Microwave-Assisted Solvothermal Synthesis of Radial ZnS Nanoribbons

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Using microwave as the heating method, radial ZnS nanoribbons have been successfully synthesized for the first time via a solvothermal procedure in enthylenediamine, combined with thermal treatment in a nitrogen flow. The resulted nanoribbons have a length up to 700 nm, a width of 10–20 nm, and a typical thickness of 3 nm.

The physical and chemical properties of nanoparticles are essentially different from those of bulk materials and largely dependent on their size, shape, and surface chemistry. It is generally accepted that one-dimensional (1D) nanostructures, including wires, rods, tubes, belts, and ribbons, can be expected to exhibit superior and fascinating characteristics and thus provide good models for investigating the physical and chemical properties on dimensionality and size[1–3] because of their anisotropic morphologies.

Tremendous research effort has been devoted to the synthesis and characterization of 1D nanoscale materials among which ZnS is one of the most attractive candidates because of its wide band gap.[4] As an important II–VI semiconductor, ZnS has extensive applications as phosphors and catalysts and also has potential utilities in electronic and optoelectronic nanodevices. However, only few papers reported on the fabrication of 1D ZnS nanostructures[5–13] especially for nanoribbons and nanobelts,[9–13] which prove very intriguing for researchers recently. ZnS nanoribbons[11] and nanobelts[12,13] possess a distinct 1D structure with a rectangular cross section and have been achieved by thermal evaporation methods employing ZnS as the raw materials.[11–13] A high reaction temperature and a reductive or protective atmosphere are required. And the products show relatively large sizes with the length of 100 μm to several millimeters, width between 40 nm and 30 μm, and thickness of tens of nanometers.

Microwave is an electromagnetic wave composed of both electronic and magnetic field components. Microwave irradiation is an efficient and distinct heating method in that the heating effect derives from the interaction of dipole moments of molecules with the electromagnetic radiation that changes its direction in high frequency. Microwave heating has been used in industry for decades. However, synthesis via microwave heating is a relatively new technique in chemistry[14] and has nowadays been developed to prepare inorganic materials.[15] Recently the applications of microwave-assisted synthetic procedures are extending to the preparation of nanoparticles,[16] owing to the unique reaction effects such as rapid volumetric heating, high reaction rates, small particle size, narrow size distribution, and high purity.[17]

In this paper, we present the first solvothermal synthesis of the hitherto smallest radial ZnS nanoribbons in enthylenediamine (en) via microwave irradiation. The nanoribbon directly obtained by this method is a complex of ZnS and en, which decomposes into pure ZnS with the wurtzite structure after annealing in a nitrogen flow.[18] The finally obtained ZnS nanoribbons have a length up to 700 nm, a width of 10–20 nm, and a typical thickness of 3 nm.

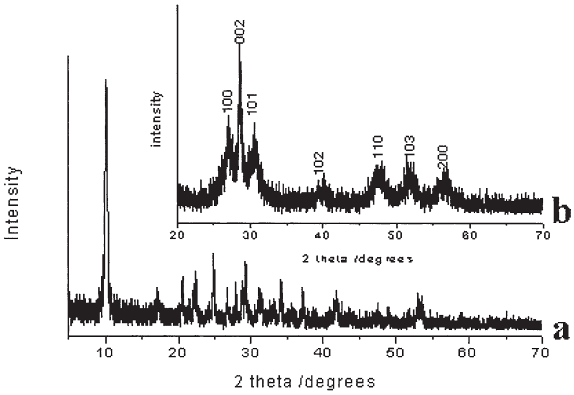

Figure 1. Wide-angle XRD patterns of (a) as-synthesized and (b) annealed ZnS nanoribbons.

Our synthesis was carried out in a microwave sample preparation system model MK-III. The system was equipped with Teflon PFA vessels that were transparent for microwave energy, working at 1200 W with a discontinuous motion to keep the pressure constant during the reaction. The pressure inside the Teflon vessels was instantaneously monitored via an optical fiber displacement sensor. In a typical synthesis, 0.065 g $Zn(NO_3)_2\cdot 6H_2O$ (0.22 mmol) was mixed with 0.17 g thiourea (Tu, 2.24 mmol) and 20 g en. The mixture was stirred vigorously to form a clear solution and then placed in the microwave system and the reactions were processed for 10 min, keeping the pressure inside the vessel at 10 atm. The products were recovered by centrifugation, washing with ethanol for several times and annealed by heating at 400 °C in a nitrogen flow for 4 h, and powders with a light-grey color were obtained.

Wide-angle X-ray Diffraction (XRD) patterns of the obtained materials are shown in Figure 1. As-synthesized ZnS products exhibit well-resolved diffraction peaks (Figure 1a), which can not be indexed as any known phase of $Zn(NO_3)_2$, Tu or ZnS. Such a phenomenon has also been observed by several researchers and it was demonstrated that the composition of this compound can be expressed by the formula ZnS (0.5 en).[18,19] The broadening of the diffraction peaks reveals the nanoscale structure of this precursor. After annealing at 400 °C in a nitrogen flow, the resulting material shows a diffraction pattern (Figure 1b) which can be indexed as the wurtzite ZnS with the lattice constants $a = 3.31$ Å and $c = 6.24$ Å. In addition, the (002) diffraction is extraordinarily intense, suggesting a preferential growth direction along [001].

