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# Synthesis of cobalt hexacyanoferrate nanoparticles and its hydrogen storage properties

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## ABSTRACT

In the present paper, we report hydrogen storage properties of cobalt hexacyanoferrate nanoparticles as a function of temperature. Cobalt hexacyanoferrate nanoparticles were synthesized by facile chemical precipitation method. The resulted compound forms FCC structure analogous to Prussian blue and is found to be stable up to 550 K. Presence of characteristic absorption bands in the range of 2000–2300  $\text{cm}^{-1}$  in IR spectra corresponds to the CN stretching frequency of Fe(III)–C=N–Co(II) sequence and this confirms the formation of Prussian blue analogues. Hydrogen adsorption studies were performed at variable temperatures. The effect of precursor concentration on hydrogen storage property has been investigated and interestingly, with increase in cobalt precursor concentration, hydrogen storage capacity is found to decrease. This correlates well with openness of the crystal structure. To the best of our knowledge, this is the first report on hydrogen storage properties of cobalt hexacyanoferrate.

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## Introduction

Use of hydrogen as energy carrier in near future could be a solution for controlling global warming and climate change owing to its high energy density and clean conversion. Hydrogen storage is a key challenge for the advancement of hydrogen technology. Therefore, a perfect hydrogen storage material is needed for advancing hydrogen economy [1]. Tremendous effort is underway to explore a variety of materials for hydrogen storage [2]. Hydrogen can be stored by different means in solid, liquid and gas phase. The solid phase hydrogen storage is safe, efficient and cost effective method

for transportation purpose [3]. Hydrogen can be stored in solid matrix by two ways, either absorption or adsorption. Materials like metal hydride, chemical hydride and different types of metal and alloys store hydrogen by absorption. Among them, metal hydride based materials show quite high hydrogen storage capacity under ambient conditions [4,5]. The main drawbacks of this type of hydrogen storage materials are high temperature of hydrogen desorption and low reversibility [6]. Physical adsorption of hydrogen is another attractive option, but bottleneck of this type of materials, for transport applications, are lower adsorption energy of hydrogen and comparatively low gravimetric density [7].

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Recently many porous materials like carbon-based materials, zeolites, Prussian blue analogues (PBA) and metal-organic frameworks (MOF) have been reported for their interesting hydrogen storage characteristics [8–10]. Among various materials, cyanide-based porous coordination compounds called Prussian blue analogue (PBA) have received much attention due to presence of coordinatively unsaturated metal site and polarisable  $\pi$  clouds around the cyanide ligands. Transition metal hexacyanoferrates are already in focus because of their unique properties such as redox behaviour and ionic conductivity [11–13]. Due to distinctive properties, the transition metal hexacyanoferrates exhibit various applications in different fields such as sensor fabrication, molecular magnets, display technologies, batteries, hydrogen storage and precipitation of radioactive element from nuclear waste [14–18]. Hydrogen storage property of this family of materials is quite interesting due to the availability of free coordination sites in anhydrous form and is clear from the recent reports [19–26] listed in Table 1.

Metal hexacyanoferrate (MHCF) can be synthesised by single or double precursor methods. However, for fine-tuning the properties of MHCF nanoparticles, control over both size and shape is very crucial. The growth of the Prussian blue analogue strongly depends on the reaction temperature, and concentration of precursors. It has been found that slow reaction condition is useful for controlling size and morphology of nanoparticles. Probable mechanism of formation of Prussian blue analogue has been discussed in earlier reports [27]. Among different MHCF, cobalt hexacyanoferrate (CoHCF) is one of the interesting transition metal hexacyanoferrate [28–31]. The redox process in CoHCF involves two different transition metal ions (Fe and Co), unlike other materials of the same class; the phenomenon is driven by a metal-to-metal charge transfer process. The electron transfer is accompanied by change of spin state of Co ion [32]. For example the complex is used for electro catalytic oxidation of captopril and degradation of neutral red dye. It can also be used for various medical applications such as biosensor for bovine insulin and

detection of L-cysteine [33]. Nanoparticles of such materials are reported to be Ferromagnetic with a Curie temperature of 19 K [34]. Many reports are available on the preparation of CoHCF nanoparticles by electrochemical, reverse micelles and microemulsion methods [35–37]. Though there is no report on direct synthesis and hydrogen storage properties of CoHCF nanoparticles with/or without any templating/added substances.

