCFs. These limitations may ultimately affect the electrocatalytic and versatile approach for making Prussian blue analogues. Accordingly, there is a need of another organic reducing agent that not

only precisely allow controlled formation of mixed metal analogues of all transition metal combination along with better crystallinity of as made nanomaterial which has been attempted in this investigation. The use of PEI has been demonstrated for the reduction of noble metal ions like gold into gold nanoparticles [(Mohammed *et al.* 2013; Sun *et al.* 2004, 2006; Wen *et al.* 2013)]. Recently, we have demonstrated that polyethylenimine (PEI) enable controlled and rapid synthesis of gold nanoparticles in the presence of formaldehyde [(Pandey *et al.* 2016)]. Accordingly, the use of PEI for controlled conversion of Prussian blue and its mixed metal analogue has been attempted. Indeed interesting finding on controlled synthesis of Cu-Fe HCFs and Ni-Fe HCFs has been recorded. The use of cationic polymer also allowed enhancing the crystalline behaviour of mixed metal hexacyanoferrate with good processability for use in both homogeneous and heterogeneous electrocatalysis. The findings based on; (i) PEI mediated synthesis of Cu-Fe HCFs and Ni-Fe HCFs nanoparticles from single precursor, (ii) Structural and elemental characterization of as synthesized mixed metal nanoparticles, (iii) electrochemical characterization of as synthesized mixed metal nanoparticles, (iv) homogeneous catalysis of hydrogen peroxide by as synthesized MHCs nanoparticles, (v) usability of these material in the electrocatalytic oxidation of dopamine, hydrazine and electrocatalytic reduction of H₂O₂ sensing; are reported in this chapter.

1.2 Experimental

1.2.1 Material and Methods

Potassium ferricyanide [K₃[Fe(CN)₆]], Potassium ferrocyanide [K₄[Fe(CN)₆], hydrogen peroxide (H₂O₂), nickel sulphate (NiSO₄) and copper sulphate (CuSO₄) were purchased from Merck, India. Polyethylenimine (PEI) (Mol wt 60,000), Graphite powder (1-2 μm), nujol oil (density 0.838 g ml⁻¹), o-dianisidine, hydrazine hydrate and dopamine were procured from Sigma Aldrich Chemical Co. India. All reagents used were of analytical grade and used without further purification. Double distilled water was used in all the experiments performed (Alga water purification system).

1.2.2 Synthesis of Cu-Fe hexacyanoferrates and Cu-hexacyanoferrates

Synthesis of Cu-Fe HCFs involves mixing of single precursor potassium ferricyanide, PEI, CuSO_4 and HCl in an optimum concentration and allowing the reaction to proceed at 60 °C for 3 hours in a vacuum oven. In a typical procedure, 70 μl aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (50 mM) and 20 μl of PEI (0.1 g/ml) are mixed together under stirring condition over cyclomixture followed by addition of 5 μl hydrochloric acid solution (6.5 M). To this add 70 μl of aqueous solution of CuSO_4 solution (0.05 M) mixed vigorously over cyclomixture and keep it at 60 °C for 3 hours in an oven. A yellow colour solution was turned into blue colour indicating the synthesis of Cu-Fe HCFs. Cu-Fe HCFs was made through the varying the molar ratio of Cu:Fe and observed in the electrochemical behaviour of these materials. Copper hexacyanoferrate (CuHCFs) was synthesized in a single step by mixing 100 μl aqueous solution of CuSO_4 (0.01 M) with 100 μl aqueous solution of potassium ferricyanide (0.01 M) containing 0.01 M KCl under stirring. The use of potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) in place $\text{K}_3[\text{Fe}(\text{CN})_6]$ under similar condition also allowed the formation of similar nanomaterial.

1.2.3 Synthesis of Ni-Fe hexacyanoferrates and Ni-hexacyanoferrates

Synthesis of Ni-Fe HCFs involves the mixing of optimum concentration of single precursor $\text{K}_3[\text{Fe}(\text{CN})_6]$, PEI, NiSO_4 and HCl and allowed the reaction mixture at 60 °C for 3 hours in oven. In a typical procedure, 70 μl aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 20 μl aqueous solution of PEI (0.1 mg/ml) was mixed over cyclomixture followed by addition of 5 μl of hydrochloric acid (6.5 M). To this solution, add 25 μl of aqueous solution of NiSO_4 was mixed and allowed to reaction happen at 60 °C for 3 hours. As a resultant of this reaction, yellow colour solution turned into blue colour indicating the synthesis of Ni-Fe hexacyanoferrate. Ni-Fe hexacyanoferrates was also synthesized by varying the molar ratio of Ni:Fe and studied the effect of the same through cyclic voltammetry. Nickel hexacyanoferrate (NiHCFs) was synthesized in a single step by mixing 100 μl aqueous solution of nickel sulphate (0.01 M) with 100 μl aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.01 M) containing 0.01 M KCl under stirring.

The use of potassium ferrocyanide ($K_4[Fe(CN)_6]$) in place $K_3[Fe(CN)_6]$ under similar condition also allowed the formation of similar nanomaterial.

1.2.4 Structural characterization of mixed metal hexacyanoferrates

Formation of mixed metal hexacyanoferrates was confirmed by UV-Vis spectrophotometer, X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) coupled with energy dispersive spectroscopy analysis (EDS). Hitachi U-2900 spectrophotometer was used for all UV-Vis spectroscopy measurements. XRD analysis was done in thin film of mixed metal analogues which was prepared by dip coating of the respective solution onto the transparent glass slides and dried at 60 °C in a vacuum oven. XRD analysis was done on a Rigaku miniflex II diffractometer using nickel filtered $CuK\alpha$ ($\lambda = 1.506 \text{ \AA}$) radiation. The crystallite size was calculated using Debye–Scherrer formula [(Zheng *et al.* 2007)]. Dilute sample was dip coated onto the Indium Tin oxide coated glass which was dried at room temperature and used for the SEM analysis. TEM analysis was performed using a TECHNAI 200 Kv TEM (Fei, Electron Optics). A dilute solution of sample was dip casted and dried at room temperature on the carbon coated copper grid (Mesh size-400) obtained from Electron Microscopy Sciences, USA. The concentration of copper and nickel in the respective solution was determined by the Atomic Absorption Spectroscopy by Shimadzu Corporation.

1.2.5 Peroxidase mimetic activity of mixed metal hexacyanoferrates

Peroxidase mimetic activity of as synthesized mixed metal analogues was performed as described earlier [(Pandey and Panday 2016b)]. In a typical procedure, peroxidase mimetic activity was performed spectrophotometrically using Hitachi spectrophotometer by measuring the formation of the oxidized product of o-dianisidine (brown in colour) at 430 nm ($\epsilon = 11.3 \text{ mM}^{-1} \text{ cm}^{-2}$) which was formed in the presence of reduced form of o-dianisidine, hydrogen peroxide and mixed metal analogues which acts as a mimetic catalyst. Each reaction was performed in 2 ml, 0.1 M phosphate buffer (pH=7.0) containing $15 \mu\text{l ml}^{-1}$ mixed

metal analogues and 50 μM o-dianisidine and varying concentration of hydrogen peroxide (0 – 25 mM) at room temperature. The variation in the absorbance as a function of time was monitored at 430 nm ($\epsilon = 11.3 \text{ mM}^{-1} \text{ cm}^{-2}$) and kinetic parameters were calculated as described elsewhere [(Pandey and Panday 2016b)].

1.2.6 Fabrication of modified graphite paste electrode

The electrochemical measurements were performed on mixed metal analogues modified graphite paste electrode. The electrode body was procured from Bioanalytical Systems, West Lafayette, In (MF 2010). The well of the electrode body was filled with active paste of composition in (w/w): Cu-Fe HCFs or Ni-Fe HCFs 2.5%, graphite powder (1-2 μm) 67.5% and nujol oil 30%. The mixture was mixed thoroughly in a blender and filled the electrode body and finally electrode surface was manually smoothed on a clean butter paper.

1.2.7 Electrochemical Measurements

All the electrochemical measurements were performed in a three electrode assembly system with a working volume of 3 ml solution on a workstation Model CHI660B, CH instruments Inc, TX. Modified graphite paste electrode, Ag|AgCl electrode (Orion, Beverly, MA, USA) and platinum plate electrode were functioned as working, reference and counter electrode respectively. Cyclic voltammetry was performed at various scan rates from 0.01 V s^{-1} to 0.3 V s^{-1} to analyze the scan rates (v) dependence on peak current density (j) on the mixed metal analogues modified graphite paste electrode. All potential given throughout text are relative to the Ag|AgCl reference electrode. Electrochemical oxidation of dopamine, H_2O_2 and hydrazine was performed on 0.1 M phosphate buffer containing 0.5 M KCl and 0.1 M NaNO_3 solution respectively. Effect of pH on the electrochemical behaviour and the stability was performed by cyclic voltammetry in 0.1 M phthalate buffer (pH= 4), 0.1 M phosphate buffer (pH=7.0) and 0.1 M borate buffer (pH=9.0) containing 0.5 M KCl.

1.3 Results

1.3.1 PEI mediated synthesis of nanocrystalline mixed metal hexacyanoferrates

The method for PEI mediated synthesis of PBNPs has been described in chapter 4 and the same method for the synthesis of Cu-Fe HCFs and Ni-Fe HCFs has been successfully explored further. The active role of each component has been studied through UV-Vis spectroscopy and visual photography of respective solutions. Figure.5.1. shows the importance of each component during the conversion of $K_3[Fe(CN)_6]$ into mixed metal analogues depending on the respective transition metal.

The possibility of utilizing $K_4[Fe(CN)_6]$ in place of $K_3[Fe(CN)_6]$ was also explored by synthesizing Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) under identical condition of 60 °C for 3 hours. The synthesis of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) made through $K_4[Fe(CN)_6]$ was confirmed by UV-Vis spectroscopy and cyclic voltammetry on respective graphite paste modified electrode in 0.1 M KNO_3 and compared with the Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) made through $K_3[Fe(CN)_6]$ and the result is shown in Figure.5.2. and Figure.5.3. which confirms that the Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) synthesized by $K_3[Fe(CN)_6]$ was better.

The temperature in the synthesis of mixed metal hexacyanoferrates was also studied by varying the temperature of the synthesis. Synthesis was carried out at room temperature, 60 °C and 90 °C for both Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) using optimized concentration of $K_3[Fe(CN)_6]$, PEI, HCl and other transition metal ions. The confirmation was done by UV-Vis spectroscopy and cyclic voltammetry of as synthesized mixed metal hexacyanoferrates using graphite paste electrode in 0.1 M KNO_3 as shown in Figure.5.4. and Figure.5.5. As can be seen, there is very less amount of synthesis of PB and mixed metal hexacyanoferrates at room temperature even keeping the reaction mixture for 4 days. As we increase the temperature, the reaction is getting faster. The synthesis of mixed metal hexacyanoferrates was done in 2 hours at 90 °C but the electrochemical behaviour was better when the synthesis was done at 60 °C in 3 hours.

It was also intended to study the role of PEI in the present method for the synthesis of mixed metal hexacyanoferrates. Synthesis of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) was performed without involving the PEI at 60 °C in 24 hours. For this, synthesis of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) was done by involving optimized concentration of $K_3[Fe(CN)_6]$, HCl and other transition metal ions and confirmed by UV-Vis spectroscopy and cyclic voltammetry. Figure.5.6. shows the UV-Vis spectroscopy and cyclic voltammetry performed on graphite paste electrode in 0.1 M KNO_3 for as synthesized mixed metal hexacyanoferrates. This justifies that there is less synthesis of mixed metal hexacyanoferrates in case of no PEI even keeping the reaction mixture for 24 hours.

1.3.2 Structural characterization

In the first instance, the formation of nanocrystalline mixed metal hexacyanoferrates was characterized by UV-Vis spectroscopy. Figure.5.1. shows UV-Vis spectroscopy of both the metal hexacyanoferrates as synthesized. Both hexacyanoferrate shows the strong absorption at 680 nm which is the characteristic peak of all the metal hexacyanoferrates. The absorptions at 680 nm can be assigned to the inter-metal charge transfer (CT) band from Fe^{2+} to Fe^{3+} in PBNPs [(Gotoh *et al.* 2007)].

As synthesized mixed metal hexacyanoferrates was further characterised by FT-IR analysis. Figure.5.7. (A) and (B) represents the FT-IR spectra of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively which shows the characteristic peaks available in the mixed metal hexacyanoferrates. Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) was further characterised by XRD analysis. Figure.5.8. shows the XRD diffractogram for the Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) mixed metal analogues respectively. This shows the common and characteristic peaks available in the mixed metal analogues. The crystallite size was calculated by Debye-Scherrer formula as described in the chapter.2 [(Zheng *et al.* 2007)]. The particle size of the mixed metal analogues has been further evaluated by SEM and TEM analysis as shown in Figure.5.9. for the Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively. These figures confirm the nanosized of as synthesized mixed metal

analogues. Energy Dispersive spectroscopy (EDS) was done for the elemental analysis of as synthesized mixed metal analogues. Figure.5.10. shows the EDS spectra of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively. This indicates the presence of the characteristic peaks assigned to the carbon, potassium, iron, and transition metal ions. The percentage atomic contents of these nanoparticles were also shown in the inset to the respective figure.

