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Microwave-assisted synthesis of Sb$_2$Se$_3$ submicron rods, compared with those of Bi$_2$Te$_3$ and Sb$_2$Te$_3$

Bo Zhou$^{1,2}$ and Jun-Jie Zhu$^{2,3}$

$^1$ Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing 210097, People’s Republic of China
$^2$ Key Laboratory of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People’s Republic of China
$^3$ Author to whom any correspondence should be addressed.

E-mail: zhbzhou@tom.com and jjzhu@nju.edu.cn

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Abstract
Orthorhombic Sb$_2$Se$_3$ submicron rods were prepared from antimony sodium tartrate and Se powder via a microwave-assisted chemical method. The products were characterized by x-ray powder diffraction (XRD), transmission electron microscope (TEM) and selected-area electron diffraction (SAED) techniques. The reaction mechanism and the morphology of the product were studied in detail in comparison with those in the syntheses of Bi$_2$Te$_3$ and Sb$_2$Te$_3$. The synthesis of Sb$_2$Se$_3$ was based on the polyol reducing process and microwaves played an important role. The morphologies of the compounds were mainly determined by their inherent anisotropic crystal structures. The optical properties of as-prepared Sb$_2$Se$_3$ were also characterized by UV–vis diffuse reflectance spectroscopy, and the bandgap ($E_g$) can be derived to be 1.16 eV, which is suitable for applications in photovoltaic conversion.

1. Introduction
One-dimensional (1D) semiconductor nanomaterials (and submicron materials), including nanorods, nanowires, nanotubes and nanoribbons, have attracted a great deal of attention because of their distinctive electronic, optical, mechanical and other properties that differ from those of the bulk materials, and their promising applications as building blocks for nanodevices [1–6]. Employing hard templates or soft structure directors is a widely used strategy to grow 1D nanostructures [7, 8]. And, as for the materials that have inherent anisotropic structures, 1D nanostructures can also be fabricated based on the natural crystal growth mechanism without using templates or structure directors [9–11].

Antimony triselenide, an important member of V$_2$VI$_3$ (V = As, Sb, Bi; VI = S, Se, Te) type main-group metal chalcogenides, is a direct bandgap semiconductor that crystallizes in the orthorhombic system. It exhibits good photovoltaic properties and high thermoelectric power (TEP), which makes it promising for applications in photochemical devices, optical devices and thermoelectric cooling devices [12–16]. Besides these, Platakis et al reported threshold and memory switching phenomena on the materials of Sb$_2$Se$_3$ [17].

Traditionally, Sb$_2$Se$_3$ was prepared by elemental reaction of antimony and selenium at high temperature [18]. Recently, some wet chemical methods have been utilized to synthesize 1D Sb$_2$Se$_3$ nanocrystals, such as the colloid route [19] and refluxing reaction [20]. However, the most widely used method is the hydrothermal/solvothermal process [21–28, 13]. Sb$_2$Se$_3$ with various 1D structures, such as nanowires [21, 22, 25, 26], nanorods [23, 27], nanoribbons [24, 28] and nanotubes [13], were successfully prepared via this hydrothermal/solvothermal process. In these syntheses, strong reductants, such as NaBH$_4$ [25, 28, 29], NaHSe [30] and Na$_2$SO$_3$ [26, 27, 31], were usually used to promote the reactions.

Here, we report a microwave-assisted polyol method for the rapid synthesis of 1D Sb$_2$Se$_3$ submicron rods. To the best of our knowledge, there is no other report on the synthesis of 1D Sb$_2$Se$_3$ via a microwave chemical method. The raw materials used here are only antimony sodium tartrate, Se powder and ethylene glycol, which acts as both solvent and reductant.
This synthesis was studied in detail in comparison with the syntheses of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ under similar conditions from the viewpoints of the reaction mechanism and the morphology of the product.

2. Experimental details

All reagents are of analytical purity and were used without further purification. The typical synthesis procedure is as follows: 2 mmol of antimony sodium tartrate (Na(SbO)C$_4$H$_4$O$_6$), 3 mmol of Se powder and 30 ml of ethylene glycol (EG) were added to a 100 ml round-bottomed flask, which was then put into a microwave oven equipped with a condenser to carry out the reaction under refluxing. The microwave frequency was 2.45 GHz and the power was set at 280 W. The microwave irradiation time was 3 h. The product was cooled, centrifuged, washed with water and ethanol for several times, and then dried at 60 °C.

The products were characterized by x-ray powder diffraction (XRD) with a Philips X'pert x-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The morphology and the microstructures of the products were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) with, respectively, a JSM-5610LV (JEOL, 150 kV, WD 10 mm) SEM and a JEM-200CX (JEOL, 200 kV) TEM. The optical properties of the solid product were characterized by a UV–vis diffuse reflectance spectrum and absorbance spectrum using a Varian Cary-5000 UV–vis–NIR spectrophotometer. The TEM image and SAED pattern of the Sb colloid were recorded by H-7650 (Hitachi, 80 kV) TEM and H-600A-2 (Hitachi, 75 kV) EM, respectively.

3. Results and discussion

Experimental results are given below, after which the synthesis mechanism and morphology are discussed, respectively.

3.1. Synthesis mechanism

The typical XRD pattern of as-prepared samples was shown in figure 1. All the diffraction peaks can be indexed to pure orthorhombic Sb$_2$Se$_3$ (JCPDS no. 72-1184). No impurities were detected. The sharpness of the peaks indicates the high crystallinity of the sample. The abnormal strengthening of the (hk0) diffraction peaks, which is most evidently shown in the (230) and (240) peaks, implies the 1D preferred growth along the (001) direction, which is confirmed by TEM and SAED investigations as discussed below.

