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Facile synthesis and optical properties of Prussian Blue microcubes and hollow Fe_2O_3 microboxes

Qiaofeng Wu [a], Guanglei Wu [b], Liuding Wang [a], Wenlong Hu [a], Hongjing Wu [a,*]

[a] Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China
[b] Center of Nanomaterials for Renewable Energy (CNRE), State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, PR China

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ABSTRACT

In this paper, we report a novel strategy for the synthesis of Prussian Blue microcubes via hydrothermal conditions by using $K_3[Fe(CN)_6]$ and glucose for the first time, and then hollow Fe_2O_3 microboxes have been successfully fabricated by calcination from a Prussian Blue microcube precursors. The phase structures and morphologies were studied using X-ray powder diffraction (XRD), scanning electronic microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED). The results depict that highly pure and single crystalline monodisperse hollow Fe_2O_3 microboxes are successfully obtained, which have a diameter ranging from 3 to 5 μm. The optical properties of the Prussian Blue microcubes and hollow Fe_2O_3 microboxes were observed by photoluminescence spectra.

1. Introduction

Hollow interior nanomaterials have received great attention because of their peculiar and fascinating application potentials [1], including catalysis [2], electromagnetic absorption [3], rechargeable batteries [4], drug delivery [5], etc. Conventional routes to synthesize hollow structures involve the growth of a shell of designed materials on various removable or sacrificial templates including hard templates such as inorganic core or polymer and soft ones, for example, microemulsion droplets and even gas bubbles [6–11]. Strategies based on other novel mechanisms, such as layer-by-layer assembly, inward diffusion, Kirkendall effect, Ostwald ripening, or partial dissolution of the cores, have also been reported recently [12–16] for more efficient production of hollow structures. One particularly appealing approach for fabricating metal oxide hollow structures on a large scale is by solid-state decomposition and/or conversion of proper solid precursors [17]. Many hollow spheres of various materials, such as metals, oxides, semiconductors, and polymers, have been successfully fabricated. However, strategies for generating more complex nonspherical hollow structures remain highly challenging. Importantly, it was found that hollow oxide nanoparticles tend to shrink and collapse at high temperatures because hollow structures with extra surface energy are energetically unstable.

In this paper, we present a particularly appealing approach to prepare hollow Fe_2O_3 microboxes using oxidative decomposition of the Prussian Blue precursor. By taking advantage of the unique reactivity and thermal behavior of Prussian Blue microcubes, we formed Fe_2O_3 microboxes by an annealing treatment and the photoluminescence properties were investigated.

2. Experimental

Potassium hexacyanoferrate (III) $K_3[Fe(CN)_6]$, glucose, and ethanol were purchased from Sinopharm Chemical

* Corresponding author. Tel./fax: +86 29 8843 1664.
E-mail address: wuhongjing@mail.nwpu.edu.cn (H. Wu).

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Reagent Co., Ltd. All the chemicals were of analytical grade and used without further purification. Distilled water was used in all experiments.

Briefly, 0.002 mol glucose ($C_6H_{12}O_6$) and 0.002 mol potassium hexacyanoferrate (III) ($K_3[Fe(CN)_6]$) were co-dissolved in 65 mL distilled water. Then, solution was magnetically stirred for 30 min at room temperature until a yellow transparent solution appeared. Then, the yellow solution was transferred into a 100 mL Teflon-lined autoclave and sealed. After hydrothermally treated at 138 °C for 48 h with a heating rate of 2 °C/min, the autoclave was allowed to cool to room temperature naturally. Finally, the final products were separated by filtering off, washed with distilled water and absolute ethanol repeatedly before oven drying at 25 °C for 24 h. The as-prepared precursors were calcined at 350 °C in air for 6 h with a heating rate of 2 °C/min from room temperature to 350 °C.

The XRD patterns of as-prepared Prussian Blue and Fe_2O_3 were examined by a Rigaku D/Max 2500 equipment with Cu Kα radiation operated at 40 kV and 40 mA while X-ray photoelectron spectrum (XPS) was also recorded with the excitation source of Al Kα line. Thermogravimetric analysis (TGA) was carried out with a temperature ramp of 10 °C/min. The morphological analyses were performed on SEM (FEI Quanta 600 FEG). In order to identify the chemical constituent of the samples, selection area electron diffraction (SAED) patterns were taken on a transmission electron microscope (TEM). Room temperature photoluminescence (PL) spectroscopy with the He–Cd (325 nm) laser line as the exciting source was used to know the optical properties of the as-prepared Prussian Blue and Fe_2O_3 in detail.