The TG curves (data not shown) illustrate that decomposition of the precursor complex starts at 200 °C and ends at ~500 °C, accompanying a total weight loss of 25.3 wt % (theory

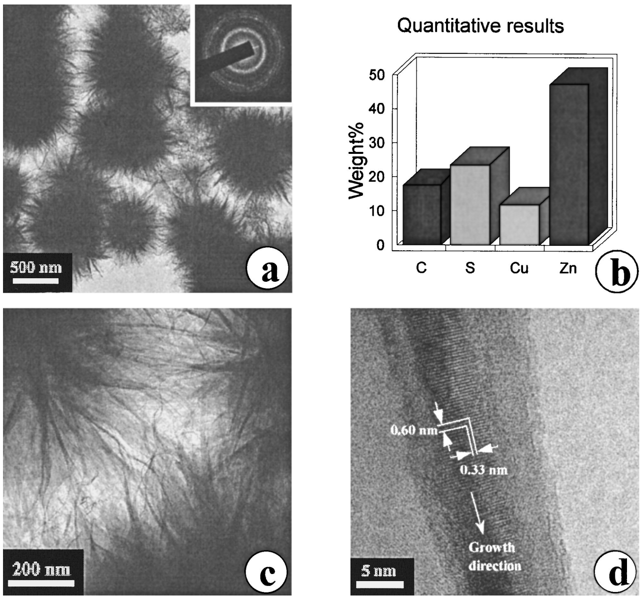

Figure 2. (a) TEM image of the as-synthesized radial ZnS nanoribbons. Inset is the corresponding SAED pattern. (b) EDX result and (c) TEM image of ZnS nanoribbons after annealing. (d) HRTEM image of a single ZnS nanoribbon.

23.6 wt %), which further confirms the above-mentioned formula of the as-synthesized complex.

The TEM image (Figure 2a) shows that the precursors with nanoribbon arrays are radially aggregated into a ball-like morphology. The selected area electron-diffraction (SAED) pattern (inset in Figure 2a) reveals the crystalline features of the as-synthesized ZnS nanoribbons. After calcination, energy dispersive X-ray (EDX) analysis of the product (Figure 2b) gives a Zn/S ratio of 1.00:0.96, indicating the obtained ZnS product has the stoichiometric composition. Figure 2c shows the representative morphologies of the resulted ZnS nanoribbons, in which aggregated bundles can be observed. The ZnS nanoribbons have a length of up to 700 nm, a width of 10–20 nm and a typical thickness of 3 nm. The high-resolution TEM image of a single ribbon (Figure 2d) reveals that the growth direction is along [001], which is reminiscent of the conclusion drawn from the strong XRD peak of (002). The *d* spacings of (100) and (001) crystallographic planes are 0.33 and 0.60 nm, respectively, which are in good agreement with the values calculated from the XRD pattern.

The intrinsic lamellar structure of the produced complex ZnS (0.5 en)[18,19] plays an essential role in the formation of ZnS nanoribbons, as demonstrated by previous researchers that lamellar structures can affiliate the formation of nanoribbons.[20] Moreover, the unique structure of the nanoribbons suggests that their growth may be largely determined by growth kinetics. In our study, thiourea releases S^{2-} upon microwave heating, serving as a sulfur source. Because of the fast and homogeneous heating effects of microwaves, a more rapid and simultaneous nucleation may take place, leading to the explosive formation of very small ZnS (0.5 en) nuclei. However, in the conventional heating method, only large platelets were observed, indicating the formation of a small number of nuclei. During the growth period, the crystallization rate is so high that a distinct preferential growth dominated owing to the anisotropic nature of ZnS (0.5 en). The inorganic and organic nutrients are consumed rapidly near the nuclei, leading to the radially grown morphologies. Upon subsequent heating, en is eliminated from the 2D ZnS nanolayers. And ZnS nanoribbons are finally obtained with a decrease in the ribbon thickness. However, if microwave heating is replaced by oven heating, much larger ZnS (0.5 en) crystals with much thicker lamellar morphologies (~400 nm) are obtained instead of nanoribbons, suggesting that only the unique heating source provided by microwave irradiation favors the formation of radial nanoribbons.

In summary, we report here that using microwave irradiation as the heating method, ZnS nanoribbons can be successfully synthesized via a solvothermal procedure. It is the first time that ZnS nanoribbons with a hexagonal wurzite structure can be achieved by chemical solution reactions. And it is the smallest ZnS nanoribbons obtained so far. We believe that microwave irradiation, as a promising heating method, may open new opportunities for the syntheses of advanced nanomaterials.

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