1.3.3 Electrochemical characterization

As synthesized mixed metal nanoparticles were further characterized by cyclic voltammetry on graphite paste electrode performed in 0.1 M KNO₃ as supporting electrolyte. It was found that the electrochemical behaviour gets affected by the varying concentration of transition metal to the iron present in the mixed metal analogues therefore the effect of transition metal was evaluated by varying concentration of transition metal ions in the respective mixed metal analogues.

1.3.3.1 -Electrochemical behaviour of mixed Cu-Fe hexacyanoferrates and Cu-hexacyanoferrates

The electrochemical behaviour of mixed Cu-Fe HCFs was studied through graphite paste modified electrode in 0.1 M KNO₃ solution and compared to that of PBNPs. The results based on the cyclic voltammetry for PBNPs, mixed Cu-Fe HCFs (different ratio) and Cu-hexacyanoferrates are as shown in Figure.5.11. As can be seen from the figure, there is a gradual change in the electrochemical behaviour of PBNPs modified electrode as a function of copper ion concentration. The result shown in Figure.5.11. (B) to (H) justify the significance of heterotransition metal atom in 3-dimensional network, since there are redox peak at - 0.2 V and 0.9 V vs. Ag|AgCl (characteristic peak of PBNPs modified electrode) and a redox peak at 0.7 V (characteristic peak of CuHCF) [Figure.5.11.(I)] [(Pandey and Pandey 2013b)]. The result shows that the mixed Cu-Fe HCFs which contains molar ratio of Cu to Fe i.e; 1:1 [Figure.5.11. (F)] tends to produce characteristic peak of CuHCFs and also of PBNPs. Figure.5.12. shows cyclic voltammogram of various as synthesized Cu-Fe HCFs in 0.1 M

KNO_3 at various scan rates between 0.01 V s^{-1} to 0.3 V s^{-1} . This shows that peak current increases as increase in the scan rate [Figure.5.13].

1.3.3.2 Electrochemical behaviour of mixed Ni-Fe hexacyanoferrates and Ni-hexacyanoferrates

The electrochemical behaviour of as synthesized Ni-Fe HCFs was studied by cyclic voltammetry (CV). Figure.5.14. shows the cyclic voltammetric behaviour of mixed Ni-Fe HCFs of varying Ni:Fe ratio modified electrode in 0.1 M KNO_3 as a supporting electrolyte. Figure.5.14. (B) to (F) shows the CV of Ni-Fe HCFs with varying molar ratio of Ni:Fe. Figure.5.14. (A) shows the CV of PBNPs made through same protocol as Ni-Fe HCFs. NiHCFs was also used for the comparative purpose to the PBNPs and Ni-Fe HCFs modified graphite paste electrode [Figure.5.14. (G)]. As can be seen from the Figure.5.14.(D) is the best composition of Ni-Fe HCFs since it contains both electrochemical behaviour of PBNPs as well as NiHCFs [(Pandey and Pandey 2013a)]. Figure.5.15. shows cyclic voltammogram of various as synthesized Ni-Fe HCFs in 0.1 M KNO_3 at various scan rates between 0.01 V s^{-1} to 0.3 V s^{-1} . This shows that peak current increases as increase in the scan rate. The plot of scan rate vs. peak current was done for the respective composition of Ni-Fe HCFs and shows that the peak current was increasing as increasing the scan rate for the as modified graphite electrode [Figure.5.16.].

The electrode behaviour of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs was studied by cyclic voltammetry in different pH buffer on graphite paste modified electrode as shown in Figure.5.17.

1.3.4 Peroxidase mimetic activity of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)

As discussed in the previous chapters, mixed metal analogues also shows the peroxidase mimetic behaviour therefore it is intended to analyze the peroxidase mimetic activity of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5). Time scan mode was used for the formation of oxidised product of o-

dianisidine which gives brown colour (absorbance maxima at 430 nm) in the presence of H₂O₂ and mixed metal analogues. The kinetic parameters of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) for the reactions were evaluated by the initial rate method. Figure.5.18. (A) and Figure.5.18. (B) shows the absorbance changes in the varying concentration H₂O₂ and a constant concentration of o-dianisidine. Figure.5.18. (C) and Figure.5.18. (D) shows that as synthesized mixed metal analogues follows the Michaelis-Menton like behaviour. The Michaelis-Menton constant (K_m) for Cu-Fe HCFs and Ni-Fe HCFs was found to be 1.5 and 4.2 mM respectively.

1.3.5 Electrocatalytic analysis of dopamine, hydrazine and H₂O₂ over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode

As synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) was used for the electrocatalytic detection of dopamine, hydrazine and H₂O₂.

1.3.5.1 Electrochemical oxidation of dopamine over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode

The electrochemical oxidation of dopamine was examined over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrode. Figure.5.19. (A) and (B) shows the voltammogram of mixed Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively on modified electrode in 0.1 M phosphate buffer (pH=7.0) containing 0.5 M KCl in the absence and presence of 2 mM and 5 mM dopamine. The electrocatalytic oxidation for dopamine was studied over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) monitored by amperometric analysis as shown in Figure.5.19. (C) and (D) by adding varying concentration of dopamine in phosphate buffer (pH=7.0) at fixed potential of 0.2 V vs. Ag|AgCl. Inset to the Figure.5.19. (C) and (D) shows the calibration curve of amperometric analysis of dopamine sensing for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) graphite paste electrode respectively.

1.3.5.2 Electrochemical oxidation of hydrazine over Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified electrode

The oxidation of hydrazine was performed on Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified graphite paste electrode in 0.1 M KNO₃ solution as an electrolyte. The cyclic voltammogram on Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) in the absence and presence of hydrazine is shown in Figure.5.20. (A) and (B) respectively. As can be seen from the figure, the oxidative current starts increasing at potential of 0.2 V vs. Ag|AgCl reference electrode. The finding was further justified by the experimental observation based on the amperometry. Figure.5.20. (C) and (D) show the typical amperometric response of Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) on successive additions of hydrazine in 0.1 M NaNO₃. Successive addition of hydrazine resulted in a significant increase in the oxidation current. Inset to the Figure.5.20. (C) and (D) show the calibration plot of Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) system respectively. The calibration plot for hydrazine determination is linear in the range of 0.5 μM to 5 mM.

1.3.5.3 Electrochemical reduction of H₂O₂ over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode

The electrocatalytic reduction of H₂O₂ was performed on Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrode in 0.1 M phosphate buffer containing 0.5 M KCl. The cyclic voltammogram on Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) in the absence and presence of H₂O₂ is shown in Figure.5.21. (A) and (B) respectively. The finding was further justified by amperometric analysis. Figure.5.21. (C) and (D) show the typical amperometric response of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) on successive additions of H₂O₂ in 0.1 M phosphate buffer containing 0.5 M KCl. Successive addition of H₂O₂ resulted in a significant increase in reduction current. Inset to the Figure.5.21. (C) and (D) shows the calibration plot of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) system respectively. The calibration plot for H₂O₂ determination is linear in the range of 0.5 μM to 1 mM.

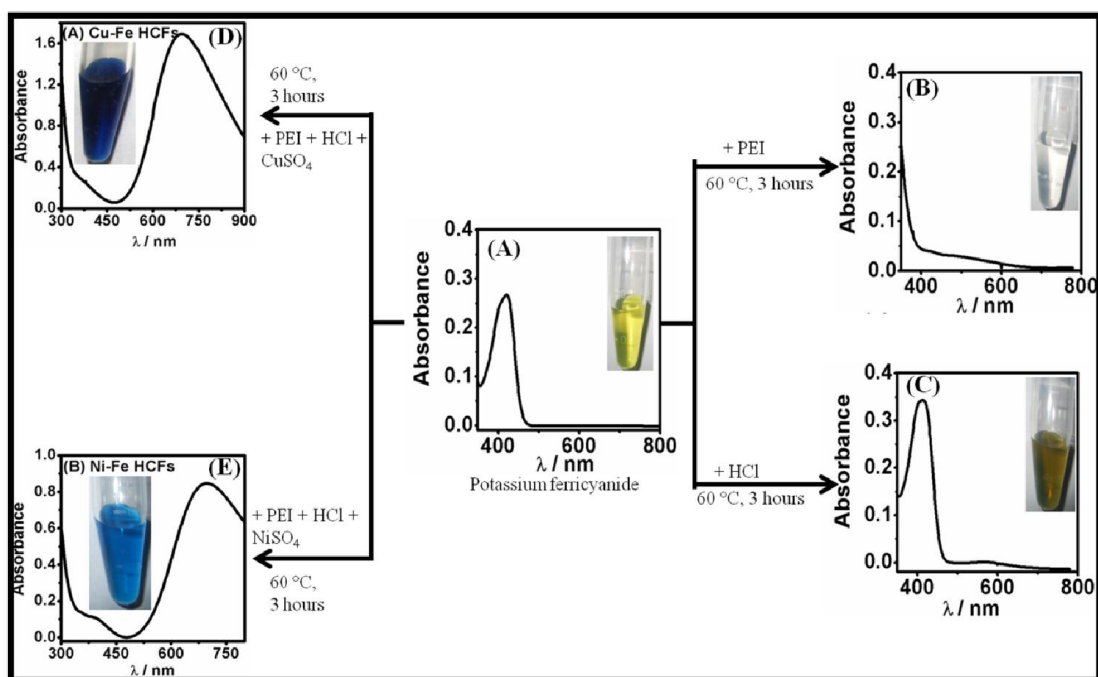


Figure.5.1. Schematic presentation of PEI mediated synthesis of Cu-Fe hexacyanoferrates and Ni-Fe hexacyanoferrates nanoparticles.

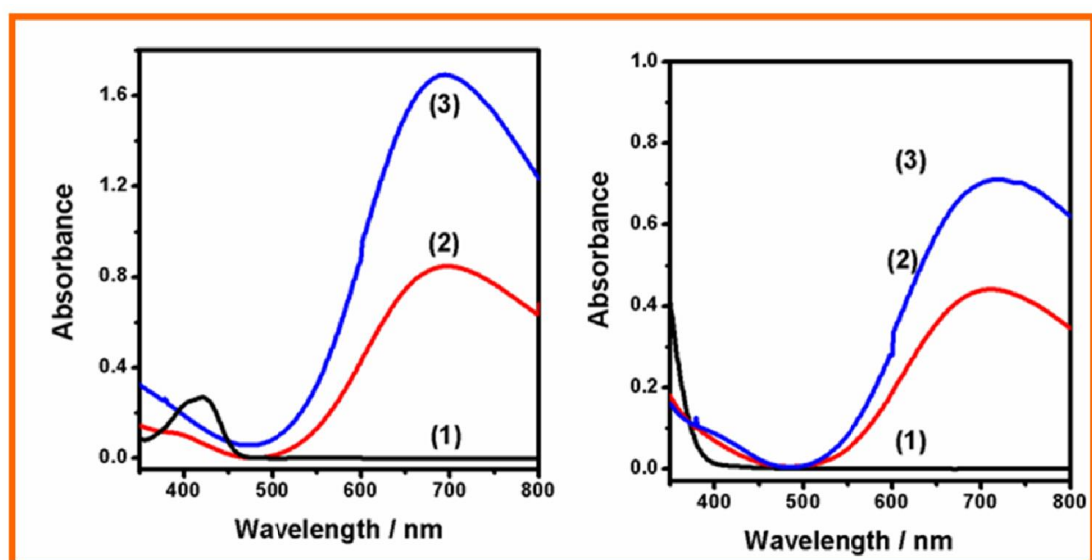


Figure.5. 2. UV-Vis spectroscopy of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) made through K₄[Fe(CN)₆] and K₃[Fe(CN)₆] at 60 °C in 3 hours.

