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Sunlight mediated photocatalytic reduction of aqueous Cr(VI) using metal hexacyanoferrate (M = Mn, Ni, Cu and Zn)

Manas Mandal^{1,2}, Krishna Chattopadhyay³, and Swapan Kumar Bhattacharya¹

¹ Department of Chemistry, Jadavpur University, Kolkata–700032, India

² Department of Chemistry, Sree Chaitanya College, Habra, 24Parganas(N)–743268, India

³ School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, West Bengal – 700032, India

e-mail: skbhatt7@yahoo.co.in

Abstract. Four different metal hexacyanoferrates, MHCF (M = Mn, Ni, Cu and Zn) were synthesized via a simple, cost effective precipitation method. The as-synthesized MHCF were characterized using XRD analysis and FESEM images were recorded for the analysis of morphology. Among the four compounds, ZnHCF exhibited most effective catalytic property for visible-light driven photoreduction of Cr(VI) to Cr(III), with excellent photochemical reducing capability of 68% within 2 h.

1. Introduction

Now a day's excessive and indiscriminate uses of organic–mineral complexes in electronic gadgets as well as inorganic compound in the wood preservation industry have progressively become the most serious matter of environmental concern [1]. Mixing of the acid wastewater from mine drainage and heavy metal like chromium from preservation industry to the ground water is very dangerous towards aquatic life and mutagenic to human [2-3]. The waste water without treatment is hazardous for ecosystem, as most of the synthetic dyes are toxic, mutagenic and carcinogenic and enhance the chemical oxygen demand (COD) of the water body. Generally, chromium (Cr) is present in compounds in two common oxidation states such as Cr(III) and Cr(VI) [4]. Amongst these, Cr(VI) is enormously toxic, carcinogenic, whereas Cr(III) is less toxic and more easily soluble in water as Cr(OH)₃. Cr (VI) is used in several industrial fields like textile production, electroplating, metal finishing, leather tanning, dyeing, etc. [5]. As a result, higher degrees of contamination due to discharges of Cr (VI) in waste water, makes the aquatic life severely harmful. Presence of Cr (VI) in drinking water causes kidney, liver, bladder, and skin cancer [6]. So, the urgent demand for effective methods for efficient reduction of Cr (VI) to Cr (III) in industrial waste water has been raised. Different methods including ion exchange, precipitation, reverse osmosis, photocatalysis and adsorption are developed [7-9]. However, each method has its own advantages along with numerous drawbacks. The photo-catalytic process is highly efficient and cost effective as compared to the other methods.

The transition metal complex like metal hexacyanoferrate has recently got attention from scientific community, as the hexacyanoferrate compound shows some unique solid state chemistry and promising applications in the field of electrochemical energy storage [10-11], electrocatalysis [12], photocatalysis [13], ion-sensing [14] etc. Jassal et al synthesized potassium zinc hexacyanoferrate nanocubes which were able to degrade Malachite Green up to 94.15% and Eriochrome Black T up to



about 76.13% under optimum condition [13]. Herein, a set of MHCF (M = Ni, Zn, Mn and Cu) was prepared using precipitation method for photocatalytic reduction of Cr (VI) under sunlight.

2. Experimental Section

2.1. Materials and Method

Manganese nitrate tetrahydrate, Nickel nitrate hexahydrate, Copper nitrate trihydrate, Zinc nitrate hexahydrate, potassium hexacyanoferrate(III), sodium hydroxide, potassium permanganate, potassium dichromate were purchased from Merck, India. All reagents were directly used for the experiment without further purification.

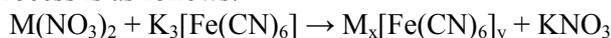
2.2. Synthesis of metal hexacyanoferrate (M = Mn, Ni, Cu, Zn)

For the synthesis of metal hexacyanoferrate (MHCF), simple precipitation method was followed. Briefly, 20 mL 0.1 M aqueous solution of $M(NO_3)_2$ [M= Ni, Cu, Zn, and Mn] was taken in a 100 mL beaker. Then 20 mL 0.1 M aqueous solution of $K_3Fe(CN)_6$ was slowly added to it under vigorous stirring condition. The solution was magnetically stirred for 1 hour. Then the solution was kept for 12 h in undisturbed condition at room temperature. After that the solid precipitate was filtered, washed with distilled water and ethanol for 4-5 times. Finally, the desired solid product (MHCF) was dried in air oven at 70°C for 6 h.

3. Results and Discussions

3.1. Formation of the Metal hexacyanoferrate:

The synthetic procedure involves the precipitation method where a quick precipitation of metal hexacyanoferrate [MHCF], where M = Mn, Ni, Cu and Zn was achieved. The chemical reaction involved in this synthetic process is as follows:



3.2. X-Ray diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was performed by Rigaku ULTIMA-III X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns of the as-prepared MHCF (M = Mn, Ni, Cu and Zn) are shown in Figure 1. The observed XRD peaks of the MHCF (M = Mn, Ni, Cu and Zn) (Table 1) are well-matched with those in the JCPDS card number 01-074-7327, 01-082-2283, 01-086-0513 and 00-038-0688, respectively.

