Sonochemical Synthesis of Antimony Trisulfide Nanowhiskers

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Antimony trisulfide (Sb_2S_3) nanowhiskers with diameters of 20–30 nm and lengths over 400 nm have been successfully prepared by a convenient sonochemical method under ambient air.

One-dimensional nanostructures, such as nanorods, nanowires, nanowhiskers and nanotubes, represent the smallest dimensions for efficient transport of electrons and excitons and are ideal building blocks for hierarchical assembly of functional nanoscale electronic and photonic structures.[1] During the past decade, materials with one-dimensional nanostructures have been the focus of much attention due to their special properties and potential applications in mesoscopic research and the development of nanodevices.[2] A variety of experimental approaches have already been reported for the preparation of one-dimensional nanostructural materials, such as nanofabrication techniques[3] and crystal growth methods by using templates[4] or crystal seeds.[5]

V–VI group metal chalcogenides $A^{V}{}_2B^{VI}{}_3$ (A = Sb, Bi, As; B = S, Se, Te) are useful semiconductors that have applications in television cameras with photoconducting targets, thermoelectric devices, electronic and optoelectronic devices and in infrared spectroscopy.[6] Sb_2S_3 is regarded as a prospective material for solar energy because of its good photoconductiviy. It has also been used in thermoelectric cooling technologies and optoelectronics in the IR region.[7] Amorphous and polycrystalline Sb_2S_3 films have been prepared by vacuum evaporation[8] and chemical bath deposition.[9] However, most of the as-prepared Sb_2S_3 films are amorphous and need to be annealed at high temperature to crystallize. Crystalline Sb_2S_3 powders can be synthesized by a solvothermal reaction of anhydrous $SbCl_3$ with Na_2S_3 in benzene solvent.[10] The resulting Sb_2S_3 powders are composed of irregular plate-like particles with an average size of ca. 150 nm. Herein, we report on a novel sonochemical method for the fabrication of Sb_2S_3 nanowhiskers. In this method, the in situ generated Sb_2S_3 nuclei could self-assemble into one-dimensional nanostructures with the inducement of high-intensity ultrasound irradiation. It is found to be a mild, convenient and efficient one-pot route to produce Sb_2S_3 nanowhiskers with uniform morphology and high purity.

All the reagents used were of analytical purity. In a typical procedure, 0.45 g $SbCl_3$ and 0.50 g thioacetamide were dissolved in 50 mL absolute ethanol. Then the mixture solution was exposed to high-intensity ultrasound irradiation[11] under ambient air for 90 min. At the end of the reaction, a dark brown precipitate was obtained. The precipitate was centrifuged, washed with absolute ethanol, distilled water and acetone in sequence, and dried in air. The final product was characterized by employing techniques such as X-ray powder diffraction (XPRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and X-ray photoelectron spectroscopy (XPS).[12]

The dimensions and morphology of the product are studied by TEM measurements. The TEM image in Figure 1A clearly reveals that the product presents needle-shaped morphology with diameters of 20–30 nm and lengths over 400 nm. Figure 1B shows the TEM image of an individual Sb_2S_3 nanowhisker together with its SAED pattern obtained from this selected area with a convergent electron beam. The SAED pattern indicates that this Sb_2S_3 nanowhisker presents a single crystalline nature and grows predominantly along the (001) direction. Figure 2 shows the XPRD pattern of the product. All the diffraction peaks can be indexed to be the pure orthorhombic phase for Sb_2S_3. The intensities and positions of the peaks are in good agreement with the literature values.[13] The as-prepared Sb_2S_3 nanowhiskers are also characterized by XPS measurements for evaluation of their composition and purity. The XPS results reveal that the as-prepared Sb_2S_3 has high purity and the Sb : S ratio is calculated to be 1 : 1.41 according to the measurements of the Sb_{4d} and S_{2p} peak areas, which indicates that the surface of the product is slightly rich in Sb.