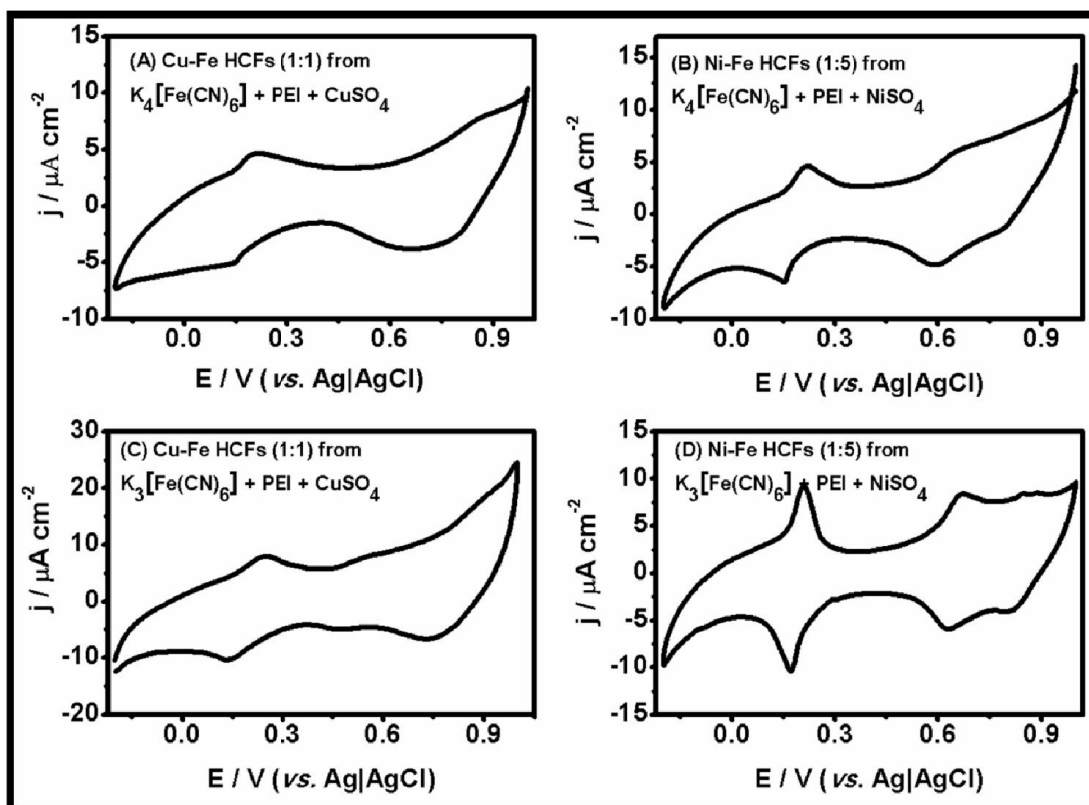


Figure.5. 3. Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) (B) Ni-Fe HCFs (1:5) [made through $\text{K}_4\text{Fe}(\text{CN})_6$ and PEI at 60°C]; and (C) Cu-Fe HCFs (1:1) (D) Ni-Fe HCFs (1:5) [made through $\text{K}_3\text{Fe}(\text{CN})_6$ and PEI at 60°C].

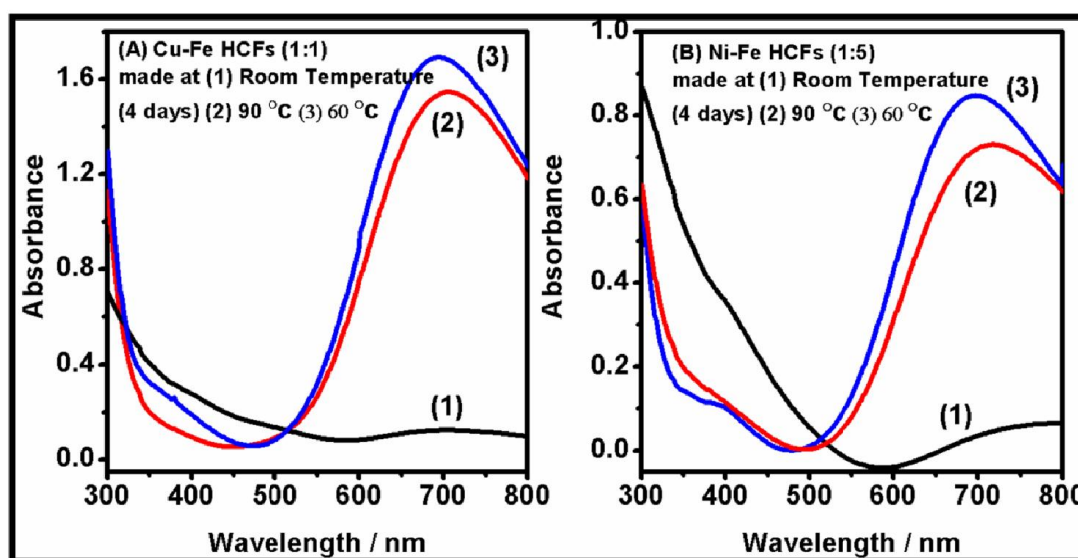


Figure.5. 4. UV-Vis spectroscopy of (A) Cu-Fe HCFs (1:1) (B) Ni-Fe HCFs (1:5) made at (1) room temperature (2) 90°C and (3) 60°C .

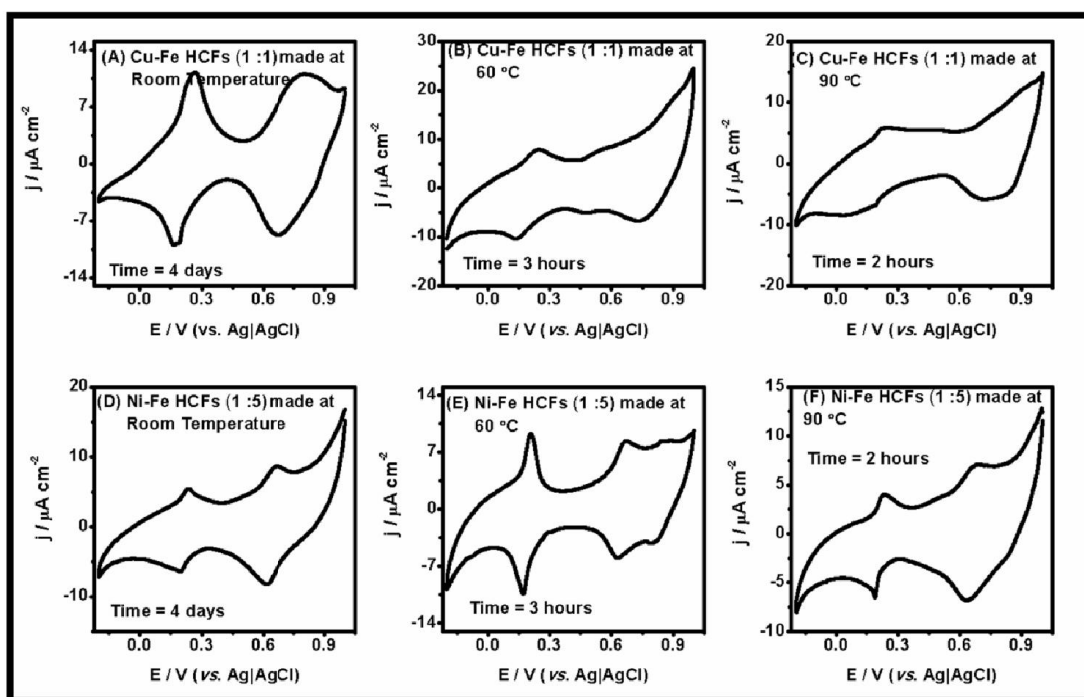


Figure.5. 5. Cyclic voltammetry of (A) to (C) for Cu-Fe HCFs (1:1) and (D) to (F) for Ni-Fe HCFs (1:5) [synthesized at room temperature, 60 °C and 90 °C] in 0.1 M KNO_3 as electrolyte.

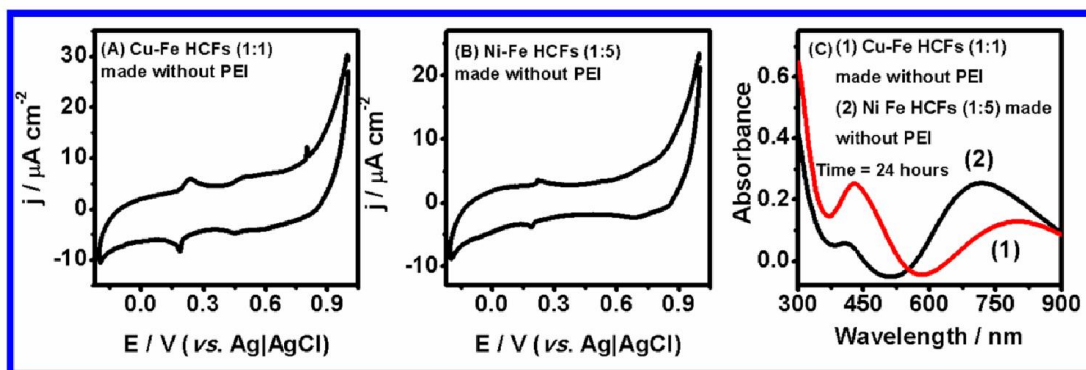


Figure.5. 6. Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) made without PEI at scan rate of 0.01 V s^{-1} in 0.1 M KNO_3 as a electrolyte; UV-Vis spectroscopy (C) of the (1) Ni-Fe HCFs (1:5) and (2) Cu-Fe HCFs (1:1) synthesized without PEI in 24 hours.

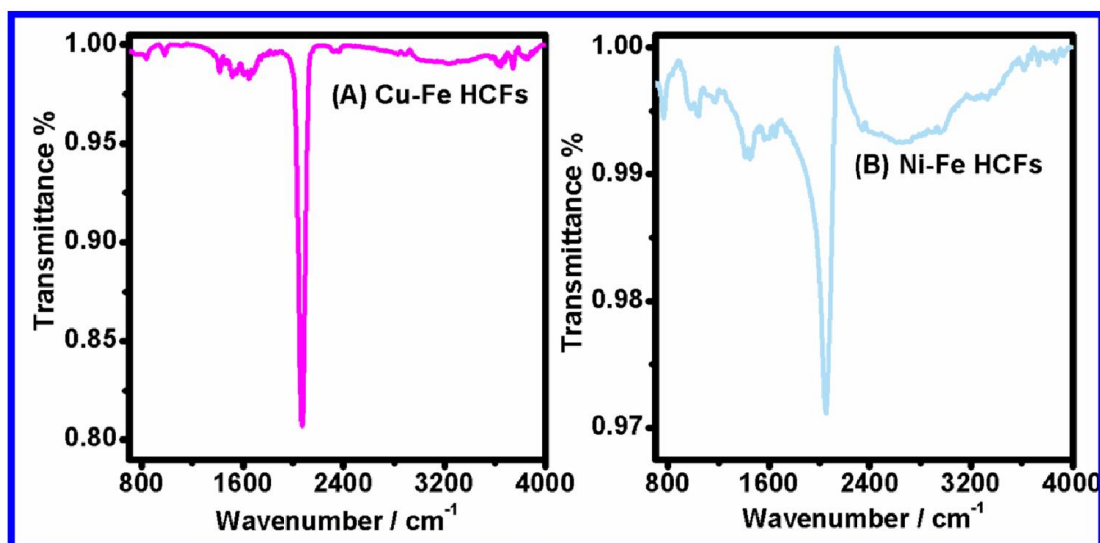


Figure.5. 7. FT-IR spectra of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5).

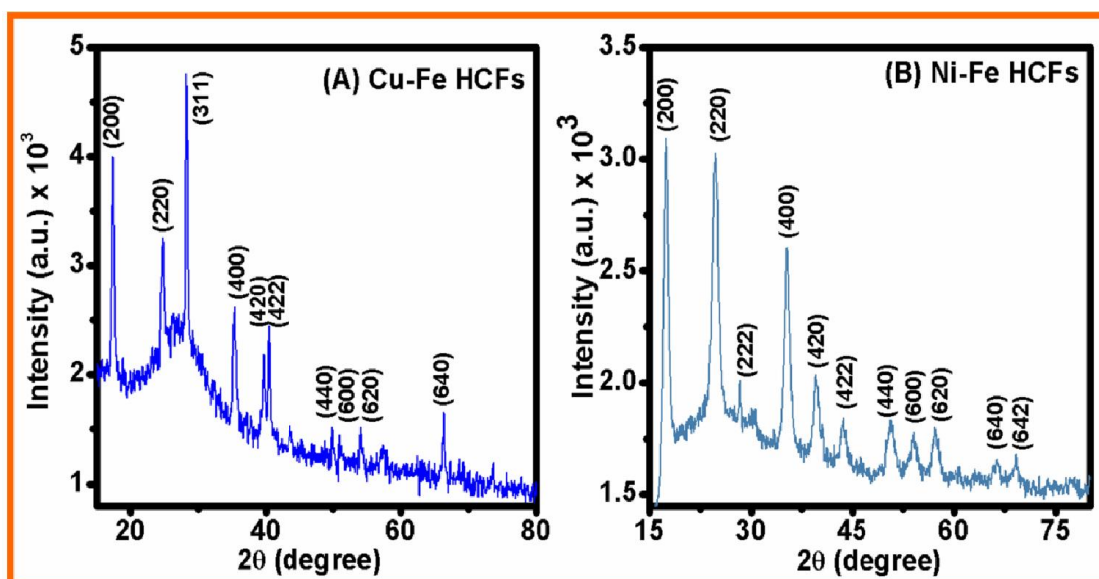


Figure.5. 8. XRD analysis of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5).

