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Synthesis and properties of Prussian blue nanoparticles prepared by using Cetyl Pyridinium Chloride as protecting agent

ABSTRACT

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A new approach for the synthesis of Prussian blue nanoparticles using the cationic surfactant Cetyl Pyridinium Chloride (CPC) as capping agent has been developed in the present work. Powder X-ray diffraction, transmission electron microscopy, UV–vis absorption spectra, and IR spectroscopy were employed to characterize the product. The TEM image showed that the Prussian blue nanoparticles with diameters of 8-22 nm were obtained. A particle size effect on optical and conductivity properties of the Prussian blue particles was observed. The higher value of activation energy for the nano compound compared to bulk Prussian blue indicates that the ionic conductions are predominant in the nano compound.

Keywords: *Nanoparticles; Transmission electron microscopy; Absorption spectra; Conductivity; X-ray diffraction.*

INTRODUCTION

In the recent years, many efforts have been made in the synthesis of metal nanoparticles because of their unusual properties and potential applications in optical, electronic, catalytic and magnetic materials and so on. The physical and chemical properties of nanoparticles are essentially different from those of bulk materials and largely dependent on their size, shape and surface chemistry [1-3].

The preparation of Prussian blue (PB) family nanoparticles has emerged as a promising subject in the past few years due to its large number of interesting properties and applications in the nanomagnetic, biosensing, electrochromic, and biomedical devices. So far, several techniques for the preparation of Prussian blue nanoparticles have been reported, in which various agents, such as sol-gel [4], mesostructured silica [5], porous alumina [6] etc were used to stabilize nanoparticles.

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These templating methods have difficulties in tuning the size of the particles over a wide range or in controlling the morphology of the product [7]. Several template free methods such as surfactant-assisted and rapid heating processes were developed to overcome such disadvantages. In this work, we present a new synthesis of Prussian blue nanoparticles using cationic surfactant Cetyl Pyridinium Chloride (CPC). In this system it could be expected that the positively charged surfactants interacts with negatively charged Prussian blue nanoparticles [8]. This method can be used to prepare Prussian blue particles with controlled sizes. The optical and conductivity properties of the newly synthesized nanoparticles are also discussed in this paper.

EXPERIMENTAL

Materials and Measurements

Solvents for synthesis, potassium ferricyanide, and FeCl_2 were obtained from Merck chemical company. Cetyl Pyridinium Chloride (CPC) was obtained from Sigma Chemicals, USA. All materials were used without further purification.

The samples were characterized by the powder X-ray diffraction (XRD) on a Bruker D8 advance instrument. Images of transmission electron microscopy (TEM) were achieved with a JEOL JEM-2100F. Infra-red spectra of the compounds were recorded as KBr pellets using a Shimadzu IR Affinity spectrometer. UV-visible spectra were recorded, by dissolving a calculated amount of the sample in appropriate solvents, on a Shimadzu UV-1800 spectrophotometer. The bulk electrical conductivity of the compound was evaluated from the complex impedance-admittance plots recorded at different temperatures ranging from room temperature to 120°C at an interval of 5°C using a Hioki 3532-50, frequency response analyzer. The plots were recorded in the frequency range from 42 Hz to 100 kHz keeping the signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was SS|electrolytefilm|SS, where SS plate (SS stands for Stainless Steel) was used as electrodes.

Synthesis

- **Preparation of Prussian Blue Nanoparticles (PB-01)**

Prussian Blue nanoparticles (PB-01) are synthesized by mixing two types of solutions together under magnetically stirring: one was a mixture of 0.9 g CPC, 25 ml ethanol and 0.083 g of potassium ferricyanide, and the other was a mixture of 0.9 g CPC, 25 ml ethanol and 0.005 g of FeCl_2 . The stirring was continued for another 30 minutes. Upon mixing, the solution turned dark blue, indicating the formation of PB. Isolation of a PB composite (PB-01) was carried out by an addition of acetone (4 mL) to the PB solution (2mL). The resultant paste like precipitate was centrifuged and washed with acetone for several times.

- **Preparation of Bulk Prussian Blue (PB-Bulk)**

The bulk Prussian blue (PB-Bulk) was prepared by mixing an aqueous $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.987 g, 0.03 M) solution (100mL) with a 0.03 M aqueous solution of FeCl_2 . The resulting blue colored precipitate was filtered and washed with methanol.

RESULTS AND DISCUSSION

The IR spectrum of PB-Bulk in the $2000\text{--}2200\text{ cm}^{-1}$ region showed a strong band at 2079 cm^{-1} associated with CN stretching in the $\text{Fe}^{2+}\text{-CN-Fe}^{3+}$ of Prussian blue (Figure 1A). The species PB-01 also shows the major ν_{cn} band at 2071 cm^{-1} in the solid state (Figure 1B). The absorption at 493 cm^{-1} and 597 cm^{-1} are assigned to metal-carbon-nitrogen bending mode [9].