Table 1. List of important powder X-ray diffraction peaks and corresponding (hkl) values of the as prepared MHCF (M = Mn, Ni, Cu and Zn)

$Mn_4[Fe(CN)_6]_{2.667} \cdot 15.84H_2O$ JCPDS No. 01-074-7327		$Ni[Fe(CN)_6]_2 \cdot H_2O$ JCPDS No. 01-082-2283		$Cu[Fe(CN)_6]_{0.667}$ JCPDS No. 01-086-0513		$Zn_3[Fe(CN)_6]_2$ JCPDS No. 00-038-0688	
2 θ (°)	(hkl)	2 θ (°)	(hkl)	2 θ (°)	(hkl)	2 θ (°)	(hkl)
16.8	(002)	17.3	(200)	17.5	(200)	9.7	(012)
23.9	(022)	24.4	(220)	24.9	(220)	13.4	(104)
34.1	(004)	35.1	(400)	35.4	(400)	14.0	(110)
38.3	(024)	39.4	(420)	39.7	(420)	16.2	(113)
42.1	(224)	50.4	(440)	43.7	(422)	19.5	(024)
48.9	(135)	53.7	(600)	50.9	(440)	21.4	(116)
52.2	(244)	56.7	(620)	54.3	(442)	24.4	(300)
55.2	(335)			57.6	(620)	28.1	(119)
63.8	(246)					32.7	(226)
66.5	(137)						

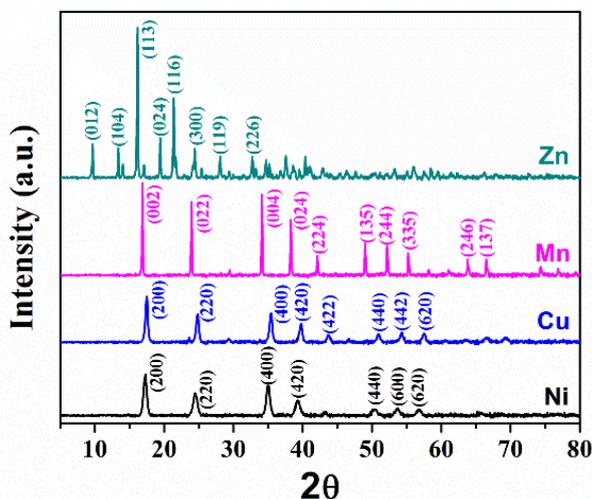


Figure 1. XRD pattern of as-prepared MHCF (M = Mn, Ni, Cu and Zn)

3.3. Morphological analysis

To investigate the surface morphology of the as-synthesized metal hexacyanoferrate (M = Mn, Ni, Cu and Zn) photo-catalysts, the field emission scanning electron microscopy (FESEM, Carl Zeiss-SUPRA 40) images were captured (Figure 2). From the FESEM of MnHCF, it can be seen that this is of cubic structure with an average length of 1 μm . The NiHCF and CuHCF are nano-sized particles. The FESEM image of ZnHCF suggests the cubic structure with an average length of 200 - 500 nm.

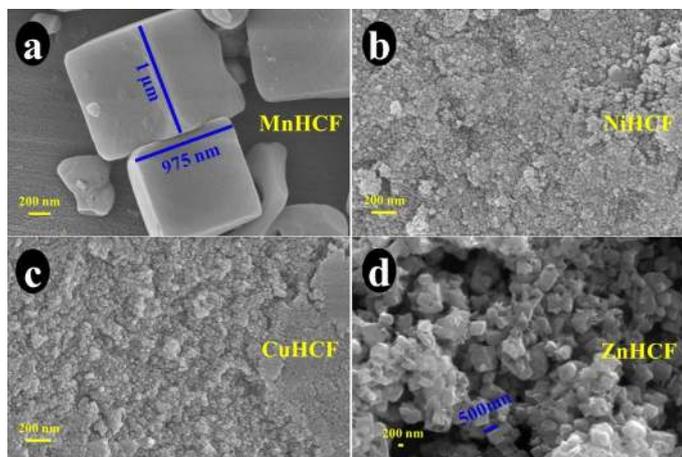


Figure 2. FESEM images of as-prepared metal hexacyanoferrate: MnHCF (a), NiHCF (b), CuHCF (c) and ZnHCF (d).

3.4 Photocatalytic Reduction of Cr(VI)

The photocatalytic reduction of Cr(VI) was performed by taking the aqueous dichromate solution containing the different as-synthesized catalyst (MHCF) under sunlight. A set of four beakers containing 25 mL 2×10^{-4} M aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ with 25 mg of different MHCF (M = Mn, Ni, Cu and Zn) was taken and stirred for 1 h in dark condition to reach the adsorption-desorption equilibrium. One blank test was also performed without catalyst. After that all the beakers were put under sunlight for 2 h with occasional shaking. The solutions were centrifuged separately time to time and the UV-vis spectra were recorded.

