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Preparation of ZnS nanotubes via surfactant micelle-template inducing reaction

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Semiconductor ZnS nanotubes, with outer diameters in the range of 37–52 nm and lengths up to 3 microns, have been successfully synthesized from solutions containing a nonionic surfactant, Triton X-100 (t-octyl-$(OCH_2CH_2)_xOH$, $x = 9,10$). The as-synthesized nanotubes have been characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). The growth mechanism of nanotubes has also been discussed.

1. Introduction

Currently, one-dimensional (1D) nanostructured materials, such as nanotubes [1–7] and nanowires (nanorods) [8–15], have attracted much attention due to their intriguing properties. These new nanoscale materials are expected to have many potential applications in both mesoscopic research and development of nanodevices [16, 17]. Demonstrations of nanotube-based devices include a prototype super-bright, paper-thin, flat-panel TV display by the Korea company SAMSUNG and artificial muscles for micro robots by the U.S. company Allied Signal [18]. The semiconductor nanotubes may also be potentially used as supercapacitors [19]. ZnS and other II–VI compound semiconductor are important materials for fabrication of many optoelectronic devices, such as optical coatings, solid-state solar cell windows, electrooptic modulators, photoconductors, field effect transistors, etc. [20]. Considerable attention has been attracted to synthesize their 1D nanostructured materials. For example, Lan *et al*. [20] synthesized ZnS nanorods by annealing precursor ZnS nanoparticles in NaCl flux. Wang *et al*. [21] prepared single-crystal ZnS nanowires by thermal evaporation of ZnS powders onto a silicon substrate with the presence of Au catalyst. Wu *et al*. [22] obtained winding ZnS nanowires from reverse micelle solutions. However, the reports about ZnS nanotubes are still very rare. So far, only one group, i.e., Dloczik *et al*. [6] reported the preparation of ZnS nanotubes by chemical conversion of ZnO columns. But the procedures and devices they employed are relatively complicated. Herein we report a simple, convenient and efficient method to synthesize ZnS nanotubes.

Surfactant micelle-template inducing reaction is a particularly efficient method to prepare 1D nanoscale materials. The surfactant molecules can form rod-like micelle when the concentration of the surfactant is 10 times above the critical micelle concentration (CMC). The rod-like micelle can act as templates to induce the growth of 1D nanoscale materials. Prof. Rao *et al*. [4] have successfully synthesized CdS nanotubes and nanowires by this method. In this letter, we reported synthesis of ZnS nanotubes using Triton X-100 micelle as templates, selecting CS_2 as sulfur source and oil phase. To the best of our knowledge, the synthesis of ZnS nanotubes by this method has never been reported before.

2. Experimental

All of the reactants and solvents used in our reaction system are analytical grade and used without any further purification. In a typical procedure, zinc acetate ($Zn(AC)_2$, 0.2772 g, 2.5 mmol) was added into a 100 ml beaker containing 20 ml distilled water, to form a transparent solution A. Next, Triton X-100 (1.05 ml), the aqueous ammonia solution (28% wt, 0.6 ml) and CS_2 (0.3 ml, 4.9 mmol) were added into a 250 ml three-necked flask containing 20 ml distilled water. Subsequently, solution A was introduced from the beaker into the flask at room temperature. Then, the flask was heated from 20 to 60°C at heating rate about 1°C/s, and kept at 60°C for 24 h. All steps above were carried out with constant stirring. The flask was then cooled to room temperature naturally. The precipitate was filtered off, washed with distilled water and absolute ethanol for several times, then dried in vacuum at 60°C for 2 h. The as-obtained white powder was collected for characterizations.