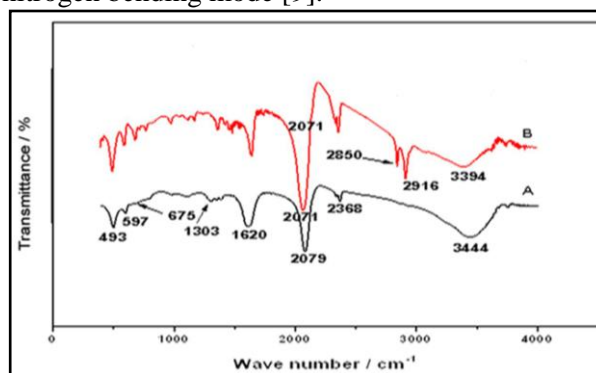


Fig. 1. FT-IR spectra of Prussian blue: (A) PB-Bulk and (B) PB-01.

The Powder X-ray diffraction patterns of the PB-01 and PB-Bulk are depicted in Figure 2(A and B). All the diffraction peaks of PB-01 appeared at the same positions as that obtained for PB-Bulk. From the width of the diffraction peaks using Sherrer's law, the average size of the crystalline domains for PB-01 as well as the PB-Bulk was found to be almost the same. This result is inconsistent with that from the TEM experiments. The particle size of the PB-Bulk was found to be over 500 nm determined from a TEM image (Figure 3A). The TEM images of the compound PB-01 are shown in (Figure 3B). All of the samples dispersed on the copper grids show a spherical morphology. The TEM image showed that very small particles with diameters of 8-22 nm were obtained.

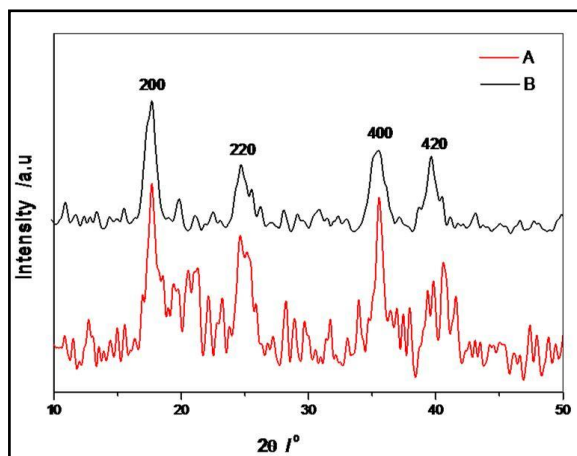


Fig. 2. X-ray powder diffraction patterns of (A) PB-Bulk and (B) PB-01.

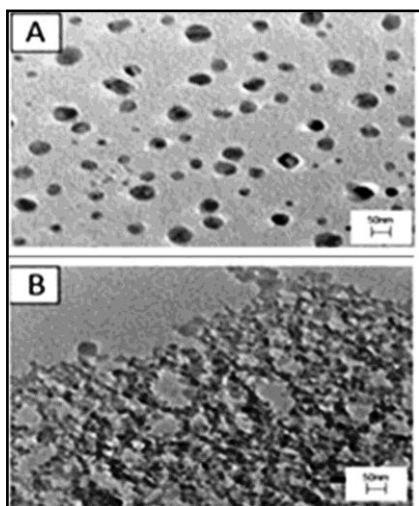


Fig. 3. TEM images of (A) PB-01 and (B) PB-Bulk.

The UV-Visible absorption of PB-01 in CHCl_3 and PB-Bulk in water are shown in Figure 4. The absorption spectra of PB-Bulk in water revealed a peak around 700 nm, which is attributed to an inter metal charge transfer (CT) band from Fe^{2+} to Fe^{3+} of Prussian blue [10]. In the case of PB-01 in CHCl_3 the peak shifted to longer wavelengths (743 nm). Such a large shift may be ascribed to hydrophobic and electrostatic interactions of the PB with the surfactant micelles.

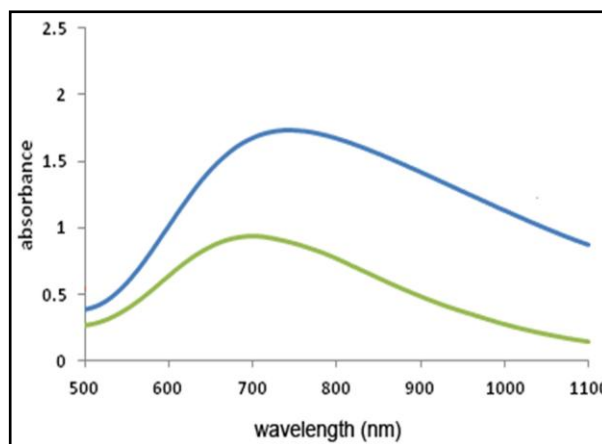


Fig. 4. UV-Visible spectra of PB-Bulk in aqueous solution and PB-01 in CHCl_3 solution.

The bulk Prussian blue is insoluble in organic solvents and this restricts applications of the molecular magnets as functional materials [11]. The PB-01 species are soluble in various organic solvents but are insoluble in water. This may be due to the reduction in the size and the surfactant assistance. The electronic spectrums of PB-01 in various solvents are shown in Figure 5.