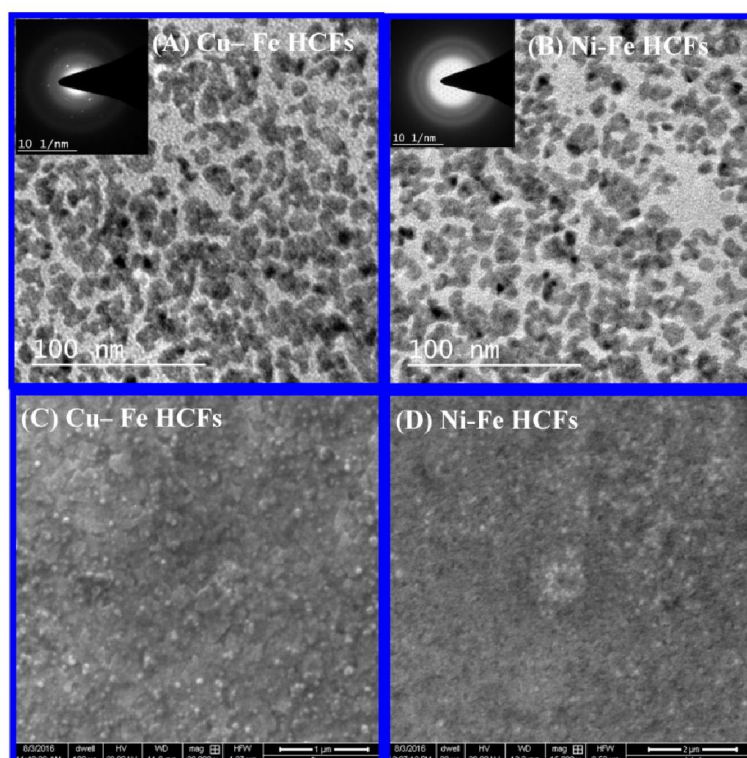


Figure.5. 9. TEM image of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5); inset to the each figure shows the SAED pattern of respective metal hexacyanoferrates; SEM image of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5).

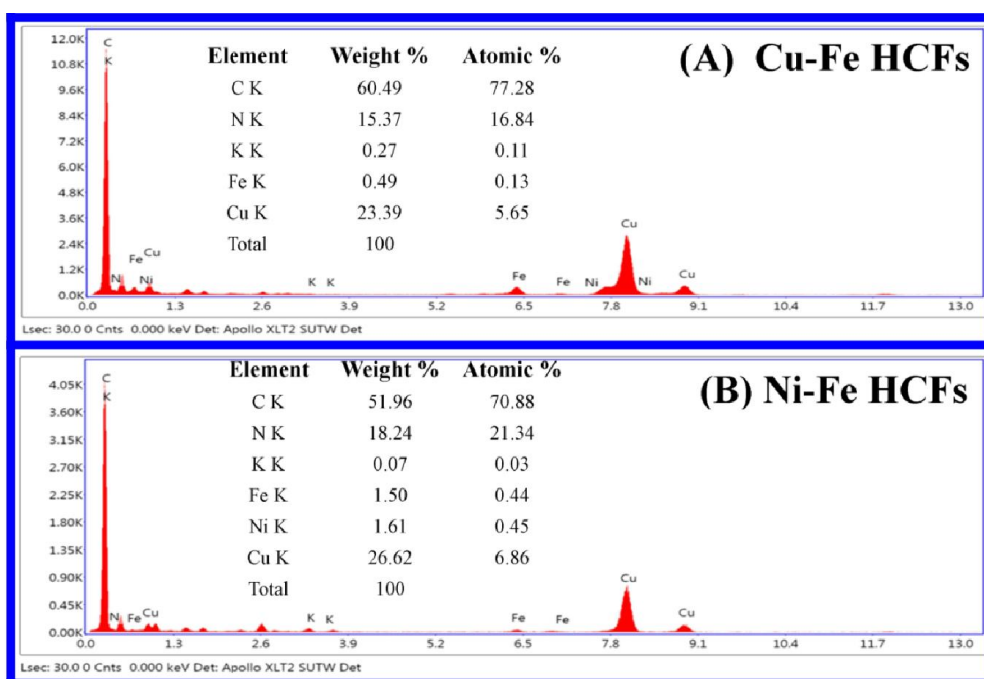


Figure.5. 10. EDS spectra of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5).

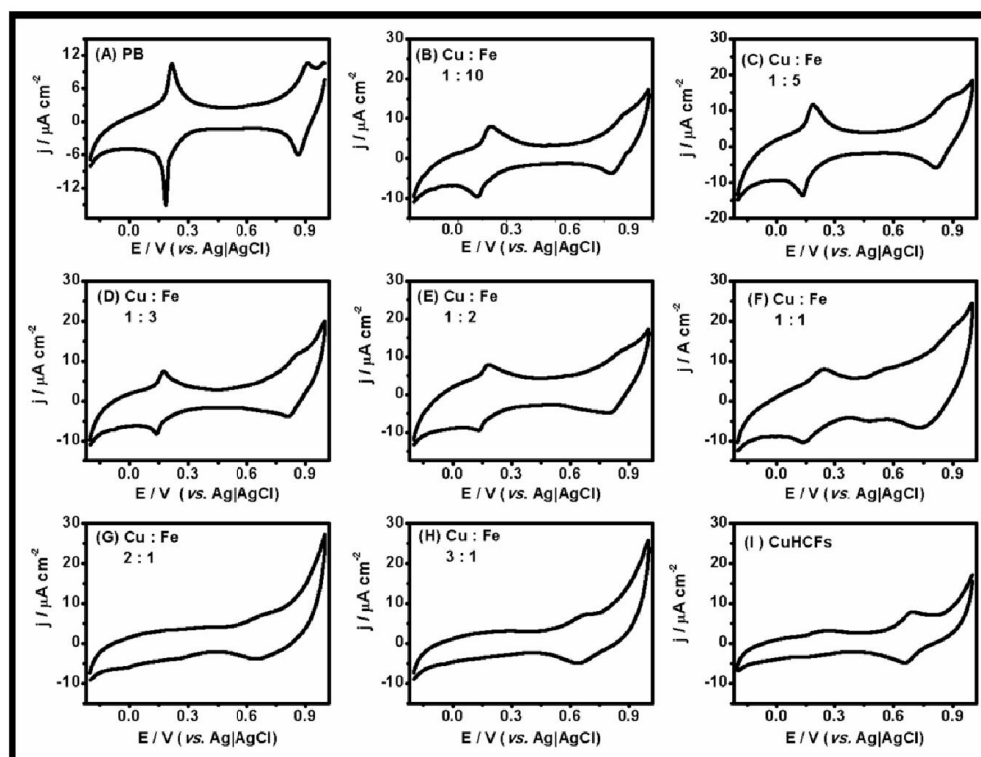


Figure.5. 11. Cyclic voltammometry response of Cu-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01 V s^{-1} made at different Cu:Fe molar ratio [A] PBNPs; [B] Cu:Fe (1:10); [C] Cu:Fe (1:5); [D] Cu:Fe (1:3); [E] Cu:Fe (1:2); [F] Cu:Fe (1:1); [G] Cu:Fe (2:1); [H] Cu:Fe (3:1); and [I] CuHCFs

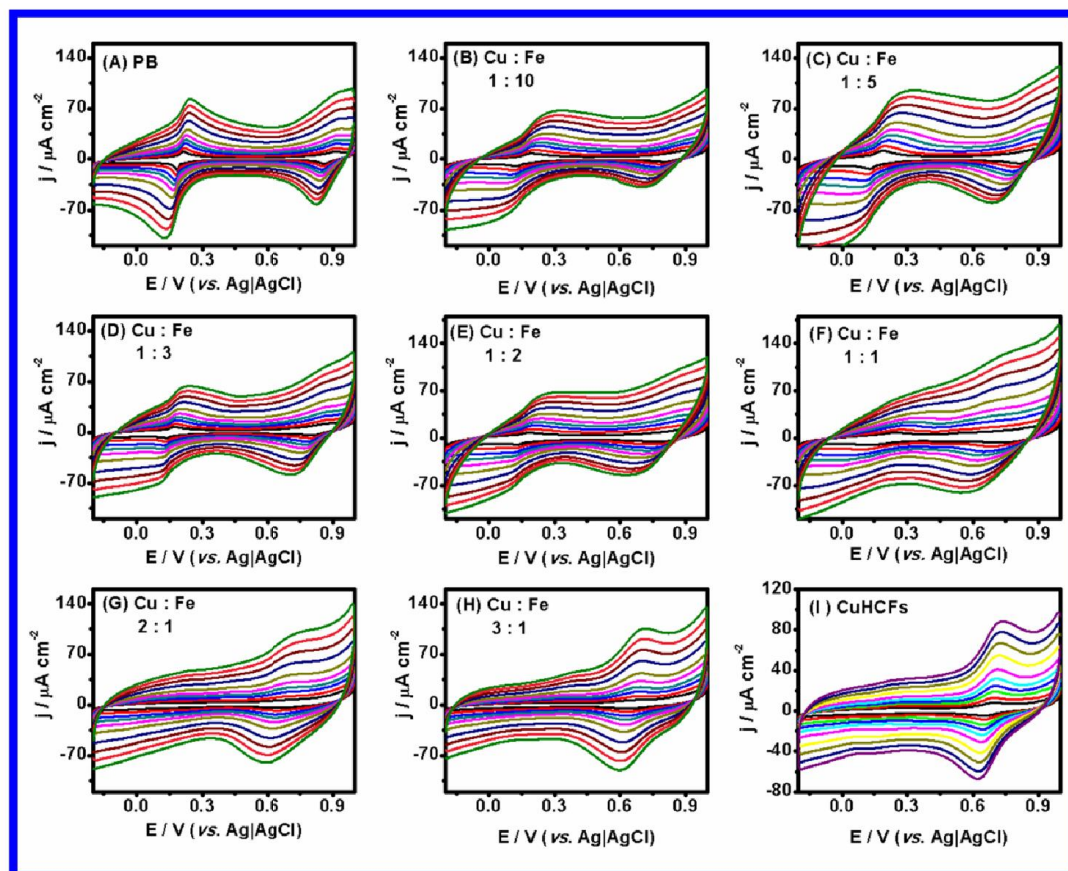


Figure.5. 12. Cyclic voltammety response of Cu-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01, 0.02, 0.035, 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.30 V s^{-1} made at different Cu:Fe molar ratio [A] PBNPs; [B] Cu:Fe (1:10); [C] Cu:Fe (1:5); [D] Cu:Fe (1:3); [E] Cu:Fe (1:2); [F] Cu:Fe (1:1); [G] Cu:Fe (2:1); [H] Cu:Fe (3:1) and [I] CuHCFs.

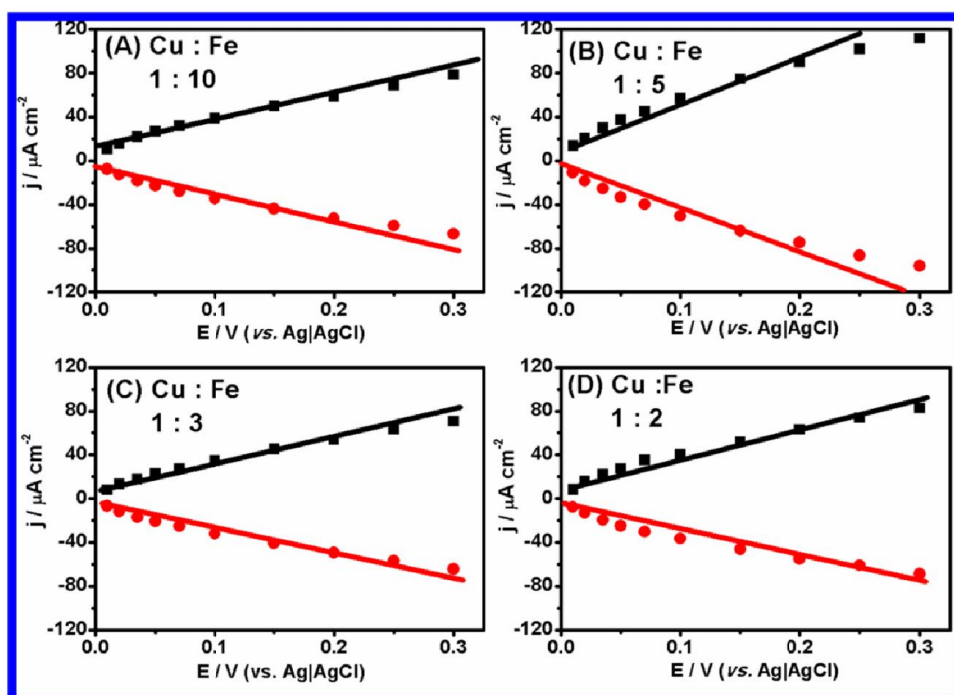


Figure.5. 13. The plots of peak current density vs. scan rate for Cu-Fe HCFs made at different molar ratio of Cu:Fe [A] 1:10 [B] 1:5 [C] 1:3 and [D] 1:2.

