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A facile hydrothermal route to the large-scale synthesis of $CoWO_4$ nanorods

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Abstract

Single-crystalline $CoWO_4$ nanorods with average diameter of 20 nm and lengths of 100 to 300 nm have been successfully synthesized by a hydrothermal method using only $CoCl_2$ and Na_2WO_4 as reaction reagents and distilled water as solvents. The structure and morphology of the nanorods were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM). This facile method does not need any seed, catalyst, surfactant, or template, thus is promising for large-scale and low-cost production with high-quality.

Keywords: Nanocrystalline materials; Hydrothermal synthesis; $CoWO_4$

1. Introduction

Over the past few decades, increasing attentions have been drawn to the synthesis of one-dimensional (1D) nanostructures, such as nanowires, nanotubes, nanorods, nanobelts and *etc.*, because of their distinct chemical and physical properties that are distinctly different from their bulk counterparts and potential applications in nanodevices as components and interconnects [1,2]. Generally, 1D nanostructures can be prepared by thermal evaporation [3], chemical vapor deposition (CVD) [4], electrodeposition [5], template-directed growth [6], solution-phase chemical methods [7] and so on. Although these strategies are widespread demonstrated effective methods to fabricate 1D nanostructures, large-scale application of these methods has been limited due to their some shortcomings, such as some methods suffering from high temperature, special apparatus, expensive templates or surfactants, and others needing complicated process, or even tedious procedures. Recently, significant efforts have been devoted to develop green method that take into account human and environmental impact in the selection of reactants and the reaction conditions for material fabrication [8,9]. Many recent studies have demonstrated that hydrothermal process is an effective and versatile route for the synthesis of 1D nanostructures in terms of low-cost, high efficiency and good potential for high-quantity production [10].

Metal tungstates, an important material of ABO_4-type ternary metal oxides, have aroused much interest due to their luminescence behavior, industrial catalysts and high potential applications [11,12]. Up to now, a number of 1D nanostructured metal tungstates have been synthesized by solution-phase methods. For example, single-crystalline $BaWO_4$ [13], $CdWO_4$ [14], $ZnWO_4$ [15], $FeWO_4$ [15], $MnWO_4$ [15], $PbWO_4$ [16] nanostructures and so on, have been successfully fabricated. However, to the best of our knowledge, few studies have been carried out concerning the synthesis of cobalt tungstate ($CoWO_4$) 1D nanostructures. Herein, we report a hydrothermal approach for the synthesis of single-crystalline $CoWO_4$ nanorods on large-scale by the reaction of aqueous $CoCl_2$ and Na_2WO_4 solutions. This method is promising for large-scale and low-cost synthesis of $CoWO_4$ nanorods with high-quality because no harmful surfactants, templates or solvents are used.

2. Experimental

In a typical process, 25 ml $CoCl_2$ aqueous solution (0.2 mol L^{-1}) was added into 25 ml Na_2WO_4 aqueous solution

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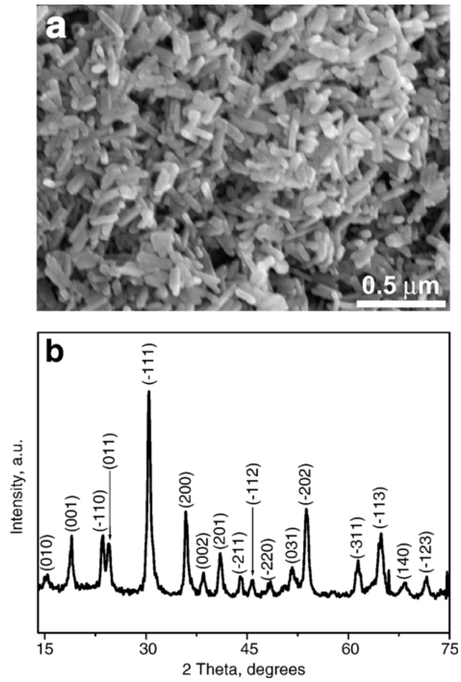

Fig. 1. (a) A typical SEM image and (b) XRD pattern of the as-synthesized $CoWO_4$ nanorods.

(0.2 mol L^{-1}) with the assistance of strong magnetic stirring to form a homogeneous precursor at room temperature. After stirring for 10 min, the final mixture was directly transferred into a 50 ml Teflon-lined stainless autoclave, filled up to 80% of its capacity. The autoclave was maintained at 160 °C for 24 h in an oven and then cooled naturally to room temperature. The precipitate was collected, filtered off and washed with distilled water and absolute ethanol several times. After drying in air at 60 °C for 60 min, the final powders were obtained.

The X-ray diffraction pattern (XRD) was recorded on a Rigaku D/max-rA diffractometer with Cu K_α radiation (λ=1.5406 Å). The morphology of the sample was examined by scanning electron microscope (SEM, Hitachi S-4700). Transmission electron microscope (TEM) and selected-area electron diffraction (SAED) studies were carried out with a JEM-100CXII microscope operated at 100 kV. High-resolution transmission electron microscope (HRTEM) images were recorded on a JEOL-2010F high-resolution transmission electron microscope, operated at 200 kV. The as-synthesized powders were first dispersed in ethanol by ultrasonic treatment. A small drop of the dispersion was transferred to a holey carbon film supported on a copper grid for TEM and HRTEM observations.