The bulk electrical conductivity of the compound was evaluated from the complex impedance-admittance plots recorded at different temperatures ranging from room temperature to 120°C at an interval of 5°C .

The ionic conductivity of PB-Bulk and PB-01 were determined from the relation $\sigma = \frac{l}{R_b} r^2 \pi$, where l is the thickness of the sample, r is the radius of the sample, R_b is the bulk resistance of the electrolyte obtained from complex impedance plot [12].

The activation energy computed from Arrhenius plot (Figure 6) of $\text{Log}(\sigma T)$ vs. $1/T$ of the compounds PB-Bulk and PB-01 are -0.104 and 0.7591 eV respectively. The higher value of activation energy for the nano compound PB-01 compared to PB Bulk indicates that the ionic conduction is predominant in this compound and is for the structural factors of the polymers as observed by Miyamoto *et al* [13].

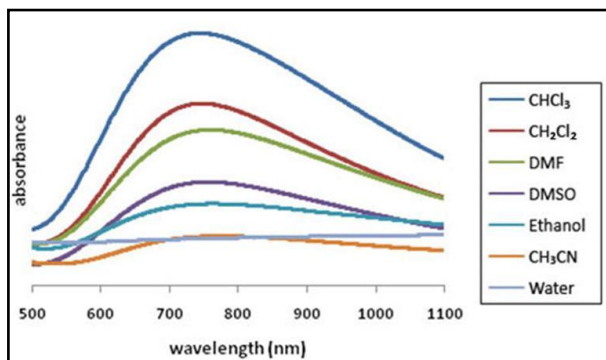


Fig. 5. UV-Visible spectra of PB-01 in various solvents.

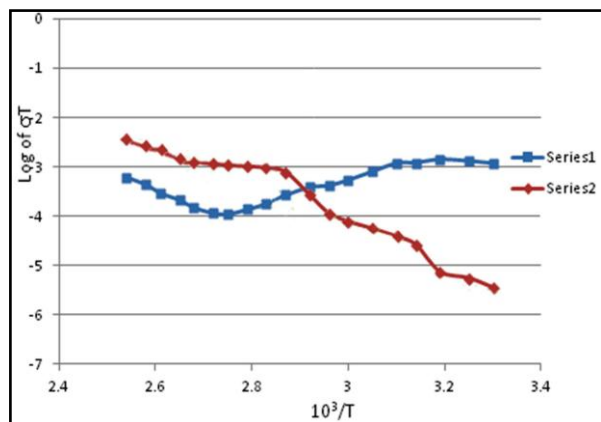


Fig. 6. Conductivity plot of the compounds PB-Bulk (Series 1) and PB-01 (Series 2)

Transport number determined from Figure 7 shows that the ionic conduction of PB Bulk is merely 12% at the very beginning of the observation and after about 50 seconds conduction gradually increases. Under the influence of the electric field Fe^{3+} ions are migrated from the compound and provide ion for conduction. Transport number of PB-01 (Figure 7) shows that it is around 76% ionic in nature and shows increase of conductivity with the rise of temperature. PB-01

is nano structured and its conductivity can be understood in terms of the free-volume model [14]. Free volume increases with the rise of temperature which in turn facilitates ion mobility and assists ion transportation.

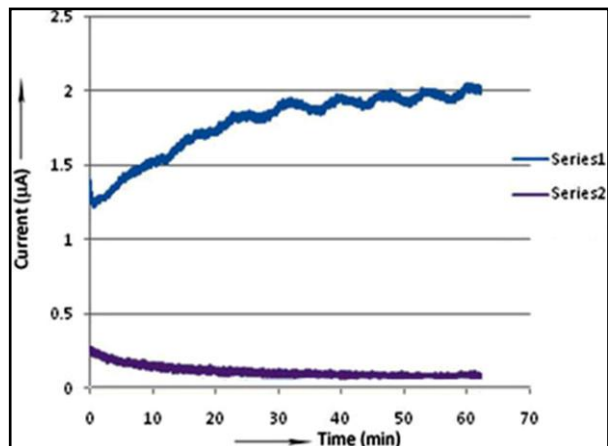


Fig. 7. Polarizing current vs. time plot of the compounds PB-Bulk (Series 1) and PB-01 (Series 2)

CONCLUSIONS

In conclusion, we present a new chemical route for preparing PB nanoparticles protected against aggregation by mixing Fe^{2+} , $\text{Fe}(\text{CN})_6^{3-}$ and CPC. The electrostatic interaction between the surfactant cationic head groups and the negatively charged PB nanoparticles may be the cause of inorganic-surfactant composites. The surfactant micelles make the PB nanoparticles soluble in organic solvents.

This is advantageous as insolubility of Bulk PB in organic media restricts its applications as functional materials. This work also demonstrated the properties such as the optical and conductivity of PB. The higher value of activation energy for the nano compounds PB-01 compared to PB Bulk indicates that the ionic conduction is predominant in the compounds.

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