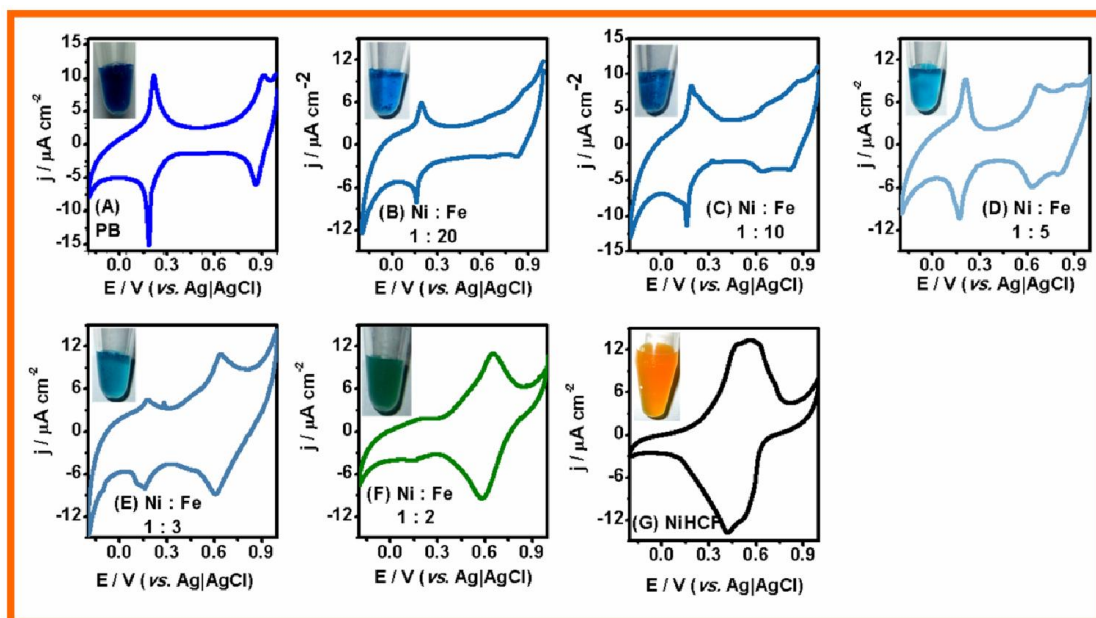


Figure.5. 14. Cyclic voltammetry response of Ni-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01 V s^{-1} made at different Ni:Fe molar ratio [A] only PBNPs; [B] Ni:Fe (1:20); [C] Ni:Fe (1:10); [D] Ni:Fe (1:5); [E] Ni:Fe (1:3); [F] Ni:Fe (1:2); [G] NiHCFs.

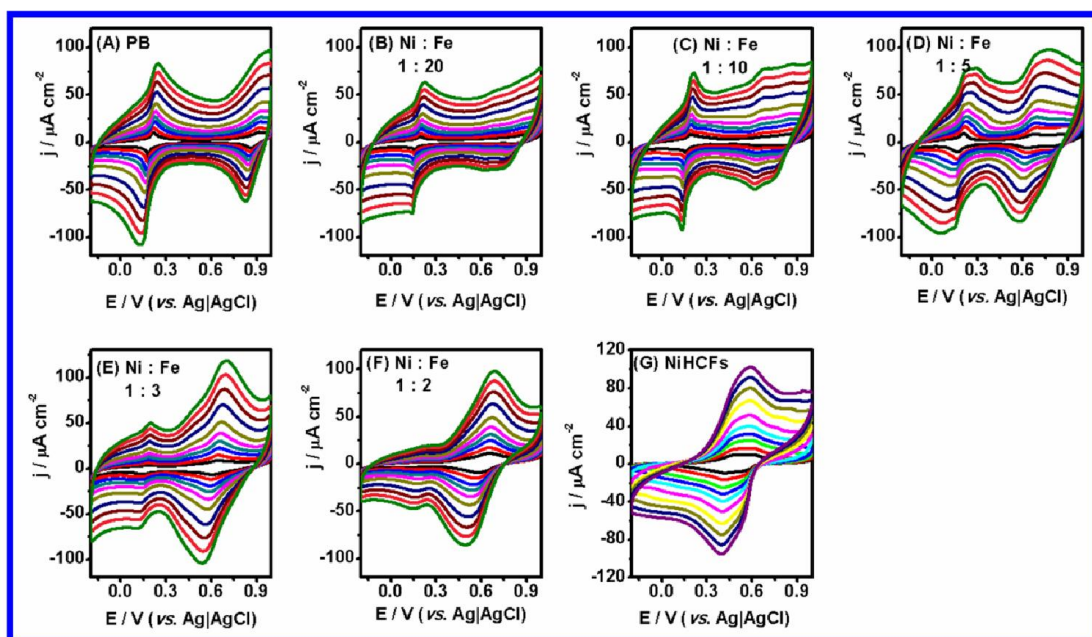


Figure.5. 15. Cyclic voltammety response of Ni-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at varying scan rate of 0.01, 0.02, 0.035, 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.30 V s^{-1} made at different Ni:Fe molar ratio [A] PBNPs; [B] Ni:Fe (1:20); [C] Ni:Fe (1:10); [D] Ni:Fe (1:5); [E] Ni:Fe (1:3); [F] Ni:Fe (1:2); and [G] NiHCFs.

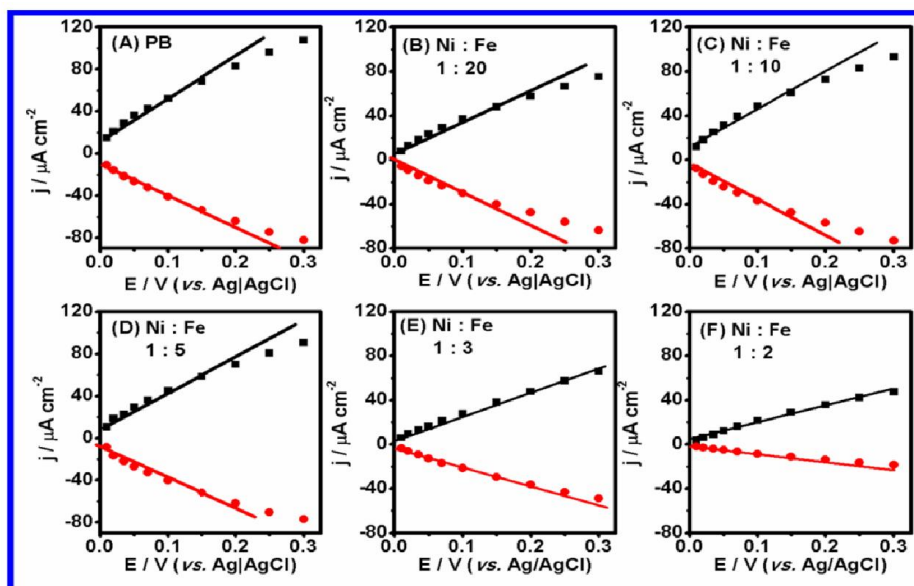


Figure.5. 16. The plots of peak current density vs. scan rate for Ni-Fe HCFs made at different molar ratio of Ni:Fe [A] PB [B] 1:20 [C] 1:20 [D] 1:10 [E] 1:5, [F] 1:3 and [1:2].

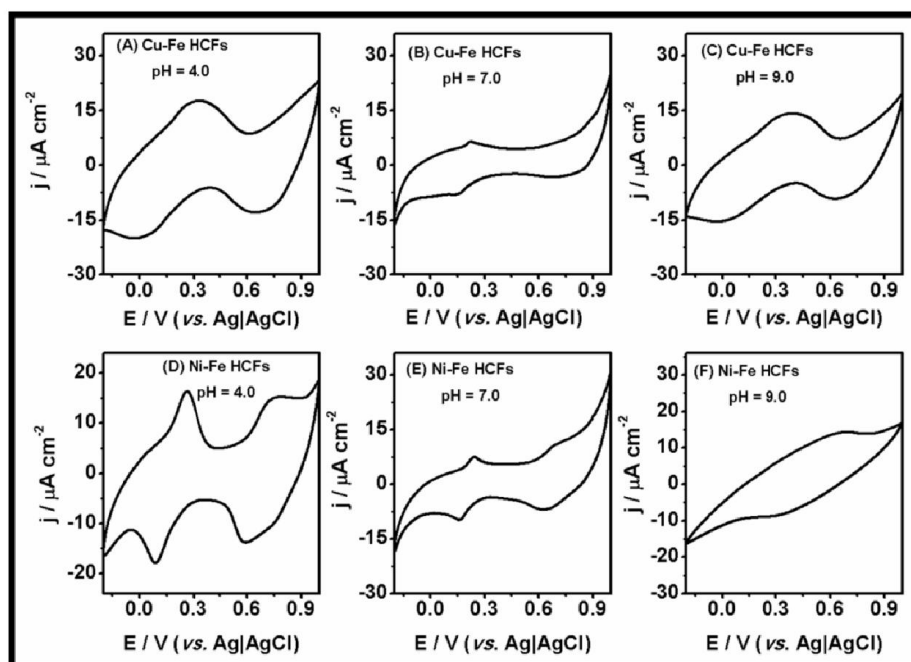


Figure.5. 17. Cyclic voltammetry of (A) to (C) for Cu-Fe HCFs (1:1) and (D) to (F) for Ni-Fe HCFs (1:5) under different pH=4.0 (phthalate buffer), pH=7.0 (phosphate buffer) and pH=9.0 (borate buffer) containing 0.5 M KCl.

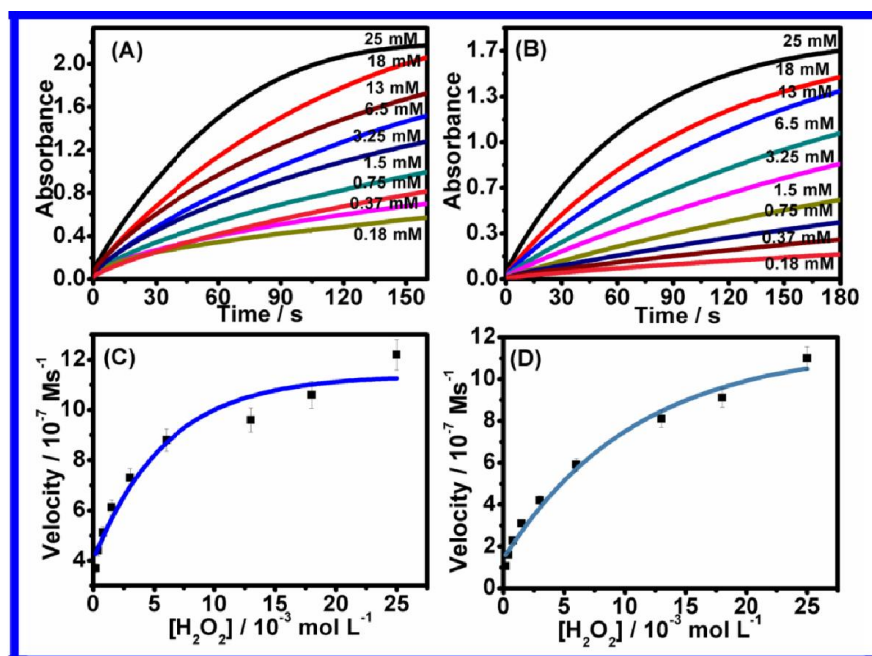


Figure.5. 18. Time dependent absorbance changes at 430 nm in the presence of different concentration (25, 18, 13, 6.5, 3.25, 1.5, 0.75, 0.75, 0.37 and 0.18 mM) of H_2O_2 and fixed concentration of *o*-dianisidine (50 μM) catalyzed by (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5); and kinetic analysis of (C) Cu:Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) with H_2O_2 as substrate.

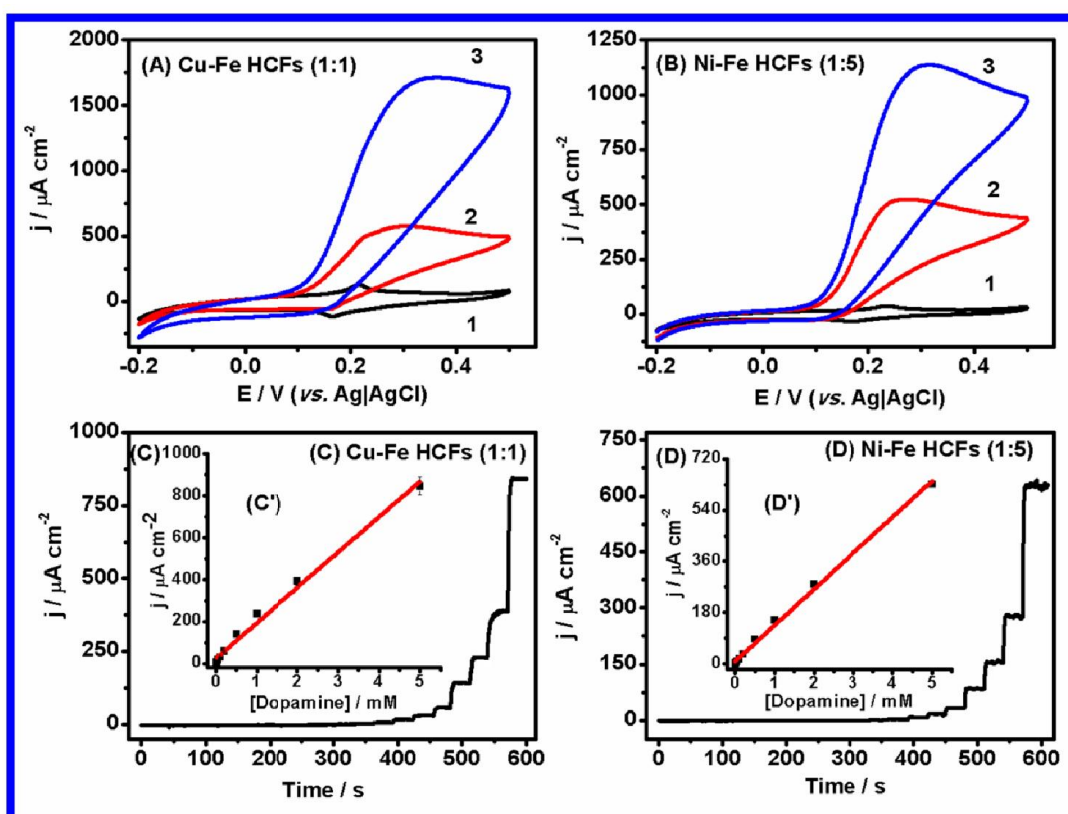


Figure.5. 19. Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) in the absence (1) and presence of (2) 2 mM and (3) 5 mM dopamine recorded in 0.1 M phosphate buffer containing 0.5 M KCl, (pH=7.0) at scan rate of 0.01 V s⁻¹; (B) amperometric response of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) modified graphite paste electrode on the addition of varying concentration of dopamine between 0.01 μ M 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.

