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A facile synthesis of $SrWO_4$ nanobelts by the sonochemical method

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ABSTRACT

$SrWO_4$ nanobelts have been synthesized via a facile and fast sonochemical route. The samples were characterized by XRD, SEM and TEM techniques. Experimental results showed that the concentration of Na_2EDTA and high-intensity ultrasonic irradiation played important roles in controlling the morphologies of $SrWO_4$. Room-temperature photoluminescence of $SrWO_4$ with various morphologies have also been investigated. Results showed that $SrWO_4$ nanobelts possessed good photoluminescent properties, suggesting that $SrWO_4$ nanobelts could be used in novel optoelectronic devices.

1. Introduction

One-dimensional (1D) nanomaterials, such as nanowires, nanorods and nanobelts, have aroused extensive attention because of their unique physical and chemical properties and potential application in nanodevices [1,2]. Therefore, much effort has been greatly focused on the synthesis of the 1D nanomaterial by a variety of methods. Among them, the sonochemical method has been extensively used in the synthesis of 1D nanomaterials [3]. When liquids are irradiated by high-intensity ultrasound, high temperatures (>5000 K), pressures (>20 MPa) and cooling rates (>1010 K/s) can be achieved upon the collapse of the bubbles [4]. The remarkable environments provide a unique platform for the growth of 1D nanomaterials.

Scheelite-type metal tungstates have received great attention because of their wide applications in photoluminescence, solid state optical masers, optical fibers, scintillating materials, humidity sensors, catalysts and so on [5,6]. Strontium tungstate ($SrWO_4$) is a typical scheelite-type tungstate and is widely used in optoelectronic industry and solid state laser system due to its luminescence behavior and stimulating Raman scattering property [7]. Recently, much works have been focused on the synthesis of $SrWO_4$ with different morphologies to enhance its physical properties and applications [8,9]. For example, $SrWO_4$ nanopeanuts and nanorods have been prepared by a solvothermal-mediated microemulsion method [10]. $SrWO_4$ with kayak-like shapes have also been synthesized via a microemulsion method [11]. However, to the best of our knowledge, no work has been reported on the synthesis of $SrWO_4$ nanobelts until now.

Herein we described the controllable synthesis of $SrWO_4$ nanobelts through a facile and fast sonochemical route. The morphologies and sizes can be readily tuned by adjusting experimental parameters. The photoluminescence (PL) spectra of the as-obtained $SrWO_4$ samples were also studied.

2. Experiment

All of the reagents were of analytical purity and used without further purification. In a typical synthesis, an aqueous solution of $Sr(NO_3)_2$ in the presence of Na_2EDTA was mixed with a Na_2WO_4 solution in a 100 mL round-bottom flask to give a final concentration of 10 mmol L^{-1} $Sr(NO_3)_2$, 10 mmol L^{-1} Na_2WO_4, and 7.5 mmol L^{-1} Na_2EDTA. The above mixture solution was exposed to high-intensity ultrasound irradiation under ambient air for 60 min. Ultrasound irradiation was accomplished by immersing a high-intensity ultrasonic probe (Kunshan Co., China, KBS-250, 6 mm diameter; Ti-horn, 20 kHz, 250 W) directly in the solution at room temperature. Finally, a white precipitate was centrifuged, washed with distilled water and ethanol, and dried in air.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/max-RA (Japan) X-ray diffractometer (Cu Kα radiation, $\lambda = 0.15406$ nm). Field-emission scanning electron microscopic (FE-SEM) images were taken on a HITACHI S-4800. The transmission electron microscopic (TEM) images were carried out on a JEOL JEM-2100. The photoluminescence (PL) spectra were measured on a HITACHI F-7000 fluorescence spectrometer at room temperature.

3. Results and discussion

Fig. 1a shows the typical XRD patterns of the as-prepared $SrWO_4$ products. All peaks of the patterns can be assigned to the tetragonal