XRD data were got from a Japan Rigaku D/max RB X-Ray diffractometer (Cu K_α radiation, $\lambda = 0.15418$ nm). The morphology was observed by transmission electron microscopy. The TEM images and SAED were taken by a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The samples used for TEM observations

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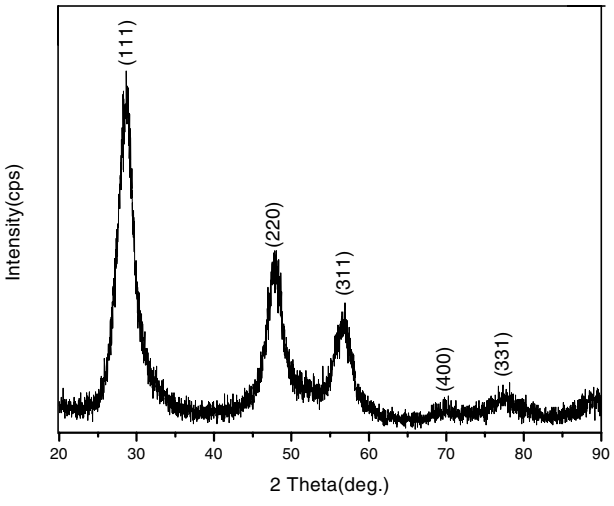

Figure 1 XRD pattern of as-synthesized ZnS nanotubes.

were prepared by dispersing some products in absolute ethanol followed by ultrasonic vibration for 10 min, then placing a drop of dispersion onto a copper grid coated with a layer of amorphous carbon.

3. Results and discussion

Fig. 1 showed the XRD pattern of as-synthesized white powder by micelle-template inducing reaction in the presence of a nonionic surfactant, Triton X-100. All diffraction peaks in the pattern could be indexed to cubic-phase ZnS with crystal constant of $a = 5.38$ Å, which were in good agreement with those of bulk ZnS crystal (JCPDS Card No. 01-0792). The broadening of the diffraction peaks was due to the small size effect. Miller indices of cubic-phase ZnS were marked in this pattern. No other crystalline impurities were detected within the detection limit indicating the as-synthesized product was of high purity. The XRD pattern suggested that the as-synthesized white powder was pure cubic-phase ZnS structure.

The morphology of the as-synthesized product was obtained from TEM (Fig. 2). Fig. 2a and b showed TEM images revealing the general morphology of ZnS nanotubes. Most of the products were tubular structure. The outer diameters ranged from 37 to 52 nm. Fig. 2c showed the TEM images of two individual nanotubes. A nanotube with length up to 3 μm was exhibited in Fig. 2c. A magnified image of the rectangular area in Fig. 2c was shown in Fig. 2d. One could see that the outer diameter and inner diameter of as-synthesized ZnS nanotube were 44 and 26 nm, respectively. The wall thickness of the nanotube was therefore around 9 nm. The SAED pattern of the nanotubes, given as an inset in Fig. 2d, showed diffuse rings indicating the polycrystalline nature of the material. The rings corresponding to $d(111) = 3.1038$ Å and $d(220) = 1.9012$ Å were clearly seen.

The growth mechanism of ZnS nanotubes might be as the following [5]:

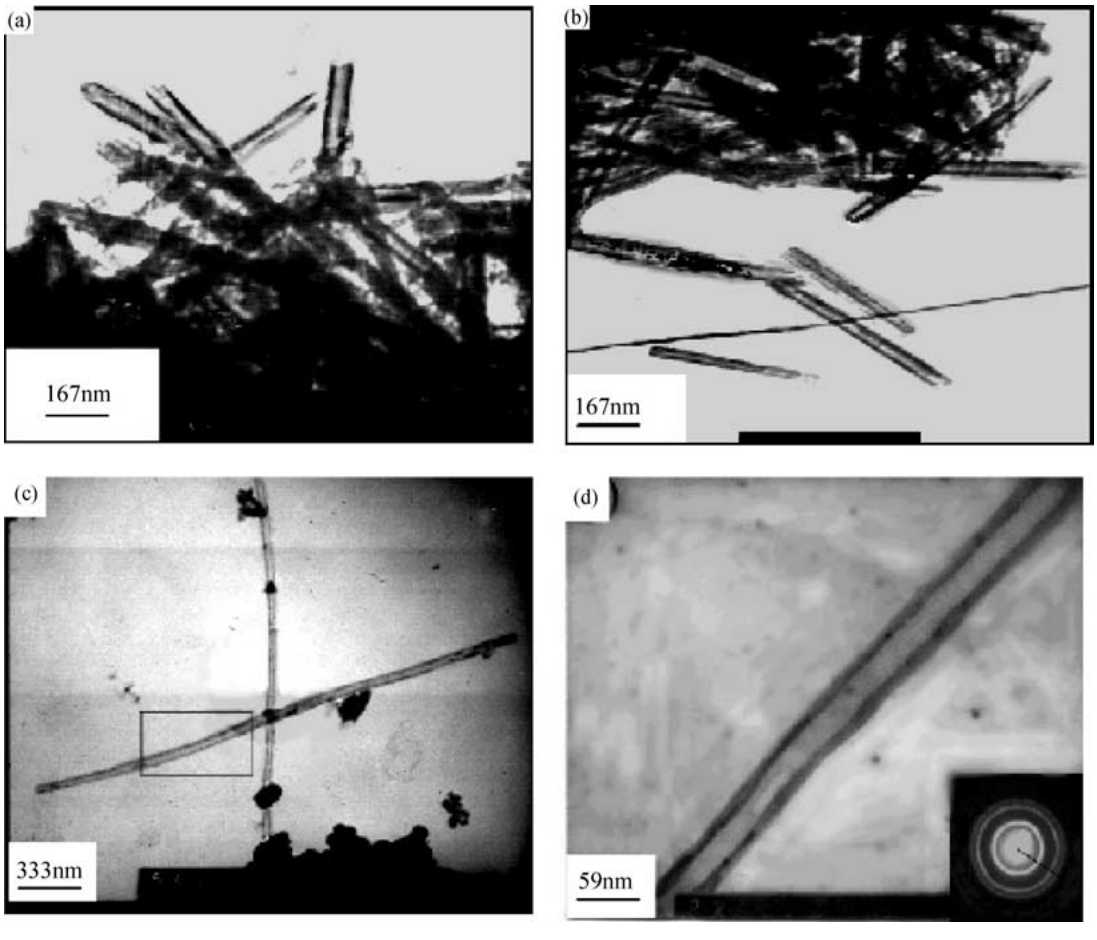

Figure 2 TEM images of as-synthesized ZnS nanotubes: (a) and (b) images of ZnS nanotubes, (c) two single relatively longer ZnS nanotubes and (d) a magnified image of the rectangular area in Fig. 2c. The inset is the SAED pattern of as-synthesized ZnS nanotubes.

