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Morphological evolution of prussian yellow $Fe[Fe(CN)_6]$ colloidal nanospheres

Jianmin Gu*, Shaoyan Fu, Cuihong Jin, Xin Liu, Yahui Gao, Jingxiao Wu, Zhenpan Bian, Hua Tian, Lin Wang, Faming Gao

Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

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ABSTRACT

A simple hydrothermal system was developed for controllable morphologies of the Prussian yellow $Fe[Fe(CN)_6]$ nanostructures in the presence of organic additives. Hollow and solid nanospheres of the Prussian yellow materials were successfully synthesized with suitable experimental conditions. It is found that the amounts of organic additives CTAB could result in the formation of the spherical nanocrystals and the hydrolysis of phosphate in the solution could play a role in the final morphology of the products. A possible formation mechanism of the Prussian yellow nanostructures is proposed.

1. Introduction

Recently, many scientists have explored the correlation between physical or chemical properties and morphology of inorganic nanomaterials driven by the excitement of understanding new science and of potential hope for applications in daily life devices [1–4]. Precise control of the morphologies of inorganic materials is often manipulated with solution self-assembly using electrodeposition method [5], sol-gel method [6], hydrothermal synthesis [7] and so on. Among these methods, hydrothermal process bears the advantage that it can initiate the nucleation in the growth of micro- and nano-crystals, and promote the formation of crystalline products to completion under non-equilibrium conditions [8], which might assist the growth of inorganic materials with special morphologies. In recent years, inorganic salt-assisted hydrothermal method that is convenient and effective, could be helpful for controlling the shape, surface nature, and structure of nanostructures [9]. In general, it is still a great challenge to develop solution self-assembly route for the controllable synthesis of various inorganic nanomaterials with tailored morphology.

Prussian blue (PB), the first synthetic coordination compound, is a mixed-valence iron-(III) hexacyanoferrate(II) compound of composition $Fe_4[Fe(CN)_6]_3 \cdot XH_2O$ with a face-centered-cubic structure, in which Fe^{3+} in the N-coordinated sites is in the high-spin state and Fe^{2+} in the C-coordinated sites is in the low-spin state [10]. Prussian blue and its analogs with different morphologies such as spheres [11], cubes [12,13], polyhedrons [14], wires [15] and tubes [16] have attracted intensive research attention due to their unique properties when applied in molecular magnets [17,18], electrochemistry [19], optics [20], hydrogen storage [21,22] and biosensors [23]. Prussian yellow $FeIII[FeIII(CN)_6]$ (PY), as the chemical oxidation of PB, displays wonderful properties in electrocatalysis and electrochromism [24]. The synthesis of PY materials needs two steps [25]: PB materials are firstly prepared and then obtained PB materials are oxidized to form PY materials. However, this synthesizing method is too complicated or unfit for the achievement of the PY nanomaterials, which is crucial for opening up possibilities for particular functional devices. Inorganic colloidal nanospheres, especially hollow nanospheres, have attracted growing attention [26] because of their potential applications in the controlled release, catalysis and drug delivery [27]. Therefore, it is of great scientific interest and technological significance for the synthesis of the PY colloidal nanospheres that may extend the application in construction of functional device.

Herein, we report the controllable synthesis of Prussian yellow $Fe[Fe(CN)_6]$ nanostructures with the hydrothermal method in the presence of organic additives. The colloidal nanospheres (hollow and solid nanospheres) of Prussian yellow nanomaterials were successfully synthesized. The spherical morphology of the PY nanocrystals is related to the amounts of organic additives CTAB. The effects of phosphate on the morphology of the PY nanomaterials

* Corresponding author.
E-mail address: jmgu@ysu.edu.cn (J. Gu).

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have been realized. Finally, we proposed a possible formation mechanism for the Prussian yellow nanomaterials. These results should give a useful enlightenment for the development of other novel inorganic nanomaterials.

2. Materials and methods

2.1. Materials synthesis

The potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$, Cetyltrimethylammonium bromide (CTAB), sodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) were all purchased from Alfa Aesar and used without further purification. In a typical synthesis, 0.48 mmol $K_3[Fe(CN)_6]$ and 0.12 mmol Na_2HPO_4 were dissolved in 12 mL distilled water under magnetic stirring for 40 min at room temperature until a transparent solution appeared. Then 0.96 mmol CTAB was added to the above solution, and placed in the ultrasonic for 40 min to form a homogeneous solution. Finally, the homogeneous solution was transferred into a 15 mL Teflon-lined autoclave and sealed. After hydrothermally treated at 140 °C for 48 h, the autoclave was cooled to room temperature naturally. The brown (Fig. S1, Supporting Information) samples were separated by centrifugation, washed with distilled water and absolute ethanol repeatedly to remove the ions of the surface before oven drying at 60 °C for 24 h. When 0.12 mmol NaH_2PO_4 was used in the reaction instead of Na_2HPO_4 without changing other conditions, yellow (Fig. S2, Supporting Information) samples can be obtained. The photographs of the dried hollow and solid nanospheres powder were shown in Supporting Information Figs. S3 and S4. These reactions were easily repeated, and the resulted structures were highly stable.

