Novel Microwave-Assisted Solution-Phase Approach to Radial Arrays Composed of Prismatic Antimony Trisulfide Whiskers

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Introduction

Dimensionality plays a critical role in determining the properties of materials due to, for example, the different ways that electrons interact in three-dimensional (3D), two-dimensional (2D), and one-dimensional (1D) structures.[1] Over the past decade, submicrometer- and nanometer-scale 1D structural materials have stimulated increasing interest as a result of their great importance in both basic scientific research and potential technological applications.[2] An important issue in the study and application of these 1D materials is how to rationally assemble atoms or other building blocks into anisotropic 1D structures with small-sized diameters (in the nanometer or submicrometer scale) but much longer lengths (up to over several micrometers) in an effective and controllable way. Although solid-state materials with submicrometer or nanoscale 1D structures can be fabricated by advanced lithographic techniques[3] or via gas-phase chemical processes,[4] solution-phase chemical synthesis is regarded as a more promising approach in terms of much lower cost and potential for high-volume production as well as tight dimension control. Among the solution-phase approaches that have already been reported, template directed[5] or crystal seed mediated methods[6] are most commonly employed to confine or catalyze the preferential 1D growth of various kinds of materials. However, exploring convenient and efficient solution-phase approaches to 1D structural materials without using any templates or crystal seeds still remains a great challenge.

Another major scientific challenge in 1D material research is to develop simple and efficient methods to create the patterns of well-arranged 1D structural materials in a predictable and controllable way. One possible route is to develop suitable hierarchical assembly techniques to put 1D structural building blocks together into functional structures.[2d] The other possibility, which is more convenient and, thus, more attractive, is to form superstructural arrays through direct one-step growth processes.

Antimony trisulfide (Sb_2S_3) is a representative V−VI group binary chalcogenide that has wide applications in target materials for television cameras, microwave switching, solar energy conversion, and various optoelectric devices.[7] Sb_2S_3 is a highly anisotropic V−VI group semiconductor with a layered structure parallel to the growth direction and crystallizes in an orthorhombic phase.[8] In the past two decades, a variety of experimental approaches have been established to prepare Sb_2S_3, in the form of either solid thin films[7,9] or ultrafine powders.[10] Herein, we develop a solution-phase growth method to fabricate radial arrays composed of prismatic Sb_2S_3 whiskers with the aid of microwave irradiation. Antimony trichloride and thiourea are used as the starting materials and *N*,*N*-dimethylformamide (DMF) is chosen as the solvent. The strong complexing action between antimony trichloride and thiourea leads to the formation of the antimony−thiourea complex, which has already been well-studied previously.[10b] The decomposition of this complex with the inducement of microwave irradiation finally results in the formation of radial arrays composed of prismatic Sb_2S_3 whiskers. This process is very convenient and efficient, free of any templates or crystal seeds, and the results are easily reproducible. It provides a novel one-pot solution-phase route that leads to the formation of 1D structural prismatic Sb_2S_3 whiskers and their simultaneous assembly into radial arrays.

Experimental Section

All the reagents were of analytical purity and were purchased from Shanghai Chemical Reagent Factory (China). In a typical procedure, 0.45 g of anhydrous $SbCl_3$ and 0.45 g of thiourea were dissolved in 50 mL of DMF. Then, the mixture solution was placed in the microwave reflux system, and the reaction was performed under ambient air for 20 min. A microwave oven with 650-W power (Sanle General Electric Corp., Nanjing, China) was used in our experiments, and a refluxing system was connected with

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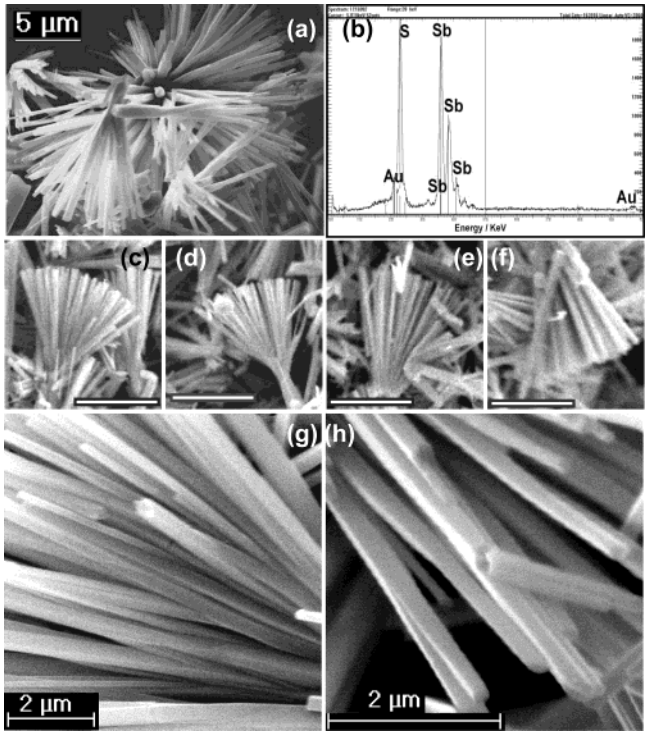