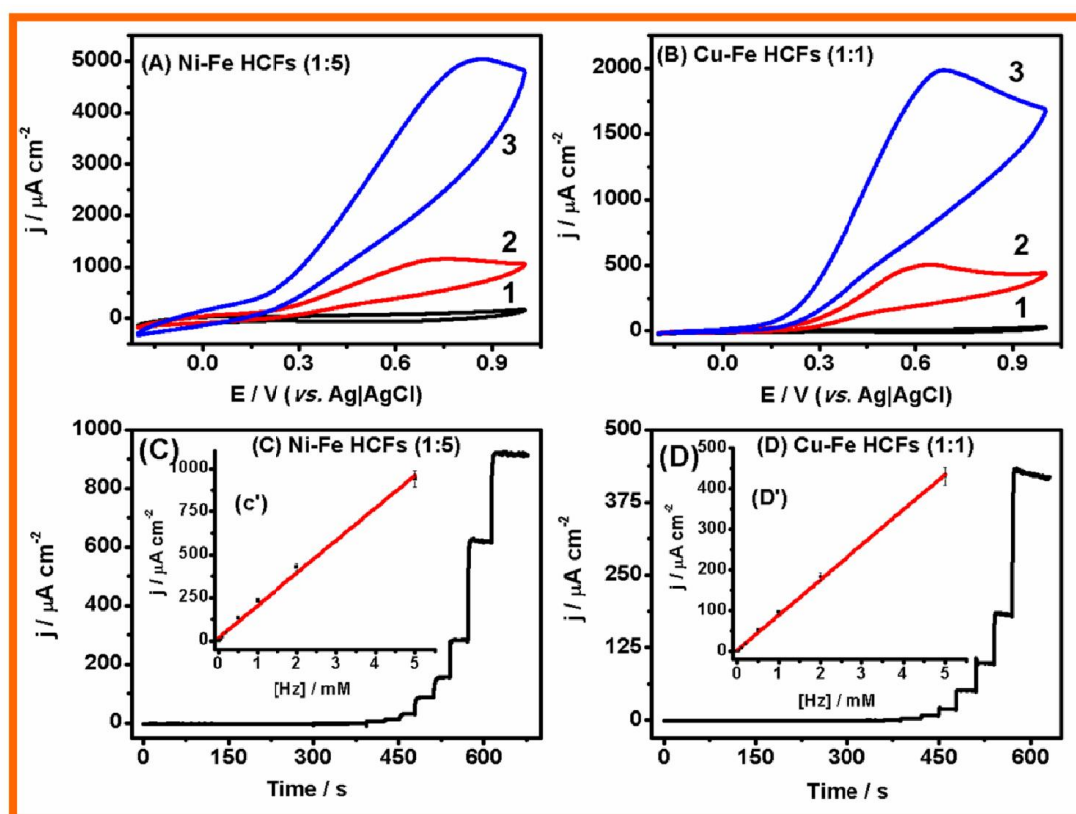


Figure.5. 20. Cyclic voltammogram of (A) Ni-Fe HCFs (1:5) (B) Cu-Fe HCFs (1:1) in the absence (1) and presence of (2) 1 mM and (3) 5 mM hydrazine recorded in 0.1M NaNO_3 scan rate of 0.01 V s^{-1} ; (B) amperometric response of (C) Ni-Fe HCFs (1:5) and (D) Cu-Fe HCFs (1:1) modified graphite paste electrode 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.

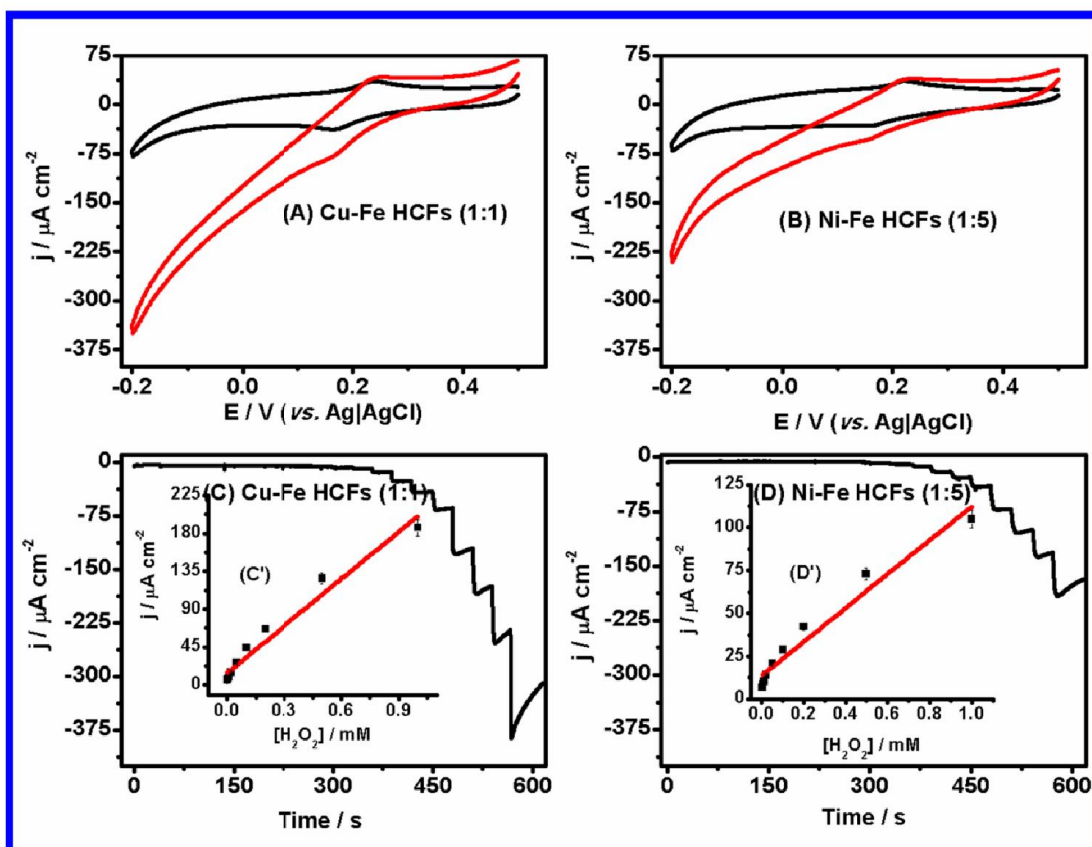


Figure.5. 21. Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) in the absence (1) and presence of (2) 1 mM H_2O_2 recorded in 0.1 M phosphate buffer containing 0.5 M KCl, pH=7.0 at scan rate of 0.01 V s^{-1} ; (B) amperometric response of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) modified graphite paste electrode on the addition of varying concentrations of H_2O_2 between $0.01 \mu\text{M}$ 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.

1.4 Discussion

1.4.1 PEI mediated synthesis of nanocrystalline Cu-Fe HCF and Ni-Fe HCFs

We have recently demonstrated the synthesis of Ni-Fe hexacyanoferrates nanoparticles involving the active participation of THF and H₂O₂. [(Pandey and Panday 2016a)] However, the same process does not allow the formation of Cu-Fe hexacyanoferrates. This could be due to the structural deformation happening by the insertion of Cu²⁺ in the 3 dimensional networks of PBNPs in the presence of THF and H₂O₂. In addition to that the crystalline behaviour of as made Prussian blue and its mixed metal analogues was significantly reduced due to the presence of high concentrations of organic moiety. Accordingly, the need of another suitable organic reducing agent overcoming such limitation is desirable that not only allows the controlled formation of mixed metal analogues of several combinations of transitions metal hetero ions but also improve the crystalline behaviour of the as made material. We have recently demonstrated the reducing ability of polycationic polymer, polyethylenimine (PEI) during the synthesis of gold nanoparticles that directed to investigate whether such reagent may be useful for efficient synthesis of Cu-Fe HCFs and Ni-Fe HCFs nanoparticles. It was found that single precursor K₃[Fe(CN)₆], PEI, HCl and Cu²⁺ or Ni²⁺ can be effectively converted into Cu-Fe HCFs and Ni-Fe HCFs nanoparticles respectively at 60 °C in 3 hours having good stability and processability as shown in Figure.5.1. During the conversion process of K₃[Fe(CN)₆] into mixed metal hexacyanoferrate, the yellow colour solution turned into blue colour solution having absorbance maxima at 680 nm. Figure.5.1.(A, B, C, D and E) depict that when all three components are present in an optimum concentration then only stable, well dispersed mixed metal hexacyanoferrates synthesized at 60 °C in 3 hours. Figure.5.1. justify the role of each component during the synthesis of mixed metal hexacyanoferrates. The finding as shown in Figure.5.1.(B) justify the conversion of white colour solution while mixing PEI to K₃[Fe(CN)₆] at 60 °C for 3 hours in absence of HCl [inset to Figure.5.1.(B)] and confirm the conversion of K₃[Fe(CN)₆] into K₄[Fe(CN)₆] as evidenced from the disappearances of absorption maxima at 420 nm which is characteristic of K₃[Fe(CN)₆]. Similarly when K₃[Fe(CN)₆] is mixed

with HCl and allowed to stand at and keep it at 60 °C for 3 hours, the conversion deep yellow colour from light yellow colour [inset to Figure.5.1.(C)] with little increase in absorbance at 420 nm along with appearance of a new peak at 590 nm [Figure.1.(C)] indicating probable break down of $K_3[Fe(CN)_6]$. Finally when all the components ($K_3[Fe(CN)_6]$, PEI and HCl) are mixed together with $CuSO_4/NiSO_4$ and allowed to stand at 60 °C for 3 hours the formation of Cu-Fe HCFs [Figure.5.1(D)] and Ni-Fe HCFs [Figure.5.1.(E)] with good Prussian blue/metal hexacyanoferrate character as evidence from the absorption maxima recorded at 680 nm. The possibility of utilization of $K_4Fe(CN)_6$ in place of $K_3[Fe(CN)_6]$ was explored by synthesizing Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) at the similar condition of mixed metal hexacyanoferrates synthesis and performed the UV-Vis spectroscopy and cyclic voltammetry of as synthesized material over graphite paste electrode in 0.1 M KNO_3 . As evidenced from the Figure.5.2 and Figure.5.3. Cu-Fe HCFs (1:1) and Ni:Fe HCFs (1:5) made from $K_3[Fe(CN)_6]$ had better absorbance maxima and better electrochemical behaviour in comparison to the material made through $K_4[Fe(CN)_6]$.

Next stage of the investigation is to understand the role of temperature on PEI mediated synthesis of Cu-Fe HCF/Ni-Fe HCF. Accordingly, the similar processes was allowed to take place at 25 °C and 90 °C respectively. The finding as shown in Figure.5.4. (A) (1) and Figure.5.4.(B) (1) reveals poor rate of Cu-Fe HCF/Ni-Fe HCF synthesis with considerable decrease in PB character as evidenced from absorption maxima recorded at 680 nm which was even observed after keeping the reaction mixture for 4 days at 25 °C. An increase in temperature from 60 °C to 90 °C caused little faster rate of conversion *i.e.* within 2 hours however the absorption maxima shows little red shift with decrease in PB character as shown in Figure.5.4. (A) (2) and Figure.5.4. (B) (2) as compared to that of recorded at 60 °C within 3 hours (Figure.5.4.(A) (3) and Figure.5.4.(B) (3)). The UV-Vis spectroscopy result was also confirmed by cyclic voltammetric experiment performed in 0.1 M KNO_3 on graphite paste electrode as shown in Figure.5.5.

