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Letter

Facile preparation, characterization and optical properties of rectangular $PbCrO_4$ single-crystal nanorods

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Abstract

Monoclinic $PbCrO_4$ nanorods, with a rectangular cross section, a typical length of 6–7 μm, a width of 80–150 nm, and a width-to-thickness ratio of 2–5, have been successfully synthesized via a simple precipitation reaction, followed by a hydrothermal treatment without using any templates and additives. The as-synthesized products were characterized with X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, scanning electron microscopy and selected area electron diffraction, UV–vis absorption spectra and photoluminescence spectra. It was found that the length of as-obtained $PbCrO_4$ nanorods relies on the pH value and the aging temperature, and the optical properties of $PbCrO_4$ nanorods depend on their length. The intensities of UV–vis absorbance of $PbCrO_4$ nanorods slightly decrease with increasing the length of nanorods. On the contrary, the intensities of room-temperature photoluminescence of $PbCrO_4$ nanorods increase with increasing the length of nanorods.

Keywords: Lead chromate; Nanorod; Rectangle; Preparation; Hydrothermal reaction; Characterization; Optical property

1. Introduction

Lead chromate ($PbCrO_4$) is an important photo-electricity solid functional material that has been widely used in decorative systems, protective systems, and mass coloration of fibers, plastics, papers, elastomers and rubbers [1–3]. In addition, it has also been used as a host material for photosensitizer, humidity-sensing resistor and so forth [4,5]. Usually, $PbCrO_4$ exists in two kinds of crystal structures: the stable monoclinic structure and the unstable orthorhombic structure [1,6]. Since the discovery of carbon nanotubes in 1991 [7], one-dimensional (1D) nanostructured materials (nanotubes, nanobelts, nanowires, and nanorods) have attracted considerable attention from the scientific community due to their distinctive geometries, novel physical and chemical properties, and potential applications in numerous areas such as nanoscale electronics and photonics [8–11]. Recently much effort has been directed toward understanding the electronic, magnetic, and optical properties of these nanostructures because these unique size- and shape-dependent properties are physically or chemically different from their bulk counterparts [12–14]. Therefore, the synthesis of lead chromate ($PbCrO_4$) nanorods with well-controlled size and shape is of great significance for its applications.

To date, there have been a few reports on the preparation of lead chromate nanorods [15–19], but few efforts were put to synthesize uniformly ultra-long and rectangular $PbCrO_4$ nanorods, and to investigate their related optical properties. Herein, we develop a facile hydrothermal route for the synthesis of rectangular $PbCrO_4$ nanorods without using any templates or additives. Excitingly, the length of the as-obtained $PbCrO_4$ nanorods can be easily manipulated ranging from several hundred nanometers to several micrometers by varying the aging temperature and pH value. The $PbCrO_4$ nanorods show the photoluminescence (PL) emission and the intensity of photoluminescence increases with increasing the lengths of $PbCrO_4$ nanorods, while the emission-band shape remains the same. To the best of our knowledge, this is the first report on the synthesis of rectangular $PbCrO_4$ nanorods with controllable length and luminescence intensity so far.

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2. Experimental

All chemicals used were of analytical grade and used as received without further purification. Aqueous solutions of K_2CrO_4 (0.5 M) and of $Pb(NO_3)_2$ (0.5 M) were first prepared as stock solutions. In a typical synthesis, 0.2 ml K_2CrO_4 aqueous solution (0.5 M) was added into 50 ml distilled water with a pH value of 3. Then, 0.2 ml $Pb(NO_3)_2$ aqueous solution (0.5 M) was quickly injected into the above solution under continuous stirring by using magnetic stirrer. This gave a final $PbCrO_4$ concentration of 2 mM. The mixture was further stirred for 5 min and then transferred into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was heated and kept at 150 °C for 24 h, and then was allowed to cool to room temperature. Finally the obtained products were centrifuged and washed with distilled water and absolute ethanol for several times. The final samples were dried in a vacuum at 80 °C for 6 h. As reference experiments, the samples were also synthesized with variation of pH value and temperatures, while all other conditions were kept the same.

The morphologies of resulting $PbCrO_4$ products were characterized with scanning electron microscopy (SEM, JSM-5610LV, Japan), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010F at 200 kV, Japan). The powder X-ray diffraction (XRD) patterns were obtained on an HZG41B-PC diffractometer using Cu Kα radiation at a scan rate of 0.05° $2\theta\,S^{-1}$ to characterize the crystalline phase of the products. UV-visible (UV–vis) absorption spectra of the as-prepared $PbCrO_4$ solid powders were recorded for the dry-pressed disk samples at room temperature on a UV–vis spectrometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as an absorption standard in the UV–vis absorption experiment. The photoluminescence (PL) spectra of the as-prepared $PbCrO_4$ solid powders were measured at room temperature on a Perkin-Elmer LS 50B luminescence spectrometer using a 400 nm excitation line.

