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Vertically aligned single-crystal zinc sulfide nanotubes with hexagonal cross-sections and optical properties

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ABSTRACT

Without the presence of any catalysts or templates, single-crystal zinc sulfide (ZnS) nanotubes have been successfully synthesized in bulk quantity by a facile and controllable process based on thermal evaporation of ZnS powders. X-ray diffraction (XRD), energy dispersed X-ray spectrometry (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used to characterize the products. The results indicate that the synthesized ZnS nanotubes are single-crystalline with hexagonal cross-sections. The diameters of the ZnS nanotubes vary from 200 to 700 nm and lengths are about several micrometers. The growth of ZnS nanotubes is controlled by the conventional rolling mechanism. And the room temperature photoluminescence (PL) indicated a stable and strong green emission centered at about 542 nm, which may result from nanotube effects.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], a large number of inorganic solids with layered or nonlayered crystal lattices have been found to form tubular nanostructures due to their hollow structure and quantum effects [2–4]. As an important II–VI semiconductor with a wide bandgap of 3.8 eV, ZnS has received much attention due to their unique optical, electrical, and optoelectronic properties [5,6] and potential applications in many aspects, such as sensors [7], lasers [8], photocatalyses [9], and light-emitting diodes [10]. Over the past decade, a considerable effort has been made to prepare and investigate ZnS tubular structures by various template routes [11–18]. For example, a sacrificial template strategy was reported to generate the ZnS nanotubes via chemical conversion of ZnO columns or nanoribbons (as templates) with H_2S [11,12], which is not environmentally friendly process. Additionally, the as-synthesized products were poly-crystal instead of single-crystal. Hu et al. [13] synthesized Sn-filled wurtzite-type ZnS nanotubes using Sn nanorods as a solid template by physical vapor deposition. However, the as-obtained samples were mixed with filling phase which would affect their performance in real devices. More recently, preparation of hollow ZnS micro/nanotubes via a sacrificial template was reported, in which the ZnO/ZnS core/shell structures were synthesized firstly, ZnS tubular structures were then obtained by selectively etching of ZnO core. However, the synthetic method was difficult and complex precursor was used [14,15]. For technological advance in the future, environmentally friendly and facile synthetic routs are desirable. In this paper, a simple and inexpensive process without any catalysts and templates is used to prepare large-scale single crystalline ZnS nanotubes with hexagonal cross-sections based on thermal evaporation of ZnS powders in N_2 flow. The growth of nanotubes is controlled by a classic rolling mechanism, which is inspired by the natural phenomena of a piece of foliage or a piece of wet paper curling into scrolls during its drying process [4]. Photoluminescence (PL) characterization of the ZnS nanotubes shows that these nanotubes exhibit a strong green emission (2.29 eV), together with a weak ultraviolet (UV) emission (3.47 eV). The prepared ZnS nanotube may have a broader application in photodetectors, display tube and LED, and may be a promising photocatalytic material due to the large surface-to-volume ratio.

2. Experimental

In a typical experiment, ZnS powders were used as starting materials without the presence of catalysts or templates. The synthesis process was carried out in a horizontal electronic resistance furnace, which was heated by silicon–carbon rods. The ZnS powders (2.0 g) were put in the front of an alumina boat, which was covered with a quartz plate to maintain a higher ZnS vapor pressure. The alumina boat was placed in the middle of the quartz tube that was inserted in the horizontal tube furnace. Prior to heating, the system was flushed with high-purity N_2 for 1 h to

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eliminate O_2. Then, under a constant flow of nitrogen gas 10 sccm and vacuum conditions ($\sim 10^{-1}$ mbar), the furnace was rapidly heated to 1000 °C, and held at the temperature for 60 min. After the system was cooled down to room temperature, a large piece of yellow wool-like products were seen in the alumina boat. The phase of the as-synthesized products was studied by X-ray diffraction (XRD) (X'pert MRD-Philips; Holland). The morphology of the samples was characterized using scanning electron microscopy (SEM) (XL 30-S-FEG; Holland). A little of the products obtained so was ultrasonically dispersed in ethanol and a drop of this sample was deposited on a holey copper grid with carbon film, and characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEOL-2010, operated at 200 kV; Japan) with energy dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED). PL measurements were carried with a He–Cd (325 nm, 15 mW) laser as an excitation source.

3. Results and discussion

Fig. 1a shows the SEM image of ZnS nanotube arrays. It can be observed that the synthesized products consist of a large quantity of nanotubes with open-ended and typical diameters of about 200–700 nm. Still, large-scale TEM image (Fig. 1b) further clearly indicates that the product consists of relatively straight tubular structure. The diameter and the wall thickness of the single ZnS nanotubes are about 200–400 nm and 100 nm, respectively. The nanotubes have high aspect ratio, and their lengths can reach about several micrometers. The SAED pattern (Fig. 1c), taken from this nanotube marked with black circle (Fig. 1b), is composed of the regular clear diffraction dots, which reveal the single crystalline nature of this nanotube. The corresponding HRTEM image is shown in Fig. 1d, where interplanar spacing of 2.92 Å is calculated in the lattice plane [103]. The nanotube with a high crystal structure is demonstrated, which is compatible with SAED mentioned above.