Figure 1. (a) Typical SEM image with low magnification revealing the overall morphology of several bunches of radial arrays composed of whiskers. (b) EDAX pattern of the Sb_2S_3 whiskers shown in Figure 1a. (c−f) Several SEM images showing individual bunches of radial arrays. The length of the bars equals 10 μm. (g and h) SEM images with higher magnifications showing sectional images of radial arrays.

the microwave oven. The microwave oven followed a working cycle of 9-s on and 21-s off (30% power). At the end of the reaction, a great amount of black precipitate occurred. After cooling to room temperature, the precipitates were centrifuged, washed with DMF, distilled water, and absolute ethanol in sequence, and dried in air at room temperature. The final product was collected for characterizations.

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDAX) analysis patterns were taken on a JSM-6301F scanning electron microscope, operated at 20 kV. X-ray powder diffraction (XRD) measurements were performed on a Shimadzu XD-3A X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.154\ 18$ nm) and a nickel filter. The acceleration voltage was 35 kV with a 150 mA current flux. Scatter and diffraction slits of 0.5 mm and collection slits of 0.3 mm were used. XRD patterns were taken of the powders attached to a glass slide, and data were collected in the 2θ range from 10 to 65°, with a scanning rate of 4°/min and a sample interval of 0.02°. The transmission electron microscopy (TEM) micrograph, selected area electron diffraction (SAED) pattern, and high-resolution transmission electron microscopy (HRTEM) micrographs were obtained by employing a JEOL-4000EX high-resolution transmission electron microscope with a 400-kV accelerating voltage. A conventional charge-coupled device video camera with a spatial resolution of 768 × 512 pixels was employed to digitize the micrographs, which were then processed using Digital Micrograph software. The samples used for the TEM and HRTEM observations were prepared by suspending the dried sample in absolute ethanol in a sonication bath for 15 min. A drop of the sample suspension was then dropped onto a copper grid coated with a layer of amorphous carbon, and the copper grid was dried in air at room temperature.

Results and Discussions

The dimensions and morphology of the product were characterized by SEM measurements. In a typical SEM image of the product, which is shown in Figure 1a, some bunches of radial arrays composed of straight and smooth

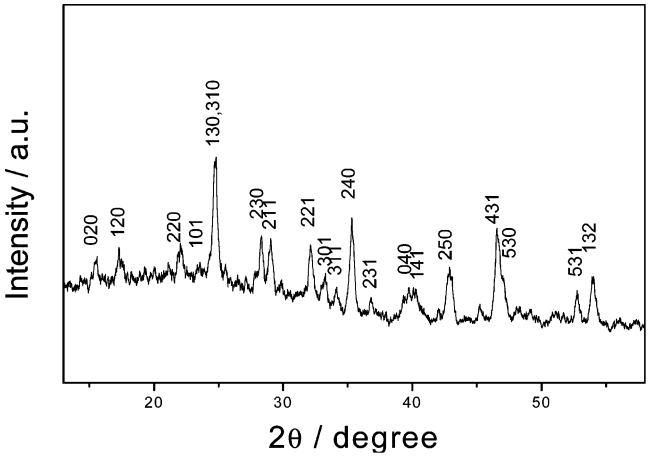

Figure 2. XRD pattern of the as-prepared Sb_2S_3 powders.

whiskers with diameters of 150−300 nm and lengths of 7−12 μm can obviously be observed. The selected area EDAX analysis pattern (Figure 1b) confirms that the image in Figure 1a contains only antimony and sulfur atoms and the atomic ratio of Sb/S is calculated to be 1:1.47, which indicates the stoichiometric relation between Sb and S in this sample. Figure 1c−f shows the SEM images of some typical individual radial arrays. It is apparent that each array is made up of a bunch of regular whiskers that grow radially from one center to form a broomlike pattern. Some SEM images with higher magnifications (Figure 1g,h) recorded on sectional regions of a radial array reveal that each whisker has a fairly uniform diameter and appears to present a regular polygonal prismatic morphology.

XRD measurements were carried out to determine the crystalline phase of the as-prepared powders. The XRD pattern of the product is shown in Figure 2. All the diffraction peaks can be indexed to be the pure orthorhombic phase for Sb_2S_3. The intensities and positions of the peaks match those data reported in the literature very well.[11] The cell parameters are calculated to be $a = 11.179$, $b = 11.280$, and $c = 3.826$ Å, which are in good agreement with the literature values.[11] No peaks of any other phases are detected, indicating the high purity of the product.