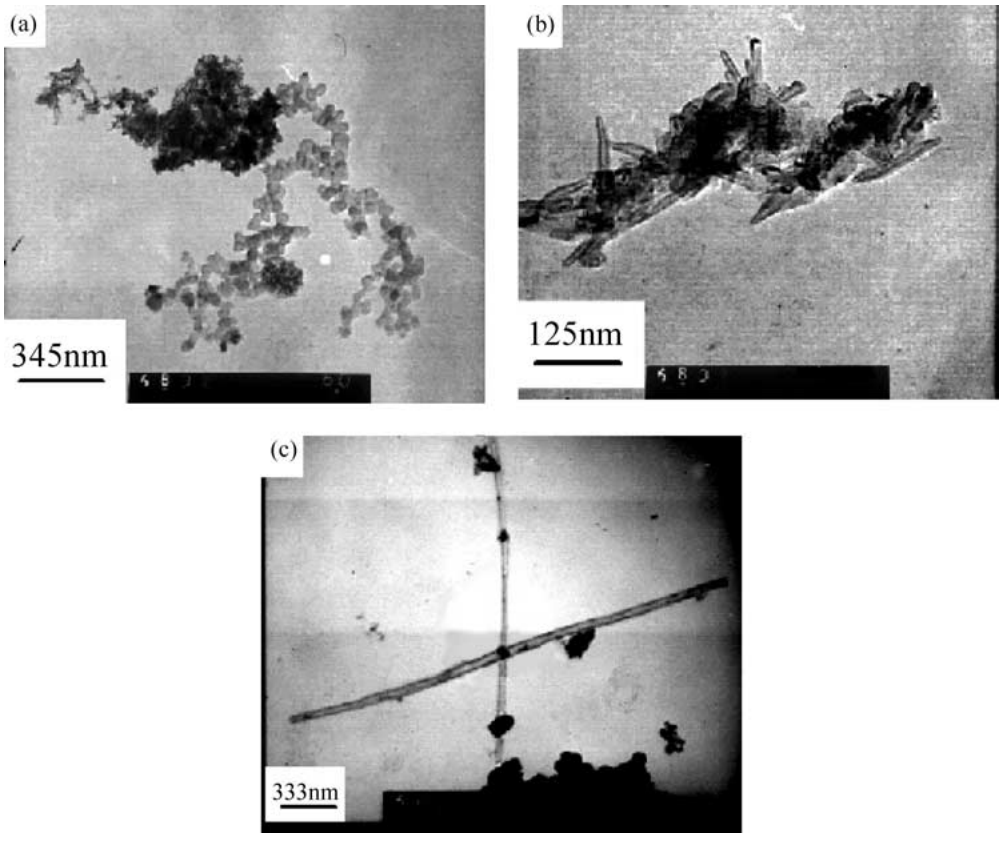

Figure 3 TEM images of as-synthesized ZnS at different reaction conditions: (a) Triton X-100 (0.70 ml), 5 h, (b) Triton X-100 (1.05 ml), 5 h and (c) Triton X-100 (1.05 ml), 24 h.

CS_2 is insoluble in water and can exist as small oil droplets in water under stirring. When the concentration of the surfactant is ten times of the critical micelle concentration (CMC), the surfactant will form both hydrophobic and hydrophilic (O/W) rod-like micelle, in which the CS_2 oil phase can be enwrapped to form CS_2 cylinders. Due to the concentration difference between CS_2 oil phase (inside) and water phase (outside) of the rod-like micelle, the Zn^{2+} and NH_3 transfer through the surfactant micelle to react with CS_2 to produce ZnS. When the unreacted CS_2 cylindric cores are removed at a temperature above the boiling point of CS_2 (46–47°C) and surfactant is removed by water and absolute ethanol, the ZnS tubular shell will be left as nanotubes. In this process, surfactant micelle play important roles of templates in confining the growth of nanotubes.

In this reaction, the molar ratio of H_2O to surfactant ($R = [H_2O]/[\text{surfactant}]$) will influence the formation of nanotubes remarkably. The quantity of surfactant decides the shape of micelle, which can be exhibited by the morphology of the final products. Fig. 3a and b showed the TEM images of as-prepared ZnS with different quantity of Triton X-100. When the quantity was 0.7 ml, ZnS could only grow into nanoparticles with mean diameters around 30 nm (Fig. 3a), so the surfactant might form sphere-like micelle. While when it was 1.05 ml, ZnS nanotubes with outer diameters around 15 nm and lengths up to 150 nm would be obtained (Fig. 3b), so we could conjecture that rod-like micelle might form at this concentration. Moreover, formation of longer and thicker ZnS nanotubes requires sufficient time. If the aging time was 24 h, ZnS could grow into nanotubes with lengths up to 3 μm and outer diameters around 42 nm. While when it was 5 h, as-obtained ZnS nanotubes would be shorter and thinner (Fig. 3c and b).

The template-directed methods provide a good control over the uniformity and dimensions of nanotubes. However, most 1D nanomaterials synthesized using this kind of methods are polycrystalline in structure, an unwanted feature that may limit their use in device fabrication and fundamental studies [23].

Inducing crystallization by rapid thermal annealing the nanotubes under appropriate conditions may be a reasonable way. Ye *et al*. [24] have synthesized single-crystal Bi_2S_3 nanotubes by adopting the conventional evaporation method using nanometer-sized Bi_2S_3 powders as starting material. So, it is promised to obtain single-crystal ZnS nanotubes at appropriate temperature and atmosphere by thermal annealing. Further research work about it needs to be carried out in the future.

4. Conclusions

ZnS nanotubes with outer diameters in the range of 37–52 nm, and lengths up to 3 μm, have been successfully synthesized through a simple surfactant micelle-template inducing reaction. The whole reaction system is made up of Triton X-100 rod-like micelle, CS_2 as the oil phase and sulfur source, $Zn(AC)_2$ as zinc source in water phase. The formation of nanotubes is remarkably influenced by the quantity of surfactant and aging time. Considering the simplicity and efficiency of this method, it is promised to be used to synthesize other metal sulfide nanotubes.

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