2.2. Characterization

The morphologies of the PY $Fe[Fe(CN)_6]$ colloidal nanospheres were characterized with Transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV) and field-emission scanning electron microscopy (FESEM, XL30, Philips, operating voltage of 20 kV). X-ray diffraction patterns (XRD) were measured using a Rigaku D/max-IIB X-ray diffractometer at a scanning rate of 4°/min with 2θ ranging from 10° to 90°, using Cu Kα radiation (λ = 1.5418 Å). The chemical compositions of the final nanomaterials were characterized with X-ray photoelectron spectroscopy (XPS). Infrared absorption spectroscopy (IR) spectrum was measured at room temperature on a FTIR spectrometer using the KBr Pellet technique.

3. Results and discussion

Fig. 1 shows the typical images of PY hollow nanospheres synthesized when the concentration of $K_3[Fe(CN)_6]$ was 0.04 M, the concentration of Na_2HPO_4 was 0.01 M and the concentration of CTAB was 0.08 M. The low-magnification FESEM image of PY hollow nanospheres indicates that spherical PY nanocrystals are formed on a large scale with diameters of 250–350 nm and shell thickness of 60 nm. (Fig. 1a) Observing from some broken spheres, it is evident that these PY nanocrystals are in hollow structure, which is further confirmed by the higher magnification FESEM image of the cracked hollow spheres (inset of Fig. 1a). The PY hollow nanospheres are further characterized with TEM to examine their fine structures. From an overview TEM image (Fig. 1b), the strong contrast between the dark edge and pale center support the fact that the PY nanospheres have a hollow interior. The thickness of shells exhibits approximate 60 nm as shown in the higher magnification TEM image (inset of Fig. 1b), which is in good agreement with FESEM observation (Fig. 1a). The photograph of the PY hollow nanospheres solution is shown in Supporting Information Fig. S1.

The composition and phase purity of the as-synthesized PY hollow nanospheres were examined using XRD. Fig. 2 presents the typical diffraction pattern of products, which can be readily indexed to a face-centered-cubic phase (space group *Fm3m*). No obvious impurity phase can be detected. The FTIR spectrum of the sample shown in Fig. S5 (Supporting Information) exhibits a peak at 2071 cm^{-1} attributed to the stretching vibration of cyanide (CN) in the PY hollow nanospheres, which is in agreement with FTIR data reported earlier [28,29]. The surface electronic states and the chemical composition of these samples were examined using XPS as shown in Fig. 3. The XPS spectrum of the surface component of the PY hollow nanospheres confirms the presence of C1s, N1s, $Fe2p_{2/3}$, and $Fe2p_{1/2}$ with binding energies of 284.6 eV, 397.3 eV, 708.3 eV and 721.3 eV, respectively [30].

When Na_2HPO_4 was changed to NaH_2PO_4, PY solid nanospheres were obtained with the concentration of $K_3[Fe(CN)_6]$ 0.04 M, the concentration of NaH_2PO_4 0.01 M and the concentration of CTAB 0.08 M (Fig. 4). It would be seen that the overall samples consist of the uniform solid nanosphere with diameters in a narrow range of 350–450 nm as shown in (Fig. 4a). A typical TEM image of the samples is presented in (Fig. 4b), which shows that the diameters of the samples are 350–450 nm, which is consistent with the observation from FESEM images. Fig. 5 shows the XRD pattern of PY

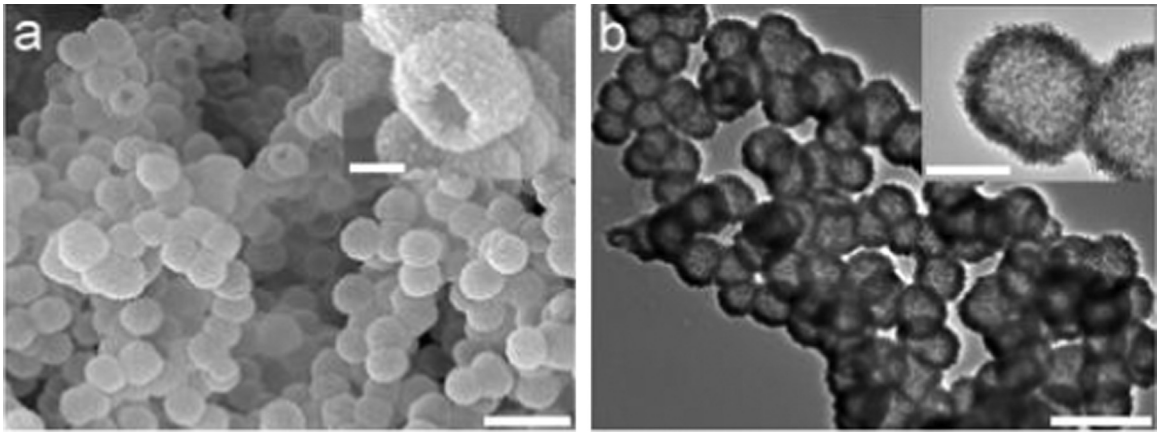

Fig. 1. (a) SEM images of the PY hollow nanospheres. (b) TEM images of the PY hollow nanospheres. Scale bars for (a) and (b) are 700 nm, and scale bars for the insets of (a) and (b) is 150 nm.