Figure 3a shows a typical TEM image of a bunch of Sb_2S_3 whiskers aligned radially to form a broomlike array. Figure 3b is the TEM image of an individual Sb_2S_3 whisker with a diameter of ∼180 nm. The inset is a SAED pattern recorded on this whisker with a convergent electron beam, which indicates that this Sb_2S_3 whisker presents a single-crystalline structure with a preferential 1D growth along the (001) crystal plane. HRTEM images recorded on individual Sb_2S_3 whiskers provide further insight into their structures. The HRTEM image recorded on an interior part of a single Sb_2S_3 whisker (Figure 3c) exhibits good crystallinity and clear lattice fringes. The interplanar spacing is measured to be about 0.801 nm, which corresponds to the (110) plane of the orthorhombic system of Sb_2S_3. The continuous (110) lattice fringes are parallel to the whisker axis. On the basis of the HRTEM observations, it is concluded that these Sb_2S_3 whiskers preferentially grow along the (001) crystal plane. The illustration of the structure of an Sb_2S_3 whisker is schematically shown in Figure 3d.

The formation process of the radial arrays of Sb_2S_3 whiskers can be reasonably divided into two stages. In

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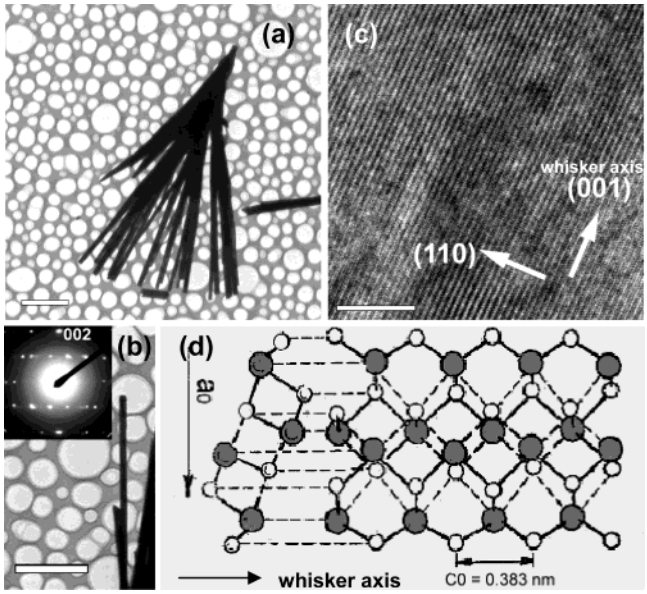

Figure 3. (a) Typical TEM image of a bunch of Sb_2S_3 whiskers aligned radially, forming a broomlike array. The length of the bar equals 2 μm. (b) TEM image of an individual Sb_2S_3 whisker with a diameter of ~180 nm. The inset is a SAED pattern recorded on this whisker. The length of the bar equals 2 μm. (c) A HRTEM image recorded on an interior part of an individual Sb_2S_3 whisker. The length of the bar equals 10 nm. (d) The illustration of the structure of an Sb_2S_3 whisker. The dark spheres represent S atoms and the bright spheres represent Sb atoms.

the first stage (nucleation stage), the antimony−thiourea complex dissolved in DMF underwent a microwave-induced decomposition process, leading to the rapid generation of Sb_2S_3 nuclei. In the second stage (crystal growth stage), the in situ generated Sb_2S_3 nuclei grew preferentially along the (001) crystal plane, which results in the formation of single-crystalline whiskers. It is noteworthy that because a bunch of whiskers grew radially from one nucleus simultaneously, radial arrays formed at the end of the crystal growth. Microwave irradiation played a critical role in both of the two stages mentioned previously. Microwaves are electromagnetic waves, containing both electric and magnetic field components.[12] In the case of a liquid-phase microwave reaction, a coupling between the oscillating electric field (2.45 GHz) and the permanent dipole moment of the molecules resulted in molecular rotations, which leads to rapid volumetric heating of the liquid phase. Such dielectric heating is capable of driving the thermal decomposition of the antimony−thiourea complex to produce Sb_2S_3 nuclei. Compared with conventional heating methods, microwave dielectric heating presents a much more rapid and simultaneous nucleation due to the fast and homogeneous heating effects of microwaves. With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be effectively avoided, providing a uniform environment for the nucleation, which is very important to the final formation of uniform and regular whiskers. Microwave irradiation is also capable of inducing the preferential 1D growth of the Sb_2S_3 crystals. One possible hypothesis of microwave-induced effects is the generation of localized high temperatures and pressures at the reaction sites to enhance the reaction rates in an analogous manner to that of ultrasound waves,[13] where both localized transient high pressures and temperatures are produced during reactions,[14] which is favorable for the 1D growth of Sb_2S_3 crystals.[10b,c] It was observed that, after microwave heating for only 5 min, the temperature of the reactant mixture reached the boiling point of DMF (152.8 °C), and then the temperature of the boiling solution remained at 153 ± 1.5 °C. The boiling solution remained transparent, and no powders appeared until 13 min of treatment. At 13 min, the precipitate of the Sb_2S_3 powders was generated rapidly, and almost all the product was formed within only 4−5 s. If the time of treatment was further prolonged to 30, 60, or even 90 min, the yield did not increase anymore, and the dimension and morphology of the product was almost kept unchanged. We have also carried out the control experiments by refluxing the reactant mixture by means of conventional heating instead of microwave irradiation. It was found that the reaction rate greatly decreased and no regular whiskers were generated even after reflux for over 2 h. Instead, only quasi-spherical grains with submicrometer sizes were obtained (see Figure 4).