Figure 3 shows the photocatalytic reduction of aqueous Cr(VI) under sunlight in the presence of the as-synthesized metal hexacyanoferrate, MHCF (M = Mn, Ni, Cu and Zn). The diversity in the efficiency of different metal hexacyanoferrate may be a result of several factors, such as composition, particle size, morphology, crystallinity, crystal defects, specific surface area, band gap, state of dispersion, adsorption capacity for Cr(VI), etc. [15]. These factors are strongly coupled with each other and hence it is hard to identify the specific function and influence of a single parameter in the photocatalytic activity of different metal hexacyanoferrates. From the Figure 3, it can be seen that as-synthesized zinc hexacyanoferrate nanocubes reveal superior photocatalytic activity when compared to other catalysts. With increasing exposure time, the main absorption band of Cr(VI) centered at 363 nm notably decreases due to decreasing the concentration of Cr(VI). It is calculated that the as-prepared zinc hexacyanoferrate nanocubes exhibit excellent photochemical reducing capability. The photocatalytic activity i.e., reducing capability of the material is calculated (Equation 1) by monitoring the decrease in the absorption intensity which is directly proportional to the Cr(IV) concentration. A decrease in absorption intensity from 1.02 to 0.33 at 365 nm implies 68% reducing capability of the as prepared ZnHCF within 2 h.

$$\text{Catalytic activity (\%)} = \frac{|(\text{Final absorption intensity} - \text{Initial absorption intensity})|}{\text{Initial absorption intensity}} \times 100 \% \quad (1)$$

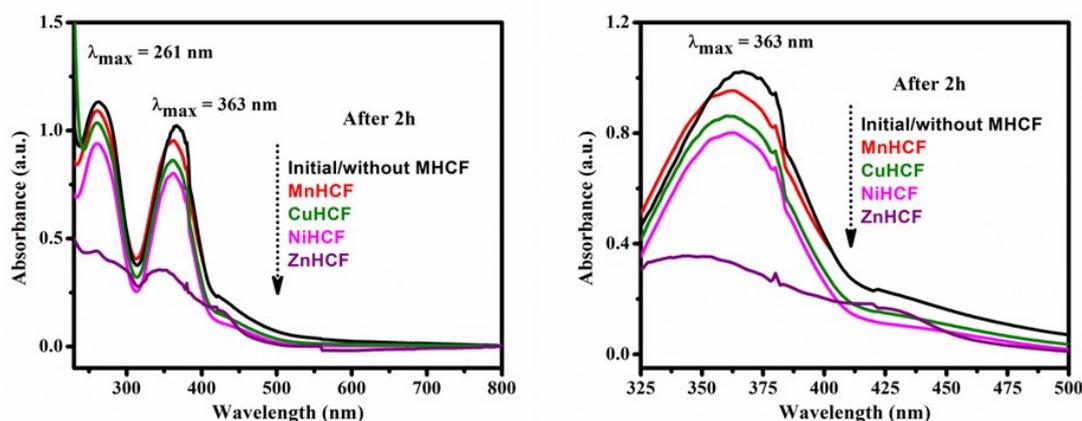
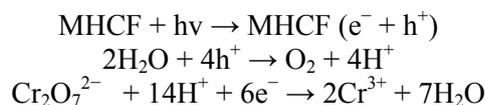


Figure 3. Photocatalytic reduction of 25 mL of 2×10^{-4} M aqueous solution of dichromate under sunlight in the presence of different MHCF (M = Mn, Ni, Cu and Zn) (25 g)

The reduction of Cr(VI) to Cr(III) is mainly carried out by the photoexcited electrons and therefore, good electron-hole pair separation is attained in this reduction process. The better photocatalytic activity of the as-prepared ZnHCF catalyst for the reduction of Cr(VI) under sunlight can be explained by taking into consideration of some unique properties of Zn which is responsible for the exceptional behaviour of ZnHCF. Zinc has a completely filled valence shell $3d$ orbitals and a narrow band gap. Due to highly dispersive nature of conduction band, the d^{10} electronic configuration supports photo-generated electron-hole separation. On photo-irradiation with sunlight, MHCF semiconductors absorb light and electrons from valence band are excited to conduction band, generating the holes in the valence band. These photoexcited electrons in conduction bands of the semiconductors reduce Cr(VI) to Cr(III) with a visual color change of the solution from leuco to colorless. The probable reaction pathway for the photocatalytic reduction of Cr(VI) under sunlight over MHCF in aqueous solution is as follows:



4. Conclusion

In summary, four different metal hexacyanoferrates, MHCF (M = Mn, Ni, Cu and Zn) were synthesized via a simple and cost effective precipitation method. The as-prepared MHCF were characterized using XRD analysis and the morphology was investigated with FESEM images. The ZnHCF semiconductor exhibited more superior catalytic property for visible-light-driven photoreduction of Cr(VI), with excellent photochemical reducing capability of about 68%. Thus the as-synthesized metal hexacyanoferrates show promising applications in the field of environmental photocatalysis.

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