We also intended to understand the role of PEI during mixed metal hexacyanoferrate formation. The mixture of optimum concentrations $K_3[Fe(CN)_6]$ and HCl was allowed to stand at 60 °C for 24 hours. The results as shown in Figure.5.6. justify appearance significant less in PB character with poor electrochemical behaviour.

The possible mechanism for the synthesis of Cu-Fe HCF/Ni-Fe HCF may involve the following steps: (i) the formation of some Fe^{3+} ions and some undissociated ferricyanide ions (ii) PEI may acts as a reducing agent and stabilizing agent which converts Fe^{3+} into Fe^{2+} ions (iii) undissociated ferricyanide ions, Fe^{2+} ions, and Ni^{2+} or Cu^{2+} ions leads to the synthesis of mixed metal hexacyanoferrates based on possible evidenced recorded in Figure.5.1.

1.4.2 Characterization of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)

1.4.2.1 FT-IR analysis

Prussian blue character is evaluated from the absorbance maxima recorded at 680 nm as shown in Figure.5.1. FT-IR spectroscopy of as made nanomaterial (Cu-Fe HCFs and Ni-Fe HCFs) as shown in Figure.5.7.(A) and Figure.5.7.(B) reveals a strong absorption peak at 2075 cm^{-1} representing the characteristic peaks of PB and its mixed metal analogues which represents to the stretching vibration of $-CN$ group for $Fe^{III}HCF^{II}$ [(Ghosh 1974; Pandey and Panday 2016b; Pyrasch *et al.* 2003a)]. Absorption bands near 3400 cm^{-1} and 1684 cm^{-2} are assigned to the O-H stretching mode and H-O-H bending mode respectively that can be assigned for the existence of interstitial forces of attraction in the sample [(Itaya *et al.* 1986; Pandey and Panday 2016a)]. The corresponding vibrations in the Ni-Fe HCFs are present at 2059 cm^{-1} , 3400 cm^{-1} and 1643 cm^{-1} which represents as described in the above part of Cu-Fe HCFs.

1.4.2.2 X-Ray diffraction analysis

As synthesized mixed metal hexacyanoferrate was also characterized by X-ray diffraction analysis. Figure.5.8. shows X-ray diffractogram of as synthesized Cu-Fe HCFs and Ni-Fe HCFs respectively. Figure.5.8. (A) shows the XRD pattern

of as synthesized Cu-Fe HCFs (1:1). There are few major peaks at c.a. 17.4°, 24.5°, 28.5°, 35.5°, 39.5°, 40.6° (2θ values) which can be assigned as (200), (220), (311), (400), (420), and (420). The crystallite size of as synthesized Cu-Fe HCFs are found to be 18.2 nm, 9.8 nm, 24.8 nm, 13.4 nm, 25.0 nm and 28.2 nm respectively. Figure.5.8. (B) shows the XRD pattern of as synthesized Ni-Fe HCFs. There are four major characteristic peaks available in Ni-Fe HCFs (1:1) which are at c.a. 17.5°, 24.7°, 35.4°, and 39.7° (2θ values). The crystallite sizes at the major peaks are 9.67 nm, 7.7 nm, 26.8 nm and 8.2 nm respectively. Some other peaks are also present at c.a. 30.5°, 43.7°, 50.7°, 54.5°, 57.4°, 66.3° and 69.2° which can be assigned as (200), (220), (400), (420), (222), (422), (440), (600), (620), (640), (642) and (822) respectively (JCPDS file no- 73-0687).

1.4.2.3 Transmission Electron Microscopy (TEM) analysis and scanning Electron Microscopy (SEM) of mixed metal analogues

Transmission Electron Microscopy (TEM) was done to evaluate the nanogeometry of as synthesized mixed metal analogues (Cu-Fe HCFs and Ni-Fe HCFs). Figure.5.9. (A) and (B) shows TEM images of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively and justify that the PEI mediated synthesis of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) are nanoparticles with almost circular in nature. The particle sizes are found in between of 5 nm to 20 nm. Inset to the respective Figure.5.9. (A) and (B) shows the SAED pattern of the respective metal hexacyanoferrate which reveals the polycrystallinity of the as synthesized metal hexacyanoferrates. As compared to the crystallite size obtained from XRD analysis is closely related to the particle size obtained from the TEM analysis for as synthesized mixed metal hexacyanoferrates. Figure.5.9. (C) and (D) shows the SEM characterization of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively which also confirms the nanoparticle behaviour of as synthesized mixed metal hexacyanoferrates.

1.4.2.4 EDS analysis of as synthesized mixed metal analogues

Elemental analysis of as synthesized mixed metal analogues was done by Energy Dispersive Spectroscopy (EDS) analysis. EDS analysis of Cu- Fe HCFs

(1:1) and Ni-Fe HCFs (1:5) are shown in Figure.5.10. (A) and (B) respectively and reveals the presence of all the essential elements available in the respective mixed metal hexacyanoferrates.

1.4.3 Electrochemical behaviour of mixed metal analogue

1.4.3.1 Electrochemistry of Cu-Fe hexacyanoferrates

Electrochemical behaviour of Cu-Fe HCFs nanoparticles was evaluated in 0.1 M KNO₃ solution by cyclic voltammetry on graphite paste modified electrode as shown in Figure.5.11. along with the similar findings on PBNPs modified electrode [(Figure.5.11.(A)]. Figure.5.11.(A) shows the voltammograms of PBNPs modified electrode revealing redox activity at - 0.2 V and ~ 0.9 V due to the redox processes of the outer sphere Fe^{2+/3+} and the inner sphere [Fe(CN)₆]^{4-/3-} couples of PB respectively [(Ricci and Palleschi 2005)]. CuHCFs is showing a set of redox couple as shown in Figure.5.11..(I) with a formal potential of approximately 0.6 V. This redox process is due to the Cu^{II}/Fe^{II} to Cu^{II}/Fe^{III} transition and is equivalent to the last redox couple in the PB system [(Siperko and Kuwana 1983)]. Figure.5.11.(B-H) shows the electrochemical behaviour of as synthesized Cu-Fe HCFs with varying molar ratio of Cu-Fe. As can be seen in the Figure.5.11.(A) there are well defined characteristic reversible peak of Prussian blue, one is at -0.2 V vs. Ag|AgCl and another is at ~ 0.9 V vs. Ag|AgCl which is the characteristic of the oxidation of Prussian white and the reduction of Prussian blue whereas the second redox couple corresponds to the oxidation of PB and the reduction of Berlin green as reported earlier [(Ricci and Palleschi 2005)]. As can be observed from the different composition of Cu-Fe HCFs [(Figure.5.11.(B) to (H)], an increase in Cu-content, the electrochemical behaviour of Prussian blue alters that justify the turning toward individual behaviour of CuHCF [Figure.5.11.(I)] [(Baioni *et al.* 2007a; Wessells *et al.* 2011a)]. The results clearly show that mixed metal analogue with the molar ratio of Cu:Fe (1:1) contains the characteristic voltammetric peaks of CuHCFs and also of PBNPs and designated as Cu-Fe HCFs (1:1). Other composition with the less molar ratio of Cu:Fe contains the PB character predominantly with the broadening in the cyclic

voltammetry. The cyclic voltammograms at different scan rate from 0.01 V s^{-1} to 0.3 V s^{-1} of as synthesized Cu-Fe HCFs are shown in Figure.5.12. The dependence of peak current on the scan rate of cyclic voltammetry was recorded at different scan rate from 0.01 V s^{-1} to 0.3 V s^{-1} and found that on increasing scan rate, the peak current increases which is shown in Figure.5.13.

1.4.3.2 Electrochemistry of as synthesized Ni-Fe hexacyanoferrates

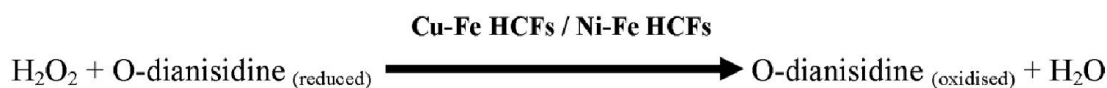
Electrochemical behaviour of as synthesized Ni-Fe HCFs was evaluated by cyclic voltammetry as a function of Ni:Fe molar ratio in Ni-Fe HCFs in 0.1 M KNO_3 solution (Figure.5.14) along with similar results on PBNPs modified graphite paste electrode. Figure.5.14.(B-F) shows the cyclic voltammetric responses recorded for Ni-Fe HCFs at variable Ni:Fe ratio whereas Figure.5.14.(A) shows the voltammograms of PBNPs modified graphite paste electrode revealing redox activity at -0.2 V and $\sim 0.9 \text{ V}$ due to the redox processes of the outer sphere $\text{Fe}^{2+/3+}$ and the inner sphere $[\text{Fe}(\text{CN})_6]^{4-/3-}$ couples of PB respectively [(Ricci and Palleschi 2005)]. On the other hand the redox property of NiHCFs as shown in Figure.5.14.(G) shows similar activity at 0.65 V [(Prabakar and Narayanan 2008)]. There are two well defined characteristic redox peaks of Prussian blue as shown in Figure.5.14.(A), the first one is at -0.2 V and another one at $\sim 0.9 \text{ V vs. Ag|AgCl}$ [(Ricci and Palleschi 2005)]. While increasing the concentration of Ni^{2+} in Ni-Fe HCFs (Ni:Fe = 1:10), the PB character starts decreasing and a new peak at $0.46 \text{ V vs. Ag|AgCl}$ starts appearing along with the PB characteristic peaks [Figure.5.14.(C)]. On further increasing the molar ratio of Ni: Fe (1:5), there is two more peaks (at $\sim 0.46 \text{ V}$ and $\sim 0.6 \text{ V vs. Ag|AgCl}$) along with characteristic PB peaks are available. At molar ratio (Ni:Fe = 1:3), again PB character decreases and NiHCFs character [Figure.5.14.(G)] starts dominating. At molar ratio (Ni:Fe = 1:2), the PB character is almost diminished showing the redox peaks at only $\sim 0.6 \text{ V}$. These findings reveal that the effect of transition metal ions on the cyclic voltammetry on the Prussian blue and its Ni-Fe HCFs and also justify the presence of other transition metal ion in the 3-dimensional crystal lattice of metal hexacyanoferrates. Since in the Ni-Fe HCFs with the molar ratio

Ni:Fe (1:5) [designated as Ni-Fe HCFs (1:5)] contains well defined PB character [Figure.5.14.(A)] as well as NiHCFs [Figure.5.14.(G)] [(Pandey and Pandey 2013a)] character that is why we choose this composition for all the study related to the as synthesized Ni-Fe HCFs [Figure.5.14.(D)]. The dependence of electrochemical behaviour on the scan rate of all the compositions like PB, Ni-Fe HCFs (1:20), (1:10), (1:5), (1:3) and (1:2) between 0.01 V s⁻¹ to 0.3 V vs. Ag|AgCl in 0.1 M KNO₃ has been recorded and shown in Figure.5.15. Peak current is low at slow scan rate while it gets increasing on increasing scan rate as shown in Figure.5.16.

The stability of Cu-Fe HCFs (1:1) / Ni- Fe HCFs (1:5) modified electrode was evaluated at different pH by cyclic voltammetry recorded in Phthalate buffer (pH=4.0), Phosphate buffer (pH=7.0) and borate buffer (pH=9.0) containing 0.5 M KCl. Both Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode show good electrochemical behaviour at pH=7.0 while at pH=9.0 both metal hexacyanoferrates modified electrode shows sluggish electrochemical behaviour. At pH 4, Ni-Fe HCF (1:5) shows relatively better redox activity whereas Cu-Fe HCF (1:1) shows sluggish redox behaviour under similar condition [Figure.5.17.].

1.4.4 Peroxidase mimetic activity of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)

Prussian blue nanoparticles and its mixed metal analogues have shown a potential material for the homogeneous detection of hydrogen peroxide [(Dutta *et al.* 2012a; Pandey and Panday 2016b; Zhang *et al.* 2014)]. Prussian blue nanoparticles and its mixed metal analogue can converts reduced form of o-dianisidine to the oxidized form of o-dianisidine which gives absorbance maxima at 430 nm in UV-Vis spectroscopy [(Dutta *et al.* 2012a; Pandey and Panday 2016b; Pandey and Pandey 2013c, d)]. Therefore, it is required to estimate the peroxidase mimetic activity of as synthesized mixed metal analogues. O-dianisidine catalyzed peroxidase mimetic reaction can be represented as:



Where o-dianisidine (ox.), o-dianisidine (red.) can be expressed for oxidized and reduced form of organic dye o-dianisidine. The peroxidase like activity was measured by steady state kinetic experiments which was carried out by varying the H_2O_2 concentration in a 2 ml phosphate buffer (pH=7.0) while keeping o-dianisidine concentration (50 μM) constant in each reaction (Figure.5.18.). Figure.5.18. (A) and (C) show the peroxidase mimetic activity of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively by varying concentration of H_2O_2 . Curve in Figure.5.18. (B) and (D) represents that as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) show the Michaelis-Menton kinetics. The Michaelis-Menton constant (K_m) for as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) are found to be 1.5 mM and 4.2 mM respectively justifying their use in the practical application.