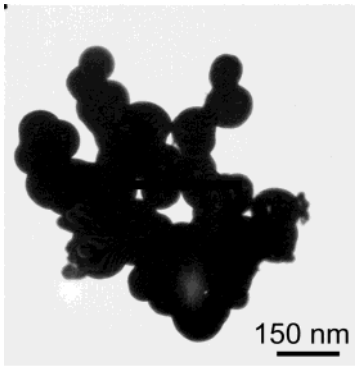

Figure 4. TEM image of Sb_2S_3 powders prepared by refluxing the reactant mixture by means of conventional heating for 2 h. The powder XRD measurement shows that this sample is orthorhombic Sb_2S_3. The EDAX result shows that the Sb/S atomic ratio of this sample is 1:1.45.

The choice of solvent is also of key importance to the formation of the radial arrays of Sb_2S_3 whiskers. Herein, DMF was chosen because of four aspects of consideration. First, because anhydrous $SbCl_3$ hydrolyzes strongly in aqueous solutions, nonaqueous solvents should be used. Second, DMF has good solubility to the precursors, providing a homogeneous medium for the microwave-induced nucleation. Third, DMF is an excellent susceptor of the microwave irradiation because of its high permanent dipole. Finally, and most important of all, DMF has a suitable boiling point and viscosity. We have also used some other solvents with a lower boiling point instead of DMF, such as ethanol, propanol, and tetrahydrofuran. In all these cases, only amorphous Sb_2S_3 powders were obtained. Figure 5a is a typical TEM image of the Sb_2S_3 powders prepared by choosing ethanol as the solvent. It is observed that this sample is composed of aggregated quasi-spherical particles with diameters of 25−40 nm. The results of the SAED and XRD measurements obviously confirm its amorphous nature. If some high boiling point solvents, such as ethylene glycol and triethylene glycol, were used, Sb_2S_3 powders with a high crystallinity

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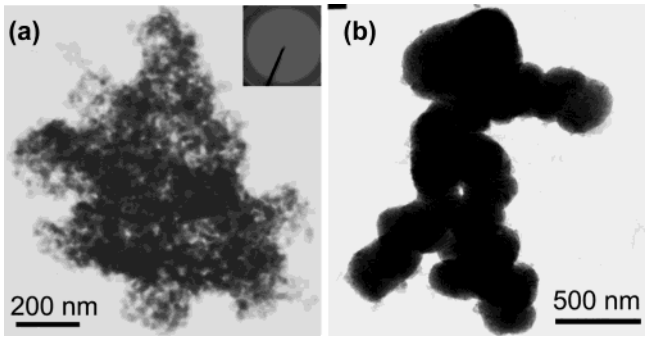

Figure 5. (a) TEM image of Sb_2S_3 powders prepared by choosing ethanol as the solvent. The inset is the corresponding SAED pattern. The Sb:S ratio of this sample is calculated to be 1:1.40 according to the EDAX results. (b) TEM image of Sb_2S_3 powders prepared by using triethylene glycol as the solvent. Powder XRD measurement shows that this sample is orthorhombic Sb_2S_3. The EDAX result shows that the Sb/S ratio is 1:1.48.

could be obtained. However, these products consisted of irregular grains. A typical TEM image of the Sb_2S_3 sample prepared by using triethylene glycol as the solvent is shown in Figure 5b. In this case, because the viscosities of these solvents are much higher than that of DMF, the preferential 1D growth of the Sb_2S_3 whiskers is inhibited and, thus, no whiskerlike products are obtained.

Conclusion

In summary, a microwave-assisted solution-phase approach to produce radially aligned prismatic Sb_2S_3 whisker arrays has been successfully established. It is a convenient one-pot method without using any templates or crystal seeds and has great potential in industrialized high-volume production. The extension of this approach may open fascinating possibilities for the fabrication and assembly of other V−VI group chalcogenide whisker arrays with wide applications in various kinds of thermoelectric and optoelectronic devices.

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