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Noncovalent supramolecular assembly of hexagonally ordered mesoscale Prussian blue analogue

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ABSTRACT

A new mesostructured Prussian blue analogue was obtained through a noncovalent templating by cetylpyridinium bromide in formamide in the presence of Co^{2+} linking ions. This phase possesses a hexagonally ordered mesostructure with a framework based on the $[Fe(CN)_6]^{3-}$ anions linked by Co^{2+} ions which was noncovalently templated with cetylpyridinium cations.

1. Introduction

The mesoporous materials with periodic organisation of channels in nanometre scale were first synthesised using an aqueous liquid–crystal-templating route by Mobil researchers nearly two decades ago [1,2]. Since then this approach has been used to prepare a wide range of mesoporous oxides [3–6]. This route has been further extended to the synthesis of nonoxidic mesostructured materials based on the assembly of tetrahedral building blocks such as metal chalcogenide complexes [7–14] and octahedral hexarhenium chalcogenide cluster anions [15–17] with various linking transition metal cations. More importantly, MacLachlan et al. used alkyl pyrazinium surfactants which can coordinate to mononuclear octahedral complex anion $[Fe(CN)_5NH_3]^{3-}$ to make a kinetically stable micellar assembly in the presence of various linking metal ions including Fe^{3+}, $Cu^{1+/2+}$, Mn^{2+}, Ni^{2+}, Zn^{2+}, Gd^{3+}, and Er^{3+} [18]. Interestingly, however, they were unable to prepare these types of materials using more conventional surfactant systems such as tetrasubstituted alkylammonium surfactants. For example, attempts to prepare mesostructured Prussian blue (PB) analogues using $(C_{16}H_{33}NMe_3)_n[Fe(CN)_6]$ ($n = 3$ or 4) only led to microcrystalline Prussian blue [18]. The reason for this may be explained by the narrow synthetic condition of such nonoxidic materials [14]. Although there have been significant advances in the design and synthesis of nonoxidic mesostructured materials, the synthesis of these materials using other compositions is a significant challenge.

Prussian blue is the first synthetic coordination compound prepared by Diesbach and Dippel in 1704 [19]. It is now denoted as an important family that includes diverse cyanometallates with similar structures and it has a rich history among artists as well as chemists. Prussian blue analogues have been extensively studied due to their properties as molecule-based magnets with a wide range of Curie points (T_c), from 9 K to room temperature, and various interesting electrochemical properties [20–24]. Especially, nano-sized Prussian blue analogues are being considered as promising candidates for nanomagnetic, biosensing, electrochromic, and biomedical applications [25–30].

We report here the first successful preparation of a new mesostructured PB analogue using $[Fe(CN)_6]^{3-}$ as a building unit in the presence of the linking ion, Co^{2+}. The resulting mesostructure was noncovalently templated by cetylpyridinium cationic micelles. The employment of cetylpyridinium cation template instead of other tetralkylammonium surfactants is a key to our success.

2. Experimental section

2.1. Characterisations

The powder X-ray diffraction (PXRD) measurement was carried out on a Rigaku Rint-2000 instrument. Elemental analysis (EA) was

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performed using EA 1110 elemental analyser for C and H, and LEO SUPRA 55 (JEOL) equipped with an EDAX Genesis 2000 X-ray Microanalysis System for Co and Fe. Images of high-resolution transmission electron microscopy (HR-TEM) were obtained with a JEOL JEM-2100F, 200 kV. The magnetic measurements were performed using a PPMS 6000 (Quantum Design Inc., USA) instrument. Diamagnetic corrections were estimated from Pascal's constants. Fourier transform infra-red spectroscopy (FT-IR) analysis was performed at room temperature on a BIORAD FTS 135 spectrometer. Thermogravimetric analysis (TGA) data were obtained under a constant N_2 flow with a heating rate of 10 K/min in the SETRAM LABSYS TG system.

2.2. Synthesis

The mesostructured material, (CTP)Co[Fe(CN)$_6$] where CTP$^+$ is a cetylpyridinium cation, was prepared by combining $K_3[Fe(CN)_6]$ and $Co(CH_3COO)_2$ in formamide in the presence of the cetylpyridinium bromide (CTPBr) hydrate, $C_{16}H_{33}C_5H_5NBr{\cdot}H_2O$. In a typical synthesis, 1.40 g (3.64 mmol based on the anhydrous form) of CTPBr hydrate was dissolved in 10 mL of formamide at 343 K. To this solution, 0.20 g (0.61 mmol) of $K_3[Fe(CN)_6]$ was added. In a separate flask, 0.15 g (0.60 mmol) of $Co(CH_3COO)_2{\cdot}4H_2O$ were dissolved in 4 mL of formamide at 343 K and added to the aforementioned formamide solution. A deep green solid formed immediately. The mixture was stirred further for 5 h at 343 K. The green solids were isolated by filtration and washed with warm water and dried at 343 K. The yield was about 75%.

3. Results and discussion

The low angle PXRD pattern of (CTP)Co[Fe(CN)$_6$] is displayed in Fig. 1. The three diffraction peaks observed in the low angle region, $2\theta = 2.58°$, 4.49°, and 5.16° which can be indexed to (100), (110), and (200) reflections with the spacing ratio of $1:\sqrt{3}:\sqrt{4}$, are a clear indication of a two-dimensional hexagonal space group *p*6mm [31,32]. The hexagonal lattice parameter, $2d_{100}/\sqrt{3}$, calculated from the PXRD pattern, is $a_H = 39.6$ Å. As with the conventional nonoxidic mesostructured materials [7,8,12,13], we do not observe Bragg diffraction peaks at wide angles, suggesting that the inorganic wall of (CTP)Co[Fe(CN)$_6$] lacks long-range order. In contrast, we were unable to obtain similar mesostructured Prussian blue analogues using Cu^{2+} or Mn^{2+} linking ions instead of Co^{2+} ion under the same synthetic conditions. No X-ray reflections from the mesostructure in a low angle region were observed. In fact, the significant role of different bridging metal ions for the formation of highly ordered mesostructures has often been observed [15–17]. We speculate that subtle variation of the coordination environments of different metal ions with $[Fe(CN)_6]^{3-}$ ion greatly affects the structural orderliness of the final mesostructures.