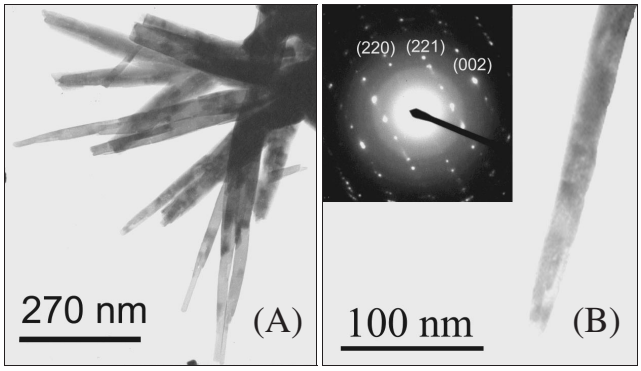

Figure 1. (A) TEM image of the as-prepared Sb_2S_3 nanowhiskers. (B) TEM image and SAED pattern of an individual Sb_2S_3 nanowhisker.

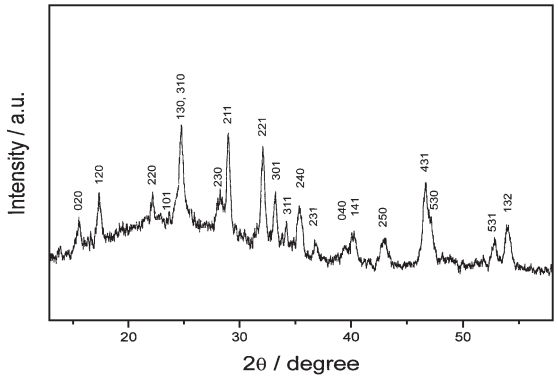

Figure 2. XPRD pattern of the as-prepared Sb_2S_3 nanowhiskers.

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When $SbCl_3$ and thioacetamide were introduced into absolute ethanol, a yellow complex was formed. Antimony salts can react with some organic compounds containing C=S bond, such as thiourea, thioacetamide and tris(*N*,*N*′-disubstituted dithiocabbamate), to produce complexes which have the tendency to decompose at suitable temperature or pressure to produce Sb_2S_3.[14] Recently, pressure-controlled synthesis of Sb_2S_3 nanorods via decomposition of Sb-thiourea under solvothermal conditions has been reported.[14] It was found that temperature, pressure and reaction time played important roles in the formation of Sb_2S_3 nanorods. In the present study, we apply ultrasound irradiation to induce the decomposition of Sb-thioacetamide complex. It is found that Sb_2S_3 nanowhiskers can be successfully prepared in an open system. Sonochemistry drives principally from acoustic cavitations: the formation, growth, and implosive collapse of bubbles in liquids.[15] When bubbles are implosively collapsed by acoustic fields in liquid, high-temperature and high-pressure fields are produced at the centers of the bubbles, providing a favorable environment for the one-dimensional growth of Sb_2S_3, even though the bulk solution surrounding the collapsing bubbles is at ambient temperature and atmospheric pressure. The unusual chain-type structure of Sb_2S_3[16] plays a critical role in the formation of the nanowhiskers. When Sb-thioacetamide complex decomposed, the in situ generated Sb_2S_3 nuclei would connect with each other and self-assemble to form chain-type structures. High temperature and high pressure produced by acoustic cavitations are favorable for the self-assembly of these nuclei, leading to the one-dimensional preferential growth of Sb_2S_3. We have also found that when the reaction was carried out under vigorous electromagnetic stir instead of ultrasound irradiation, no Sb_2S_3 nanowhiskers were obtained even after 5 hours' reaction. The details of the one-dimensional preferential growth of Sb_2S_3 nanowhiskers via such an ultrasound-induced decomposition process of Sb-thioacetamide complex are still under study.

In summary, a novel sonochemical method for the preparation of Sb_2S_3 nanowhiskers has been successfully established. It may also provide a promising way to direct the one-dimensional growth or assembly of some other functional inorganic materials.

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11 Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China; 1.2 cm-diameter; Ti-horn, 20 kHz, 100 W/cm^2) immersed directly in the reaction solution.
12 XPRD measurements were performed on a Shimadzu XD-3A X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm). TEM images and SAED picture were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The XPS spectra were recorded on an ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source and choosing C1s (284.6 eV) as the reference line.
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