



# Polyethylenimine mediated synthesis of copper-iron and nickel-iron hexacyanoferrate nanoparticles and their electroanalytical applications



P.C. Pandey \*, Digvijay Panday, Ashish Kumar Pandey

Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India

## ARTICLE INFO

### Article history:

Received 25 June 2016

Received in revised form 8 August 2016

Accepted 19 August 2016

Available online 2 September 2016

### Keywords:

Polyethylenimine

Copper-iron hexacyanoferrate

Nickel-iron hexacyanoferrate

Peroxidase mimetic activity

Electrocatalysis

Cyclic voltammetry

Amperometry

## ABSTRACT

We report herein polyethylenimine mediated synthesis of copper-iron hexacyanoferrates (Cu–Fe HCFs) and nickel-iron hexacyanoferrates (Ni–Fe HCFs) nanoparticles from single precursor potassium ferricyanide [ $K_3[Fe(CN)_6]$ ]. It has been found that  $Cu^{2+}$  or  $Ni^{2+}$  are converted in respective mixed metal hexacyanoferrate (Cu–Fe HCF or Ni–Fe HCF) nanoparticles having average size of 5 nm to 30 nm in the presence of  $K_3[Fe(CN)_6]$ , polyethylenimine (PEI), and HCl at 60 °C in 3 h with following major findings: (i) the process allow to control the desired molar ratio of Cu:Fe or Ni:Fe in the respective mixed metal hexacyanoferrate nanoparticles justifying controlled transition of Prussian blue character to respective metal hexacyanoferrate (CuHCF/NiHCF) as evidenced from cyclic voltammetric measurements, (ii) the process also allow the conversion of similar nanoparticles when  $K_3[Fe(CN)_6]$  is replaced by  $K_4[Fe(CN)_6]$  with poor electrochemical behaviour, (iii) the process also allow the synthesis of Cu–Fe HCFs/Ni–Fe HCFs at 25 °C in 4 days and within 2 h at 90 °C with significant variation in electrochemical behaviour of respective nanomaterial, (iv) Cu–Fe HCFs show better electrocatalytic activity for dopamine and  $H_2O_2$  sensing while the same for Ni–Fe HCFs is better for hydrazine sensing, and (v) both Cu–Fe HCF and Ni–Fe HCF nanoparticles display good homogeneous catalytic activity as peroxidase mimetic with Michaelis–Menten constant ( $K_m$ ) to the order of 1.5 mM and 4.2 mM respectively. The as made nanomaterials have been characterized by UV–vis spectroscopy, Fourier Transformation Infrared Spectroscopy (FT-IR), X-ray diffraction analysis (XRD), Energy Dispersive Spectroscopy analysis (EDS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and cyclic voltammetry.

© 2016 Elsevier B.V. All rights reserved.

## 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 [1–4]. 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 has been exploited in the electrochemical energy storage, electrochemical sensing of hydrazine, dopamine, and NADH and many more [2,5–8].

Although many reports on the synthesis of Prussian are available in literature however the controlled nucleation of these materials has 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 [9–15]. Recently, we have demonstrated controlled conversion of Prussian blue and its 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 [2,13–18]. 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  $32.1 s^{-1}$  [15,17]. Similar process allows controlled synthesis of super peroxidase mimetic mixed metal hexacyanoferrate [2,17]. 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 [14]. THF-HP enables the conversion of potassium hexacyanoferrate into PBNPs at room temperature in 12 h. THF-HP is also capable of reducing noble metal cations into respective

\* Corresponding author.

E-mail address: [pcpandey.apc@iitbhu.ac.in](mailto:pcpandey.apc@iitbhu.ac.in) (P.C. Pandey).

nanoparticles in the presence of 3-APTMS [19,20] whereas  $K_3[Fe(CN)_6]$  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 [13] and indeed interesting finding on the synthesis of Prussian blue and its Ni–Fe HCF has been recorded [13]. It was found that  $K_3[Fe(CN)_6]$  undergo controlled conversion in to well disperse PBNPs in the presence of tetrahydrofuran (THF), hydrogen peroxide ( $H_2O_2$ ) at 60 °C in 20 min. The same method efficiently enabled the synthesis of Ni–Fe hexacyanoferrate [16]. 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, and (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 [21–24]. Recently, we have demonstrated that polyethylenimine (PEI) enable controlled and rapid synthesis of gold nanoparticles in the presence of formaldehyde [25]. 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 HCF and Ni–Fe HCF 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) applications of as made nanomaterials in electrocatalytic sensing of dopamine, hydrazine and  $H_2O_2$  are reported in this manuscript.