3. Results and discussion

The XRD pattern of $PbCrO_4$ nanorods obtained in a typical synthesis condition is shown in Fig. 1a. All the reflection peaks can be readily indexed to a pure monoclinic phase (space group: $P2_1/n$ (14)) of $PbCrO_4$ with lattice constants $a = 0.712$ nm, $b = 0.743$ nm, $c = 0.679$ nm and $\beta = 102.42°$, which are in good agreement with the literature values (JCPDS: 73-2059). The reaction between K_2CrO_4 and $Pb(NO_3)_2$ can be expressed as follows:

$$K_2CrO_4 + Pb(NO_3)_2 \rightarrow PbCrO_4\downarrow + 2KNO_3 \quad (1)$$

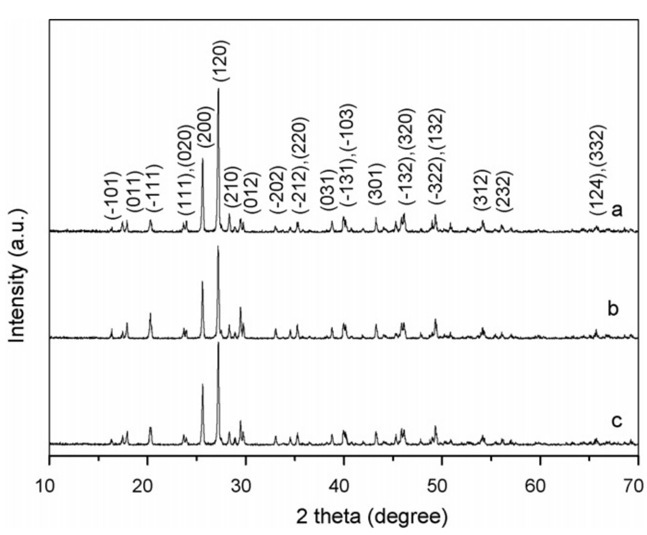

Fig. 1. XRD patterns of $PbCrO_4$ nanorods obtained at different pHs and aging temperatures: (a) pH 3, $T = 150$ °C; (b) pH 7, $T = 150$ °C; (c) pH 7, $T = 25$ °C.

The morphology and size of the resulting product are observed with SEM and TEM. Fig. 2a shows a representative SEM image of the products obtained in a typical synthesis condition. It can be seen that the products are predominantly composed of long and straight nanorods, with a typical length of 6–7 μm, a size of 80–150 nm, and a high length-to-size ratio of 40–80. The structures of the products were further examined using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Fig. 2b shows the low magnification TEM image of typical $PbCrO_4$ nanorods. As can be seen from Fig. 2b, the nanorods show uniform size over their entire lengths, and some of the nanorods stick together. Fig. 2c shows an amplified TEM image of the as-prepared $PbCrO_4$ nanorod. It can be seen that cross-section of $PbCrO_4$ nanorod is rectangle. After carefully examining many $PbCrO_4$ nanorod samples, it was found that the width, thickness and a width-to-thickness ratio of $PbCrO_4$ nanorods are about 80–150 nm, 30–50 nm and 2–5, respectively. The selected area electron diffraction (SAED) pattern (inset in Fig. 2c) taken from a single nanorod and recorded from the [0 1 0] zone axis indicates that the nanorods are single crystals with a preferential growth direction along the [1 0 1] direction. Fig. 2d is a typical HRTEM image of a single-crystalline $PbCrO_4$ nanorod, which shows the clearly resolved interplanar distance $d_{-2,0,2} = 0.269$ nm and $d_{3\,0\,1} = 0.203$ nm, and further confirms that the nanorods grow along the [1 0 1] direction.

To find out the influence of pH value and aging temperature on the morphology and size of $PbCrO_4$ nanorods, a set of experiments were carried out with variation of pH value and temperatures. When pH value was decreased and other reaction conditions were kept the same, no obvious morphological change was observed for $PbCrO_4$ nanorods (corresponding SEM pictures are not shown here). However, when pH value was increased to 7, the as-obtained products were mainly short rectangular nanorods with an average length of about 2–3 μm (Fig. 3a). The corresponding XRD pattern of the as-obtained nanorods at pH 7 is shown in Fig. 1b. Comparing Fig. 1b with a, it can be found that the two XRD patterns are almost the same except for the obvious weakening of the (1 2 0) diffraction peak in Fig. 1b, indicating that the obtained products in this case are still monoclinic $PbCrO_4$. This confirms that adjusting pH value will not affect the phase composition of $PbCrO_4$ crystal, and a low pH value is favorable for the crystallization and growth of $PbCrO_4$ nanorods. This may be due to the fact that a low pH value extends the induction time of $PbCrO_4$ precipitation [20], but how does pH exactly affect on the formation of $PbCrO_4$ nanorods is still unclear.

Further investigation showed that when the aging temperature was varied to room temperature (25 °C) and all other conditions kept the same, only some shorter rectangular nanorods with a length range from several hundred nanometers to several micrometers were obtained (as shown in Fig. 3b). Corresponding XRD pattern (as shown in Fig. 1c) can also be well indexed to monoclinic $PbCrO_4$ phase. On the basis of the above experiment, it can be concluded that a low aging temperature is unfavorable for the growth of $PbCrO_4$ nanorods, but has no influence on the phase structure. This may be ascribed to the lack of Ostwald