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$_2$WO$_4$ 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$_2$WO$_4$ 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$_2$WO$_4$ aqueous solution...
(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$_\alpha$ radiation ($\lambda=1.5406$ 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 CoWO$_4$ 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 $\beta=90^\circ$. 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. 1. (a) A typical SEM image and (b) XRD pattern of the as-synthesized CoWO$_4$ nanorods.

![Fig. 1](image1.png)

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) EDS spectrum of the nanorods. The inset in (d) shows the corresponding FFT pattern.

![Fig. 2](image2.png)
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 CoWO₄ 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 CoWO₄ 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 CoWO₄ nanorods could also be explained by this theory in our system since the synthesis condition of CoWO₄ 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 CoWO₄ 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.

References