## 2. Experimental

### 2.1. Material

Potassium ferricyanide [ $K_3[Fe(CN)_6]$ ], Potassium ferriyanide  $K_4[Fe(CN)_6]$ , hydrogen peroxide ( $H_2O_2$ ), nickel sulphate ( $NiSO_4$ ) and copper sulphate ( $CuSO_4$ ) were purchased from Merck, India. Polyethylenimine (PEI) (molecular weight of 60,000), Graphite powder (1–2  $\mu m$ ), nujol oil (density 0.838 g/ml), *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 (Elga Water Purification System).

### 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 h in a vacuum oven. In a typical procedure, 70  $\mu l$  aqueous solution of  $K_3[Fe(CN)_6]$  (50 mM) and 20  $\mu l$  of PEI (0.1 g/ml) are mixed together under stirring condition over cyclomixture followed by addition of 5  $\mu l$  hydrochloric acid solution (6.5 M). To this add 70  $\mu l$  of aqueous solution of  $CuSO_4$  solution (0.05 M) mixed vigorously over cyclomixture and allowed to stand at 60 °C for 3 h in an oven. A yellow colour solution was turned into blue colour indicating the synthesis of Cu–Fe HCFs. Cu–Fe HCF 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 by mixing 100  $\mu l$  aqueous solution of  $CuSO_4$  (0.01 M) with 100  $\mu l$  aqueous solution of potassium ferricyanide

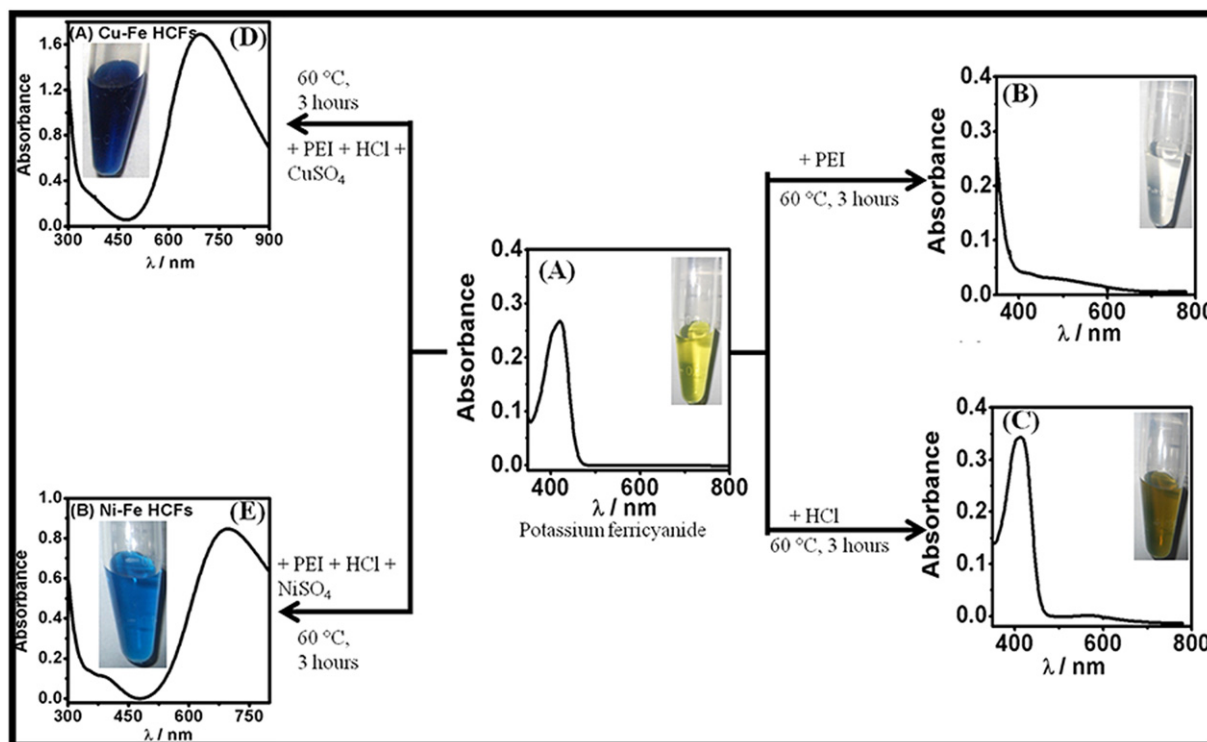


Fig. 1. Schematic presentation of PEI mediated synthesis of Cu–Fe hexacyanoferrates and Ni–Fe hexacyanoferrates nanoparticles.

Download English Version:

<https://daneshyari.com/en/article/6477149>

Download Persian Version:

<https://daneshyari.com/article/6477149>

[Daneshyari.com](https://daneshyari.com)