In the present paper, we report the synthesis of CoHCF nanoparticles by simple precipitation method in solution. Samples were characterised using X-ray diffraction (XRD), Energy Dispersive X-ray (EDX), X-ray photoelectric spectroscopy (XPS), Infrared (IR) spectroscopy, Thermogravimetry (TG), Secondary Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Hydrogen storage properties of synthesized samples have been studied in detail at various temperatures (173–273 K). In order to understand the hydrogenation behaviour, the heat of hydrogen adsorption and entropy are also evaluated. Further, to see the effect of precursor concentration on hydrogen adsorption property of CoHCF, samples were prepared by changing precursor concentration and investigated for H storage properties and the results are correlated with crystallinity of the sample. Finally we could show decent structural stability of the sample after few hydrogen adsorption desorption cycle. In light of its ease of preparation/modification, better stability and low costs, CoHCF may hold great potential for hydrogen storage applications.

## Experimental detail

Potassium hexacyanoferrate (KHCF) (Merck Milipure, Mumbai, India), Polyvinyl alcohol (PVA-MW = 1,25,000, SD Chemical Ltd, Mumbai India) and cobalt chloride hexahydrate  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck Milipure, Mumbai, India) were used as received. Cobalt hexacyanoferrate (CoHCF) nanoparticles

**Table 1 – Hydrogen adsorption data of some Prussian blue analogues (PBA) reported in the literature.**

Sr. No.	Sample	Hydrogen storage capacity(wt%)	Temperature (K)	Hydrogen pressure	Reference
1	$\text{Mn}_3[\text{Co}(\text{CN})_6]$	1.6	77	900 torr	[19]
2	$\text{Fe}_3[\text{Co}(\text{CN})_6]_2$	1.4	77	900 torr	[19]
3	$\text{Co}_3[\text{Co}(\text{CN})_6]_2$	1.5	77	900 torr	[19]
4	$\text{Ni}_3[\text{Co}(\text{CN})_6]_2$	1.4	77	900 torr	[19]
5	$\text{Cu}_3[\text{Co}(\text{CN})_6]_2$	1.8	77	900 torr	[19]
6	$\text{Co}_3[\text{Co}(\text{CN})_6]_2$	1.3	77	760 torr	[20]
7	$\text{Zn}_3[\text{Co}(\text{CN})_6]_2$	1.2	77	760 torr	[20]
8	$\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$	1.79 and 1.2	75 and 85	900 torr	[24]
9	$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	2.2 and 2.1	75 and 85	900 torr	[24]
10	$\text{Ni}_2[\text{Fe}(\text{CN})_6]$	0.9	77	890 torr	[22]
11	$\text{Mn}_2[\text{Fe}(\text{CN})_6]$	0	77	890 torr	[22]
12	$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	1.6	77	890 torr	[22]
13	$\text{Co}_2[\text{Fe}(\text{CN})_6]$	0.7	77	890 torr	[22]
14	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	1.6	77	890 torr	[22]
15	$\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$	~3.0	77	140 bar	[25]
16	$\text{FeFe}(\text{CN})_6$	0.91	77	77 bar	[26]
17	$\text{Fe}(\text{Py})\{\text{Ni}(\text{CN})_4\}$	1.46	77	77 bar	[26]
18	$\text{Co}(\text{Py})\{\text{Ni}(\text{CN})_4\}$	2.19	77	77 bar	[26]
19	$\text{Ni}(\text{Py})\{\text{Ni}(\text{CN})_4\}$	2.34	77	77 bar	[26]

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