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Cobalt-doped disulfide nanotubes prepared by exfoliation–intercalation–hydrothermal adulteration

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Abstract

Cobalt-doped disulfide nanotubes were fabricated by a technique of exfoliation–intercalation–hydrothermal adulteration. WS_2 and MoS_2 powder was used as primary materials and was exfoliated into single layer by *n*-butyllithium. Then Co^{2+} cations entered into MoS_2 and WS_2 matrix through a hydrothermal process with $CoCl_2$ aqueous solution. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDX), respectively. XRD results indicate that multimetal disulfide can be prepared by this approach. TEM images show that the morphology of the products is bamboo-like nanotube with open-end, tip-end and joint. HRTEM images show that the tip-end, joint and wall of bamboo-like nanotubes are of inorganic fullerene-like (IF-like) nanostructures. EDX results show that the components of bamboo-like nanotubes are Co, Mo, W and S. A possible formation mechanism of bamboo-like nanotubes was suggested.

Keywords: Inorganic compound; Nanostructures; Intercalation reaction; Chemical synthesis; X-ray diffraction

1. Introduction

Following the discovery of fullerene-like structure of disulfide compounds, considerable attention has been focused on the fabrication of disulfide nanocompounds. Various reports on the structure, synthesis, and properties of such IF-like structures and inorganic nanotubes are published, together with the possible application [1,2]. Up to date, fullerene-like structures of disulfide compounds have been synthesized successfully by a lot of approaches, such as heating thin films in air atmosphere [3,4], gas-phase growth [5,6], electron irradiation [7], STM induced crystallization [8], microwave plasma [9], solvothermal method [10,11], γ-irradiation method [12], hydrothermal method [13], gas–solid reaction method [14–16], catalyzed transport method [17,18], heating WO_3-coated single-walled carbon nanotube bundles [19,20], thermal decomposition method [21,22], electrochemical/chemical synthesis [23] and the reaction of MoO_3 nanobelts and S [24]. While fabricating such metal disulfide in the chemical approaches, we find problems in structure controlling. For instance, the formation of MoS_2 or WS_2 polyhedron or onion crystal is, similar to the carbon onion, a rare event [9]. Moreover, the chemical methods generally are difficult for products in mass. Tenne had declared that when the amount of IF nanoparticle per batch exceeded 15g in gas–solid reaction, the quality of IF nanoparticles would deteriorate [16]. In order to obtain multimetal disulfide IF nanoparticles in mass, we need a new approach.

Since 1970s, lamellar disulfide has been intensively studied, especially the intercalation technique [25–27]. During intercalation, the coordination patterns of lamellar disulfide changed greatly along with a lot of defects, which enable the doping of other ions [28,29]. On the other hand, after transition metal cations entered WS_2 or MoS_2 matrix, the band properties of the matrix and bond angles of S–M–S changed [22,29]. These characteristics can be observed in the characterization of multimetal disulfide IF nanoparticles as-fabricated.

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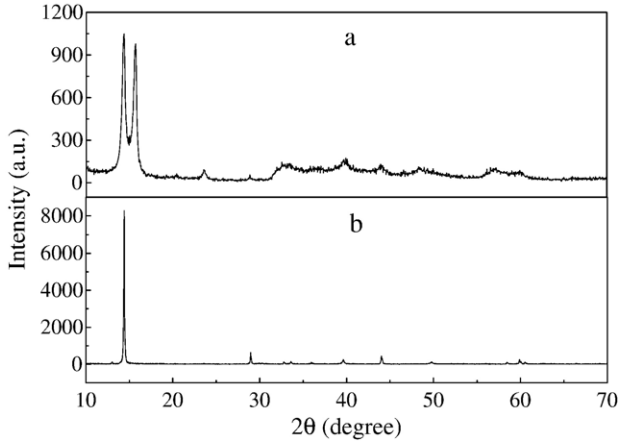

Fig. 1. XRD patterns of the samples (a) powder exfoliated by butyllithium and (b) product.

In this paper, disulfide nanotubes were prepared on a large scale by exfoliation–intercalation–hydrothermal adulteration, using the mixture of WS_2 and MoS_2 powder as precursors. The results show that the morphology of the products is bamboo-like nanotubes with IF-like nanostructures. A possible formation mechanism of bamboo-like nanotubes was suggested.