3. Results and discussion

A typical SEM image of the as-synthesized $CoWO_4$ nanorods is shown in Fig. 1a. The SEM image indicates that the obtained product is composed of large-scale nanorods, with diameters ranging from 10 to 30 nm and length in 100–300 nm. The SEM observation also demonstrates that almost 100% yield of CoWO4 nanorods can be easily obtained by this simple method. Fig. 1b shows the XRD pattern of the $CoWO_4$ nanorods. All diffraction peaks can be perfectly indexed to the monoclinic structure phase of $CoWO_4$ (JCPDC 15-0867) with cell constants of a=4.9478 Å, b=5.6827 Å, c=4.6694 Å and β=90°. No characteristic peaks from impurities are detected, indicating that the products are highly phase-pure. The relatively broad peaks probably result from the small diameter of the as-synthesized $CoWO_4$ nanorods.

Fig. 2a displays a representative low-magnification TEM image of the as-synthesized $CoWO_4$ nanorods. High-magnification TEM image (Fig. 2b) shows that the nanorods have an average diameter of about 20 nm and lengths in 100 to 300 nm, which is in agreement with the SEM observation. As also can be seen from the TEM image, some nanorods tend to self-assembled to form bundles. Fig. 2c shows the corresponding SAED pattern taken from the selected nanorods in Fig. 2b, which is very sharp, indicating that the product is highly crystalline. Fig. 2d shows a HRTEM image of an individual nanorod, and the clear lattice fringes also demonstrate its single-crystalline nature. The observed lattice spacing of 0.34 nm and 0.47 nm in Fig. 2d correspond to the (110) and (001) planes of the monoclinic $CoWO_4$, respectively. These are also reflected in the corresponding fast Fourier transform (FFT) pattern (inset in Fig. 2d). HRTEM image reveals that the $CoWO_4$ nanorod grows along [001] direction. Energy dispersive X-ray spectrum (EDS) (Fig. 2e) shows only high-intensity peaks for Co, W and O, together with the Cu and C peaks generated from carbon film supported copper grid. Quantitative analysis shows that the molar ratio of Co to W to O is about 1:1:4, which is in agreement with the nominal composition of $CoWO_4$.

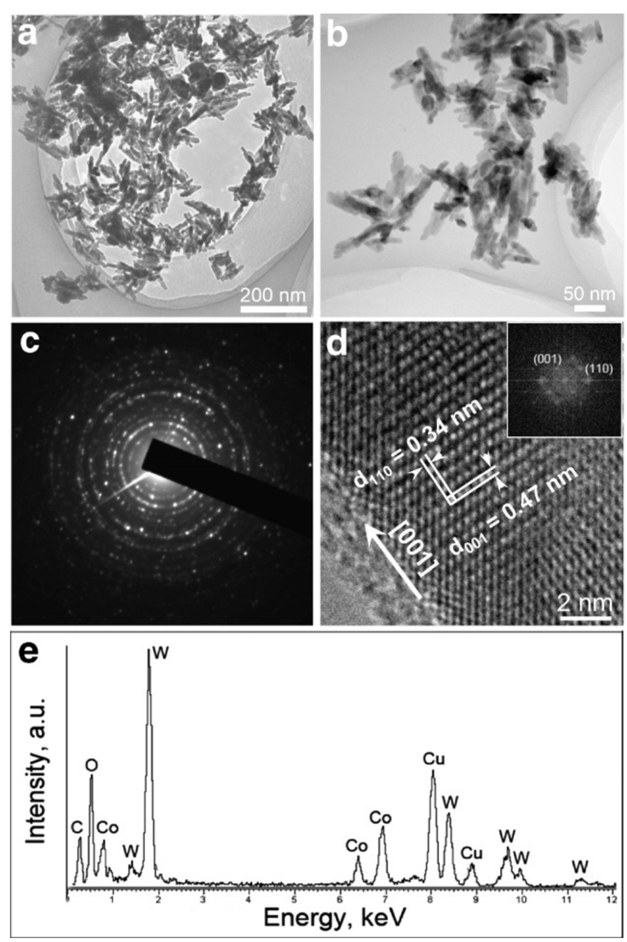

Fig. 2. (a) Low and (b) high magnification TEM images of the $CoWO_4$ nanorods, (c) a SAED pattern taken from the nanorods, (d) HRTEM image of an individual $CoWO_4$ nanorod and (e) EDX spectrum of the nanorods. The inset in (d) shows the corresponding FFT pattern.

It is well known that the crystal growth is controlled by the extrinsic and intrinsic factors, including the degree of supersaturation, diffusion of the reaction, surface energy, crystal structure and *etc.* in the solution reaction system [17,18]. Regarding to the formation mechanism of the $CoWO_4$ nanorods through hydrothermal approach, it is clear that the growth process is not surfactant-assisted or template-directed, because no surfactants or templates are introduced into the reaction system. The formation of $CoWO_4$ nanorods can be thought to be having a habit to form this morphology due to its crystal structures. Yu et al. [15] have recently reported the general synthesis of metal tungstate nanorods by the hydrothermal process without using templates or surfactants and found that the formation mechanism of the nanorods can be explained by the spherical diffusion model well. In the spherical diffusion model, there is a spherical diffusion layer of solute around each crystal during diffusion-controlled lateral growth [15]. Therefore, the formation process of $CoWO_4$ nanorods could also be explained by this theory in our system since the synthesis condition of $CoWO_4$ nanorods is similar to the previous study [15].

4. Conclusions

In conclusion, we have reported a facile hydrothermal approach for the large-scale synthesis of $CoWO_4$ nanorods with a diameter of 10 to 30 nm and lengths in 100–300 nm without using any surfactants or templates. This method does not need any seed, catalyst, surfactant, or template, thus is promising for large-scale and low-cost production with high-quality and might also be extended to synthesize other 1D nanostructures of metal tungstates.

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