XRD pattern is shown in Fig. 2a, all the diffraction peaks can be indexed to wurtzite-type ZnS with lattice constants of $a=0.3825$ nm and $c=0.6270$ nm (JCPDS no. 10-434). No other diffraction peaks corresponding to oxides or impurities have been found, indicating that the final product is highly crystallized with high purity. From the EDS spectrum (shown in Fig. 2b), we can see that only Zn and S peaks are observed together with the Cu peaks which are generated by the copper grid. Furthermore, according to the quantification of the EDS peaks, the atomic ratio of Zn and S is close to the stoichiometry ratio of ZnS (1:1), which confirms a stoichiometric composition of ZnS.

To investigate the formation mechanism of ZnS nanotubes, ZnS samples in different deposition times are obtained and the structure growth processes are examined by SEM. As shown in Fig. 3, we postulate that the nucleation and growth of the ZnS nanotubes involve three stages: the formation of ZnS layered structures at the initial stage (Fig. 3a), the layered structures roll up to form half-pipe structures (Fig. 3b), and the subsequent growth of nanotubes (Fig. 3c). When the system was heated, the nuclei under thermodynamic conditions may agglomerate and self-assemble into lamellar structures firstly. Since no catalyst-assisted techniques or template-confined synthesis is used in the experiment, ZnS vapor can be solidified directly when ZnS nanopowders are evaporated up to vapors during the heating process. We think the layered nanostructures of ZnS may be a vapor–solid (VS) growth process. The lamellar intermediates subsequently rolled up from the edges because sufficient energy was provided to overcome the strain energy barrier. The driving force lies in the built-in asymmetry of the unit cell along one zone axis and the thermal stress existing at high temperature [4]. After 60 min of heating treatment, all the half-pipe structures bent and rolled up to form vertically aligned 1D nanotubes (Fig. 3c). When the interaction between neighboring nanolayers is reduced at the edges of the layer, nanotubes will form through the rolling of these lamellar nanostructures [18]. As a result, we believe that these nanotubes were grown through the well-known rolling mechanism.

The room temperature photoluminescence (PL) of the ZnS nanotubes was examined and shown in Fig. 4. The emission spectrum reveals that the as-synthesized product has a weak UV emission at 357 nm and a strong green emission band centered at 542 nm. Usually, two emissions are observed from semiconductor nanomaterials – excitonic and trapped luminescence. The excitonic emission is sharp and located near the absorption edge,

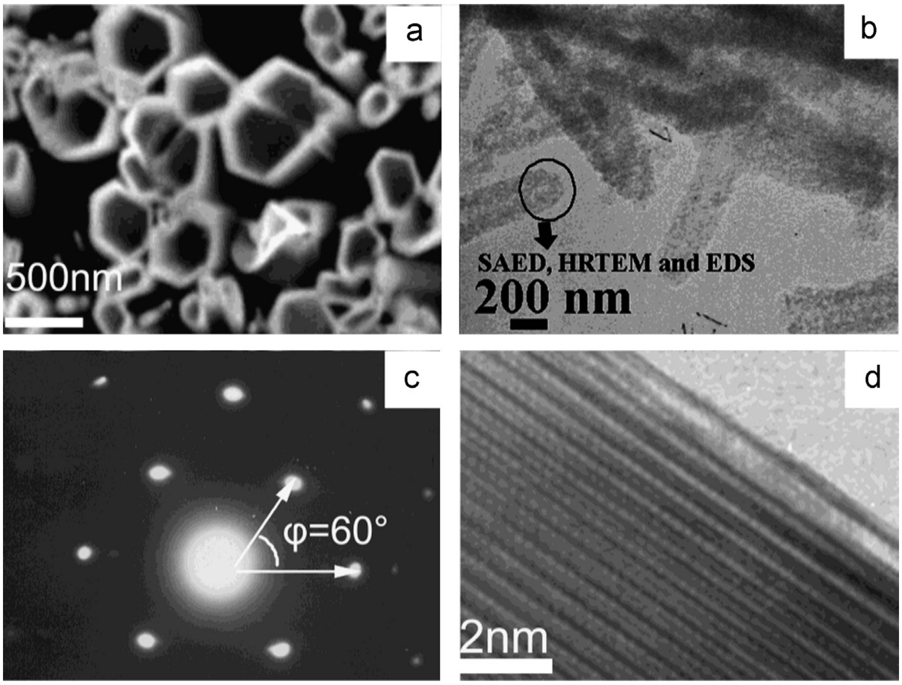

Fig. 1. Morphologies of ZnS nanotubes. (a) SEM. (b) TEM. (c) SAED. (d) HRTEM.