The pore size and periodicity in the mesostructure of (CTP)Co[Fe(CN)$_6$] were confirmed directly by HR-TEM in Fig. 2. A highly ordered hexagonal phase can be seen from the image. Both the perpendicular and parallel channels relative to the longitudinal axis are observed. An approximate pore–pore distance of 40 Å was estimated from the HR-TEM image, which agrees well with the value obtained from the PXRD data, $a_H \sim 39.6$ Å. The hexagonal symmetry of the pores was further exemplified convincingly, by electron diffraction pattern observed from the sample. The insert in Fig. 2 shows the electron diffraction pattern of (CTP)Co[Fe(CN)$_6$] with hexagonal indexing of the diffraction spots.

Infra-red spectra for CTPBr, $K_3[Fe(CN)_6]$, and (CTP)Co[Fe(CN)$_6$] are shown in Fig. 3. Curve c shows a broad band at 2080 cm^{-1}, corresponding to the stretching vibration mode of the cyanide group in the (CTP)Co[Fe(CN)$_6$] material. Additionally, most of the bands from CTP cation (curve b) appear in the spectrum for (CTP)Co[Fe(CN)$_6$]. It is a concrete evidence for the presence of intact CTP$^+$ cations and $Fe(CN)_6^{3-}$ moieties in the product. Compared with the starting complex (curve a), the (CTP)Co[Fe(CN)$_6$] exhibits a vibration mode of cyanide shifted to a lower frequency by 28 cm^{-1}. This shift may be attributable to the coordination of the cyanide ligands to the Co^{2+} ions in the material. Moreover, curve c shows a broad band around 3426 cm^{-1}, which is characteristics of O–H stretching bands and may originate from the adsorbed water.

We also investigated the chemical composition of (CTP)Co[Fe(CN)$_6$]. The elemental analysis showed weight percentages of 55.21 and 7.35% for C and H, respectively. The atomic metal ratio of Co/Fe was close to 1, which we confirmed from the EDX analysis. The calculated values for $C_{27}H_{38}CoFeN_7$ are C 56.36, H 6.66, Co 10.24, Fe 9.71, and N 17.04%. The thermal behaviour of the product was studied with TGA. Fig. 4 shows a small weight loss of about 2% from room temperature to 429 K, corresponding to desorption of adsorbed water that was shown in the FT-IR spectra. Most weight loss (~75%) occurred in the region between 429 and 773 K. This

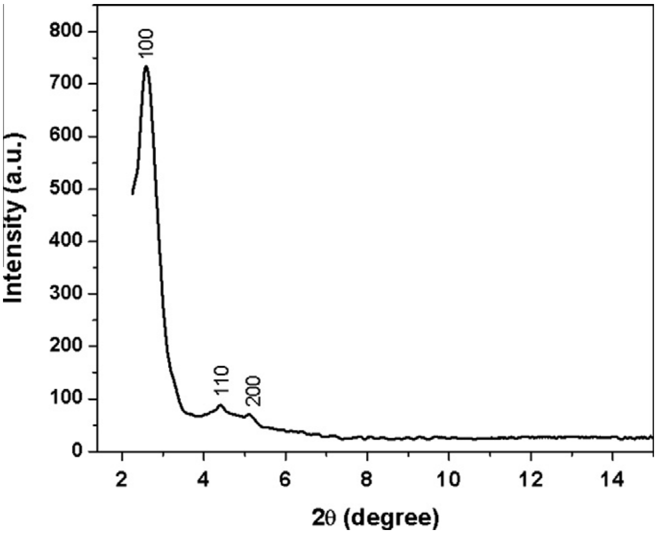

Fig. 1. PXRD pattern of (CTP)Co[Fe(CN)$_6$].

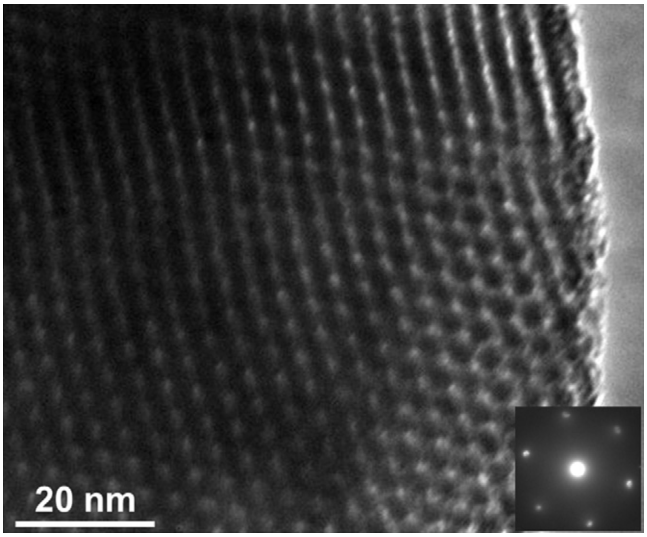

Fig. 2. TEM image and corresponding selected area diffraction pattern of (CTP)Co[Fe(CN)$_6$].