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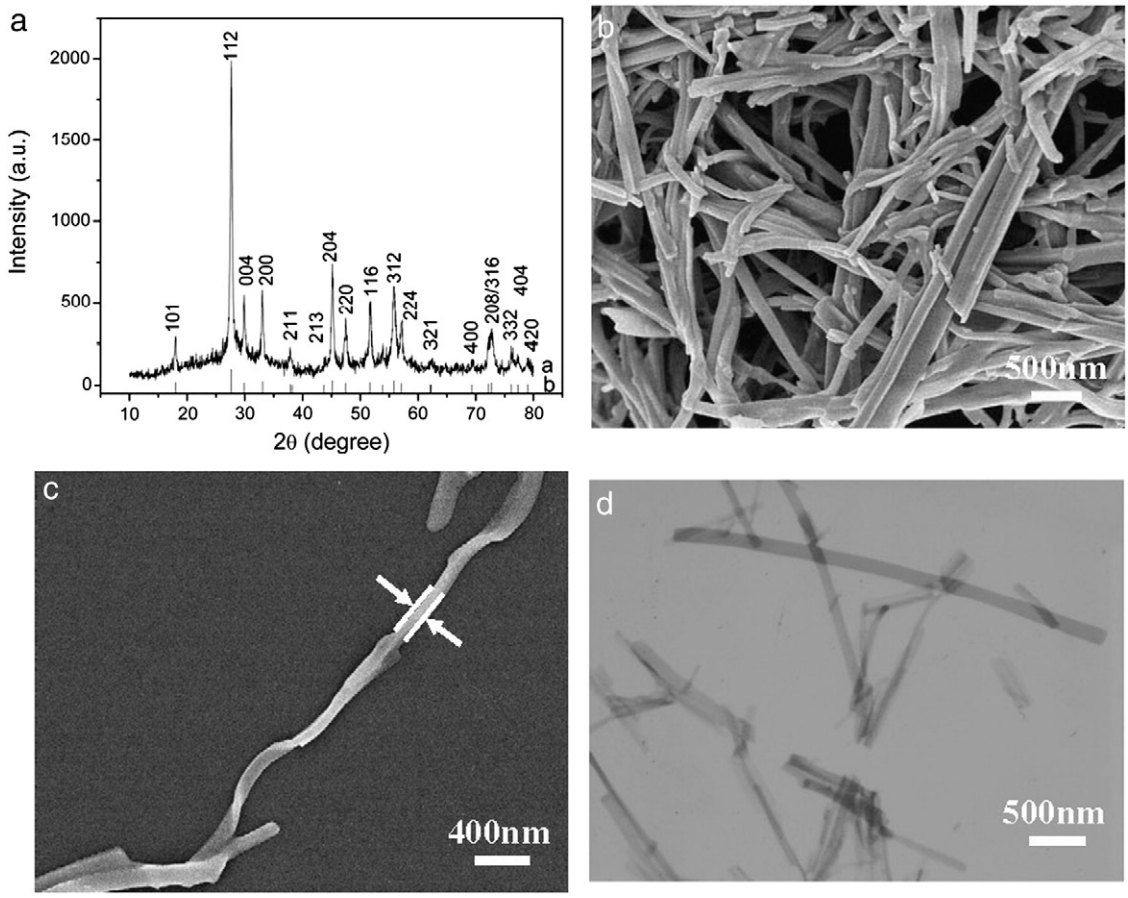

Fig. 1. (a) XRD patterns of the as-prepared $SrWO_4$ samples and standard tetragonal $SrWO_4$ (JCPDS No.08-0490); (b) FE-SEM image, (c) (c) a single nanobelt FE-SEM image, and (d) TEM image of the as-prepared $SrWO_4$ samples.

phase $SrWO_4$ with a lattice constant ($\alpha = 5.416$ Å and $c = 11.95$ Å), which are in good agreement with JCPDS No. 08-0490. It can be considered that the as-obtained samples have a good crystallinity and no other impurities were observed in the products.

The typical FE-SEM image is shown in Fig. 1b. It can be seen that the product represents a belt-like morphology with width of 50–300 nm and length of several micrometers. Single nanobelt shown in Fig. 1c indicates that the thickness of the nanobelt is about 50 nm. TEM image in Fig. 1d further confirms that the width is in the range of 50–300 nm and the length can reach several micrometers even to tens of micrometers.

It was found in our experiment that the concentration of Na_2EDTA has significant effects on the morphology of $SrWO_4$ nanostructures. When we adjusted only the concentration of Na_2EDTA, and other reaction conditions were kept constant, the morphology of the products changed obviously. If the experiment was carried out without Na_2EDTA, the product contained irregular morphologies (Fig. 2a). When the concentration of Na_2EDTA was 2.5 mmol L^{-1}, the products are a sphere-like morphology with a diameter of 1–2 μm (Fig. 2b). It can be clearly seen that an individual sphere is composed of tens of similar nanoparticles, and these nanoparticles are connected with each other with random orientation. With the concentration further increasing to 5.0 mmol L^{-1}, the sample was mainly nanobelts with a width of 50−100 nm, and a length of 50–1000 nm, as shown in Fig. 2c. In addition, there are also some nanoparticles existing in the final product. However, while the concentration of Na_2EDTA was 7.5 mmol L^{-1}, the morphology of the sample only consists of the nanobelts. A large number of nanobelts with a width of 50–100 nm and a length of 1–2 μm can be observed in Fig. 2d. If the concentration was further increased to 10.0 mmol L^{-1}, the morphology was kept unchangeable (Fig. 2e).

Consequently, the morphology of $SrWO_4$ could be adjusted by the concentration of Na_2EDTA. This might be attributed to the coordination effect of Na_2EDTA. Under a relatively low concentration of Na_2EDTA, $EDTA^{2-}$ ions are few, so the formation of $SrWO_4$ is mainly a homogeneous nucleation, and the sphere morphology is obtained. In high concentrations, Sr^{2+} ions are surrounded and coordinated by $EDTA^{2-}$ ions. Furthermore, $EDTA^{2-}$ ions can be selectively adsorbed onto some surfaces of crystals facets, which could significantly decrease the growth rates of these surfaces and lead to highly anisotropic growth [12]. As a result, nanobelt is the final morphology.

In addition to the concentration of Na_2EDTA, high-intensity ultrasonic irradiation is another important influence factor on the shape of the $SrWO_4$ products. When experiments were conducted in vigorous electric stirring and the other reaction condition kept constant, $SrWO_4$ dumbbell-shaped with a diameter of 2 μm and a length of 6 μm (Fig. 2f) could be obtained in the final products. So, high-intensity ultrasonic irradiation plays an important role in the preparation of $SrWO_4$ nanobelts.

The PL properties of $SrWO_4$ with various morphologies were also studied. Fig. 3 shows the room-temperature emission spectra of $SrWO_4$ nanobelts, dumbbells and sphere morphologies using the same excitation line of 350 nm. All of the three morphologies of $SrWO_4$ exhibited similar emission peaks at about 467 nm. The emission peak might be ascribed to the $^1T_2 \rightarrow {}^1A_1$ transition of electrons within $[WO_4]^{2-}$ anions [13]. For most emission spectra of