1.4.5 Electrocatalytic oxidation of dopamine, hydrazine and hydrogen peroxide over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)

Typical applications of as made mixed metal hexacyanoferrate has been examined in the detection of biologically important analyte like dopamine, hydrazine and H_2O_2 . The electrochemical application of these nanomaterials was examined over graphite paste electrode.

1.4.5.1 Electrocatalytic oxidation of dopamine over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode

Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrodes were used for the electrocatalytic oxidation of dopamine. Electrocatalytic oxidation of dopamine was performed by cyclic voltammetric in absence (1) and presence (2) and (3) of 2 mM and 5mM dopamine as shown in Figure.5.15. (A) and Figure.5.19. (B) for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively. There is an increase in anodic current at 0.1 V vs. Ag|AgCl in the presence of dopamine justifying the electrocatalytic oxidation of dopamine over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrode. Electrocatalytic oxidation of dopamine was quantified by amperometry. Since dopamine undergoes direct oxidation above 0.3 V vs. Ag|AgCl accordingly the amperometric

sensing of the same is recorded at 0.2 V vs. Ag|AgCl to avoid the contribution due to direct oxidation of dopamine. The amperometric response of dopamine sensing was performed by addition of increasing concentrations of dopamine (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 150, 300, 700, 1000, 2000 and 5000 μM respectively in 0.1 M phosphate buffer, pH=7.0 at 0.2 V vs. Ag|AgCl. The amperometric response of dopamine analysis recorded at 0.2 V vs. Ag|AgCl is shown in Figure.5.19. (C) and Figure.5.19. (D) for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively. The sensitivity of dopamine sensing was found to be 192.4 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and 129.0 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode respectively. The dependence of anodic current on the concentration of dopamine was linear between 0.5 μM to 5 mM for both the electrodes. The lowest detection limit was found to be 100 nM and 0.5 μM for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode respectively [Inset to the Figure.5.19. (C) and Figure.5.19. (D)].

1.4.5.2 Electrocatalytic oxidation of hydrazine over Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified electrode

As synthesized Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified graphite paste electrodes were explored for the detection of hydrazine in 0.1 M NaNO_3 . Figure.5.20. (A) and Figure.5.20. (B) shows the cyclic voltammograms in the absence (1) and presence (2) and (3) of 1 mM and 5 mM hydrazine in 0.1 M NaNO_3 over Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified graphite paste electrode respectively. The electro-oxidation of hydrazine was recorded close to 0.3 V vs. Ag|AgCl reveals at the surface of Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified electrodes. Hydrazine undergoes direct oxidation above 0.4 V vs. Ag|AgCl accordingly the amperometric sensing of the same is recorded at 0.3 V vs. Ag|AgCl to avoid the contribution due to direct oxidation. The amperometric response of hydrazine sensing was performed by addition of increasing concentration of hydrazine (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 150, 300, 700, 1000, 2000 and 5000 μM respectively in 0.1 M 0.1 M NaNO_3 at 0.3 V vs. Ag|AgCl. Figure.5.20 (C) and Figure.5.20 (D). shows the amperometric

response for hydrazine oxidation at 0.3 V *vs.* Ag|AgCl under stirring for Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified electrodes. The sensitivity of electroanalysis was found to the order of 221.9 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and 97.4 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ with the lowest detection limit of 50 nM and 0.2 μM for Ni-Fe HCFs (1:5) and Cu-Fe HCFs (1:1) modified graphite paste electrode respectively. The dependence of anodic current on the concentration of hydrazine was linear between 0.5 μM to 5 mM.

1.4.5.3 Electrocatalytic reduction of H₂O₂ over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode

As synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) possesses the Prussian blue character therefore it is intended to do the electrocatalytic reduction of H₂O₂ over Cu-Fe HCFs (1:1) and Ni-Fe (1:5) modified graphite paste electrodes. Electrocatalytic reduction of H₂O₂ was performed over these modified electrode in 0.1 M phosphate buffer (pH=7.0) containing 0.5 M KCl. Figure.5.21. (A) and Figure.5.21. (B) shows the cyclic voltammograms of in the absence (1) and presence (2) of 1 mM H₂O₂ in 0.1 M phosphate buffer containing 0.5 M KCl over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrodes. The amperometric response of H₂O₂ sensing was performed by addition of increasing concentration of H₂O₂ (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 150, 300, 700, 1000, 2000 and 5000 μM) in 0.1 M phosphate buffer, (pH 7=0) at 0.0 V *vs.* Ag|AgCl. The electrocatalytic reduction of H₂O₂ was measured by amperometric analysis over these modified electrodes at fixed potential of 0.0 V *vs.* Ag|AgCl. The sensitivity of electroanalysis was found to the order of 203.2 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and 112.9 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ with the lowest detection limit of 0.2 μM and 2 μM for Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified graphite paste electrode respectively. The dependence of anodic current on the concentration of H₂O₂ was linear between 0.5 μM to 1 mM for both Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode [Inset to the Figure.5.21. (C) and Figure.5.21. (D)].

1.4.6 Stability and Reproducibility

Stability of the present systems was evaluated by repetitive experiments on cyclic voltammetry for 100 continuous cycles at 10 mV s^{-1} . The peak current was found to be decreases by 4% after 100 cycles justifying better stability of the modified electrode.. The reproducibility of these modified electrodes were examined by cyclic voltammetry in the reaction system containing 2 mM dopamine in case of Cu-Fe HCFs electrode whereas 1 mM hydrazine in case of Ni-Fe HCFs electrode for 20 repetitive cycles at 10 mV s^{-1} . It was found that the oxidation peak potential of dopamine and hydrazine was not changed and the anodic peak current was decreased by less than 3.9 %. The relative standard deviation (RSD) of the current response to 2 mM dopamine at 0.2 V was found to be 3.2 % for 12 successive measurements in case of Cu-Fe HCFs electrode surface. The relative standard deviation (RSD) during hydrazine (1 mM) sensing at 0.3 V was found to be 2.8 % for 12 successive measurements in case of Ni-Fe HCFs electrode surface.

Summary

The thesis entitled “Studies on nanocrystalline Prussian blue and its mixed metal analogue for analytical application” has been divided into following five chapters:

1. General Introduction.
2. Tetrahydrofuran and hydrogen peroxide mediated synthesis of nanocrystalline Prussian blue nanoparticles and its analytical applications.
3. Tetrahydrofuran and hydrogen peroxide mediated synthesis of nanocrystalline Nickel-iron hexacyanoferrates nanoparticles and its analytical applications.
4. Polyethylenimine mediated Synthesis of nanocrystalline Prussian blue nanoparticles and cooperative self assembly of gold nanoparticles on polycationic surface and their analytical applications.
5. Polyethylenimine mediated synthesis of nanocrystalline mixed metal analogues and their analytical applications.

Chapter 1 describes an overview of metal hexacyanoferrates (MHCFs) in special reference to Prussian blue. An extensive survey on the structure, synthesis of Prussian blue nanoparticles (PBNPs) and its mixed metal analogues was reported followed by their use in the field of medical, environmental, energy storage devices *etc.* The utilization of PBNPs and its mixed metal analogues in the development of electrochemical sensor was critically reviewed. Later, definition of the problem, objective of the present programme and the work plan is reported.

Chapter 2 describes the tetrahydrofuran (THF) and hydrogen peroxide (H_2O_2) mediated synthesis of nanocrystalline Prussian blue nanoparticles (PBNPs) and their characterization through various techniques like AFM, FT-IR, XRD, TEM and through electrochemical. We found that potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ in the presence of THF and H_2O_2 at $60\text{ }^\circ\text{C}$ gets converted into stable nanocrystalline PBNPs with the crystallite size of 14.0 nm which shows good electrochemical behaviour. As synthesized PBNPs was used for the electrochemical reduction of H_2O_2 . The as synthesized PBNPs was also explored its peroxidase mimetic activity in the presence of *o*-dianisidine. The Michaelis–Menten constant (K_m) and the maximal reaction velocity (V_{max}) for H_2O_2 analysis

was found to be 0.49 mM and $6.03 \times 10^{-7} \text{ M s}^{-1}$ justifying the use of nanomaterial as perfect peroxidase replacement.

Chapter 3 describes THF and H_2O_2 mediated synthesis of nanocrystalline Nickel-iron hexacyanoferrates (Ni-Fe HCFs). It was observed that in the presence of THF, H_2O_2 , NiSO_4 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ gets converted into Ni-Fe HCFs at 60°C in 30 minutes. As synthesized Ni-Fe HCFs was characterized by FT-IR, XRD, SEM, TEM and EDS. The crystallite size was found to be 11 nm and the particle size was 31 nm. As synthesized Ni-Fe HCFs showed differential redox activity depending upon the molar ratio of Ni:Fe. As synthesized Ni-Fe HCFs was found to water soluble therefore it could be used for both homogeneous and heterogeneous catalysis. So, Ni-Fe HCFs was efficiently used for the electrocatalytic oxidation of hydrazine and homogeneous detection of H_2O_2 . Ni-Fe HCFs show excellent peroxidase mimetic activity with the Michaelis–Menten constant (K_m) and V_{max} in the order of 1.5 mM and $3.06 \times 10^{-7} \text{ M s}^{-1}$ respectively for H_2O_2 mediated oxidation of o-dianisidine thus representing novel material for both homogeneous and heterogeneous catalysis.

Chapter 4 describes polyethylenimine (PEI) mediated synthesis of nanocrystalline PBNPs and their assembly to the gold nanoparticles (AuNPs). It was observed that in the presence of PEI, HCl and $\text{K}_3[\text{Fe}(\text{CN})_6]$ converts into PBNPs at 60°C in 3 hours. As synthesized PBNPs was water dispersible and stable. It was also found that by mixing gold chloride salt into the as synthesized PBNPs leads to the synthesis of AuNPs assembled PBNPs within 5 minutes at 60°C . Both PBNPs and AuNPs assembled PBNPs was characterized by XRD, TEM analysis and cyclic voltammograms. The crystallite size of PBNPs was found to be 42 nm with the particle size of 5 – 25 nm. These materials were used for the electrocatalytic reduction and oxidation of H_2O_2 and homogeneous reduction of H_2O_2 as peroxidase mimetic materials. It was found that electrocatalytic efficiency of PBNPs was further increased on the incorporation of AuNPs.

Chapter 5 describes the PEI mediated synthesis of nanocrystalline mixed metal analogues like copper-iron (Cu-Fe HCFs) and nickel-iron hexacyanoferrates (Ni-Fe HCFs) at 60°C in 3 hours. As synthesized mixed metal analogues was characterized by FT-IR, XRD, TEM, EDS and cyclic voltammetry. We observed

that the cyclic voltammograms of as synthesized mixed metal hexacyanoferrates depends upon the molar ratio of iron to respective transition metal. Therefore, it could be possible the tuning of redox potential of PBNPs justified the controlled incorporation of hetero-transition metal ions in the 3-dimensional cubic lattice. As synthesized mixed metal analogues were further explored for the possibility of replacement of peroxidase enzyme as peroxidase mimetic materials. Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) have excellent peroxidase mimetic activity with Michaelis–Menten constant (K_m) to the order of 1.5 mM and 4.2 mM respectively. Mixed metal analogues were used for the electrocatalytic oxidation of dopamine, hydrazine and H_2O_2 over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) respectively.

Future Projection

This Ph.D. work covers the challenges associated with the synthesis of processable Prussian blue nanoparticles (PBNPs) and its mixed metal analogues having potential applications for many biological analytes. Moreover, the applicability of the present work involves single precursor based synthesis of PBNPs and its mixed metal analogues which have been utilized for the electrochemical sensing of hydrogen peroxide, hydrazine and dopamine. Applicability of these mixed metal nanoparticles as peroxidase mimetic reveals the perfect material for the replacement of peroxidase enzyme in biological reactions. However, the properties related to the magnetic, optical and secondary cell of such PB based nanomaterials have not been worked. The utilization of these materials in ferromagnetism, charging-discharging and optical behaviour of such nanomaterials would be helpful for the development of practical devices. In additions to these, the nanocomposite materials with as synthesized PBNPs and mixed metal analogues could improve the sensitivity and selectivity and have the possibility in the development of electrochemical sensor / biosensor for variety of analytes.

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List of Publications

1. Pandey, P.C., **Pandey, D.**, Singh, R., 2012. Extraction and Purification of Purple Membrane for Photochromic Thin Film Development: Application in Photoelectrochemical Investigation. *Appl. Biochem. Biotechnol.* 168(4), 936-946.
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3. Pandey, P.C., **Panday, D.**, Pandey, G., 2014. 3-Aminopropyltrimethoxysilane and organic electron donors mediated synthesis of functional amphiphilic gold nanoparticles and their bioanalytical applications. *RSC Adv* 4(105), 60563-60572.
4. Pandey, P.C., **Panday, D.**, 2016. Tetrahydrofuran and hydrogen peroxide mediated conversion of potassium hexacyanoferrate into Prussian blue nanoparticles: Application to hydrogen peroxide sensing. *Electrochim. Acta* 190, 758-765.
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