3. Results and discussion

3.1. Structure and morphology

X-ray diffraction (XRD) of the samples was measured as shown in Fig. 1a. XRD analysis reveals that all the samples obtained can be indexed to the pure cubic structure $Fe_4[Fe(CN)_6]_3$ (JCPDS 73-0687, space group *Fm3m*, $a=b=c=10.13$ Å, $\alpha=\beta=\gamma=90^\circ$). The peaks located at $2\theta=17.64^\circ$, 25.00°, 35.56°, 39.88°, 43.56°, 51.24°, and 57.8° were assigned to the (200), (220), (400), (420), (422), (440), and (620) reflections of the Prussian Blue, respectively [18]. No evidence was found for the existence of impurities in the samples. The thermal decomposition process for the Prussian Blue microcubes was examined by thermal gravity analysis (TGA). As indicated by TGA (Fig. 2), the Prussian Blue microcubes underwent significant weight loss mainly below 350 °C, during which Prussian Blue decomposed into iron oxide. Zhang et al. [17] reported that the Prussian Blue microcubes underwent significant weight loss mainly below 320 °C, during which Prussian Blue decomposed into iron oxide. At a relatively low temperature of 350 °C, the Fe_2O_3 microboxes retained well the size and cubic shape of the Prussian Blue precursor particles. However, such Fe_2O_3 microboxes underwent further crystal growth at increased temperatures. Therefore, the whole thermal transformation process was characterized by two major phases: thermally induced oxidative decomposition of the Prussian Blue microcubes and further crystal growth of Fe_2O_3. So, the reason for the weight loss in 550–670 °C range is further crystal growth of Fe_2O_3 microboxes.

The chemical compositions of the Prussian Blue microcubes were examined by X-ray photoelectron spectroscopy (XPS). To further understand the electronic states of the elements, we paid more attention to the higher-resolution spectra. Graat and Somers [19] reported from the study of iron oxide films that Fe^{3+} exhibits the two characteristic peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at 711.2 and 724.3 eV, with two satellite peaks at 719.5 and 733.6 eV, respectively. For the Fe^{2+}, the two characteristic peaks appear at 709.8 and 722.8 eV, with two satellites at 716.4 and 730.0 eV, respectively. Fig. 1c clearly shows that the two characteristic peaks (708.18 and 720.88 eV) for the Prussian Blue coincide with those of literally reported for Fe^{2+} of $[Fe(CN)_6]^{4-}$. Moreover, an additional XPS peak at 712.18 eV can be attributed to the Fe^{3+} of Prussian Blue. As shown in Fig. 1b, the center of electron binding energy of C 1s is 284.18 eV, and the main peak of the N 1s (Fig. 1d) core-level spectra is fitted with three components at 402.38, 399.28, and 397.28 eV, signifying the existence of C–N ($[Fe(CN)_6]^{4-}$) in the samples [20]. On the basis of the higher-resolution spectra of C 1s, N 1s and Fe 2p, we could conclude that Prussian Blue nanocrystals were successfully synthesized. Fig. 1f shows the survey spectrum of the Prussian Blue sample. In comparison with that of Fe_2O_3, the XPS survey spectrum of the Prussian Blue indicates the presence of C, N, O and Fe elements, which originates from Prussian Blue.

Fig. 3 presents a high-magnification SEM image of a perfect Prussian Blue microcube with mean size of ~3 μm, showing that these microcubes have smooth surfaces. A transmission electron microscopy (TEM) image of a single microcube clearly demonstrated its solid and dense nature without discernible porosity (Fig. 3d).

Fig. 4a and b shows SEM images of hollow Fe_2O_3 microboxes prepared by annealing Prussian Blue in air, from which monodisperse hollow Fe_2O_3 microboxes can be clearly seen with the typical size in range of 3–5 μm. The hollow Fe_2O_3 microboxes retained well the size and cubic shape of the Prussian Blue precursor. XRD analysis (Fig. 1a) confirmed that the sample was composed of standard patterns of γ-Fe_2O_3 (JCPDS card 39-1349) and β-Fe_2O_3 (JCPDS card 39-0238). For hollow Fe_2O_3 microboxes, the detailed Fe 2p spectrum of the samples corresponding to the binding energies was depicted in Fig. 1c, which shows that the binding energies related to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are about 710.78 and 724.18 eV, respectively. It can be clearly seen that shakeup satellite structures at higher binding energy sides (717.88 eV) of the main peaks are the fingerprints of the electronic structure of Fe^{3+} and indicate that Fe^{2+} is absent. The ratio of atomic concentrations calculated from the O 1s (Fig. 1e) and Fe 2p peak areas deviates from the theoretical value of 1.5 (The actual value is 9.5), suggesting OH and O_2^- groups on the surface [21].

TEM (Fig. 4c and d) clearly shows the white contrast at the center of the microcubes with the black thick shell, suggesting the hollow center inside the microcubes. Hence, during the oxidative decomposition of Prussian Blue, Fe_2O_3 grew into a relatively smooth and dense crystalline shell,