2. Experimental

The mixture of WS_2 (AR>99% 700–1100 nm, ACROS ORGANICS) and MoS_2 (AR>99% 300–700 nm, ACROS ORGANICS) powder with the weight ratio of 1:1 (WS_2 powder: 15 g, MoS_2 powder: 15 g) was exfoliated by 2.2 M of *n*-butyllithium in a container under N_2 atmosphere at room temperature for a week, rinsed by hexane for six times and dried in vacuum of 0.01 Pa at 60 °C. The as-prepared samples were put into an autoclave of 50 ml lined with Teflon as inner wall, which filled with 35 ml of 2 M $CoCl_2$ aqueous solutions. The temperature of the autoclaves was raised to 180 °C and maintained for 72 h, and then cooled down to room temperature to obtain the designed products. After rinsed by deionized water for six times, the products were dried at 80 °C.

The resulting products were characterized by XRD, TEM, HRTEM and EDX, respectively. X-ray diffraction (XRD) was performed with a D8 ADVANCE X-ray at room temperature, using quartz monochromator Cu Kα1 radiation source (λ=0.1541 nm) under a voltage of 36 kV and a current of 36 mA. The XRD patterns were recorded with a step size of 0.020° from 10° to 75° for exfoliated samples and 5° to 85° for products, and a step time of 0.3 s. Transmission electron microscopy (TEM) was performed with JEM-2000 under a voltage of 160 kV and a current of 89 mA. Before characterization, the samples were dispersed ultrasonically in ethanol and dropped onto Cu-grid coated with carbon membrane. High-resolution transmission electron microscopy (HRTEM) was performed with JEM-2010, equipped with EDX, under a voltage of 200 kV and a current of 101 mA, using the same sample TEM investigated.

3. Results and discussion

Typical XRD patterns of the samples at different stages are shown in Fig. 1. XRD patterns of the mixture of WS_2 and MoS_2 powder exfoliated by butyllithium are shown in Fig. 1a. The preeminent characteristic of XRD patterns of the mixture is double peaks, and the intensity of double peaks is much stronger than that of the other peaks, as shown in Fig. 1a. This indicates that the mixture powder was exfoliated into single layer [28]. The double peaks exhibited MoS_2 and WS_2 phases, respectively. XRD patterns of the products are shown in Fig. 1b. The products are mixture of 2H and 3R disulfide phases (JCPS card 87-2416 and 86-2308). Based on Fig. 1b, one conclusion can be drawn that no impurity phase exists in the products.

The morphology of the products is shown in Fig. 2. The typical morphology of nanotube is displayed in Fig. 2a and e. TEM image in Fig. 2a reveals the presence of long, well-defined bamboo-like nanotube with the length of over 2.0 μm. The nanotube is bamboo-like with several joints and the distance between the joints is irregular. The diameter of the nanotube is about 160 nm at the left end and becomes smaller and smaller from the one end to the other end, then closes at one end from the TEM observation. The open-end of nanotube is shown in Fig. 2b and its diameter is about 160 nm. The wall of the nanotube contains two sheets (Fig. 2b). The details and interior structures of

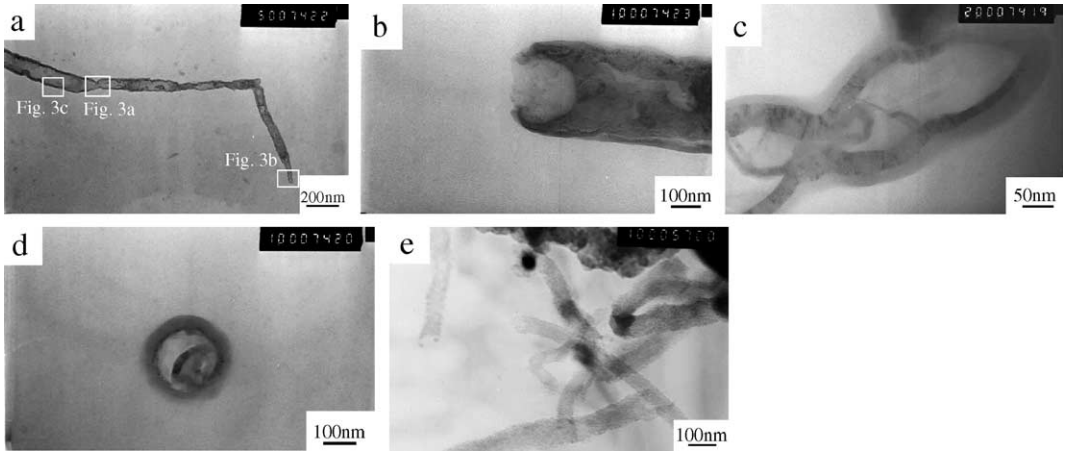

Fig. 2. TEM images of bamboo-like nanotubes. (a) Morphology, (b) open-end, (c) tip-end and joint, (d) cross section and (e) typical morphology.