This synthesis procedure is similar to that of Bi$_2$Te$_3$ [32] and that of Sb$_2$Te$_3$ [33]. However, the mechanisms seemed different from each other. As reported previously, the synthesis of Bi$_2$Te$_3$ in EG was based on the polyol process, in which Bi(III) was first reduced by EG to metallic Bi, as XRD proved. Then this reduced Bi reacted with Te powder to produce Bi$_2$Te$_3$. The synthesis of Sb$_2$Te$_3$, as discussed elsewhere [33], was based on the disproportionating reaction of Te, in which Te$^{2-}$ was produced and then reacted with Sb III to produce Sb$_2$Te$_3$. However, in the synthesis of Sb$_2$Se$_3$, neither reduced Sb was detected by XRD nor was the disproportionation of Se needed.

First, in the synthesis of Sb$_2$Se$_3$, no reduced Sb was detected. When the reaction time was not long enough and the reaction was not completed yet, only unreacted Se (the XRD peaks of which were marked with ‘*’ and could be indexed to hexagonal Se, JCPDS no. 06-0362), but no reduced Sb, was found among the produced Sb$_2$Se$_3$, as the XRD pattern shown in figure 2 indicates. This result seems to deny the synthesis mechanism based on the reduction of Sb(III), according to which Sb should be detected during the reaction. Two other facts also seemed to confirm this conclusion. One is that, when antimony sodium tartrate was microwave heated in EG without Se, no solid Sb was obtained, no matter if NaOH was added or not. This means that EG was not a strong enough reductant to reduce Sb(III) to solid metallic Sb, though it can reduce Bi(III) to metallic Bi [32]. The other one is that, when Sb powder and Se powder were microwave heated together in EG, almost no Sb$_2$Se$_3$ was obtained even after reaction for 3 h. Sb and Se remained unreacted. This means that it is hard for the powders of these two elements to react directly under this condition. The synthesis of Sb$_2$Se$_3$ was too slow to be detected.

Second, the synthesis of Sb$_2$Se$_3$ is not based on the disproportionation of Se, either. If it were, NaOH would...
accelerate the disproportionating reaction and the synthesis of Sb₂Se₃. However, we found that, when NaOH was added to the reaction system, neither Sb₂Se₃ nor Se was obtained. Instead, Sb was found as the only product. This can be seen from the XRD pattern shown in figure 3. All the diffraction peaks can be indexed to hexagonal Sb, JCPDS no. 71-1173. There are three reagents that might reduce antimony: EG, Se and Se²⁻. Since no solid Sb was obtained without addition of Se or NaOH, as discussed above, we suggest that Se²⁻ was the one that worked. Otherwise, if EG worked, Se should not be necessary; and if Se worked, NaOH should not be necessary. The reduction of antimony is suggested via the following mechanism: firstly, Se disproportionates in an alkali medium to give Se²⁻ (equation (1)).

\[
\text{Se} \rightarrow \text{Se}^{2-} \quad (1)
\]

Since \( \phi_{\text{Se}^{2-}} = -0.77 \text{ V} \); \( \phi_{\text{Zn}} = -0.76 \text{ V} \), Se₂⁻ is a reductant even stronger than Zn (equation (1)). Se₂⁻ then reduces Sb(III) to metallic Sb (equation (2)):

\[
\text{Sb}^{3+} + 2\text{Se}^{2-} \rightarrow \text{Sb} + \text{Se}_2 \quad (2)
\]

The Se produced in equation (2) disproportionations again in equation (1). The total reaction can be represented as

\[
3\text{Se} + 6\text{OH}^- \rightarrow \text{SeO}_3^{2-} + 2\text{Se}^{2-} + 3\text{H}_2\text{O} \quad (1)
\]

\[
3\text{Se}^{2-} + 2\text{Sb}^{3+} \rightarrow 2\text{Sb} + 3\text{Se} \quad (2)
\]

Equation (5) is a much faster reaction. The resulting consumption of Sb (colloid) drove equation (4) to the right and thus made the reduction of antimony and the synthesis of Sb₂Se₃ complete.

To prove the formation of Sb colloid, we dissolved antimony sodium tartrate in EG and then heated the solution in a microwave oven for 3 h. Though almost no solid was produced, we centrifuged the liquid obtained in a tube. Once centrifuged, we inclined the tube very carefully to decant the upper 2/3 of the liquid, then added absolute ethanol into the tube to the original volume. The liquid in the tube was mixed up thoroughly by shaking and ultrasonication, and then was centrifuged again. This cycle was repeated four times. On the last time, most of the liquid was decanted and only ~1 ml was left at the bottom, from which the sample for TEM observation was made. Figure 4 shows the TEM image and the SAED pattern of the sample. Most of the particles were of diameters smaller than 20 nm. The diffraction rings in the SAED pattern indicated their crystallinity. The calculated \( d \) value was consistent with that of hexagonal Sb (JCPDS no. 71-1173).

Another notable fact is that microwaves played an important role in this synthesis of Sb₂Se₃. When the reaction...
was carried out solvothermally at temperatures as high as 180 °C and for times as long as 30 h, which was 10 times that needed under microwave irradiation, a large amount of Se remained unreacted among the produced Sb₂Se₃. This can be seen from the XRD pattern shown in figure 5, in which peaks marked with '#' can be indexed to Sb₂Se₃, and those stronger peaks marked with '*' can be indexed to Se.

3.2. Morphology of as-prepared Sb₂Se₃

The morphology of as-prepared Sb₂Se₃ was investigated with TEM and SAED, and was found to be rod-like as the XRD result implies. From the SEM and TEM images shown in figures 6(a)–(c), it can be seen that these rods were mainly 100–200 nm in diameter, and with lengths ranging from several micrometers to more than ten micrometers. A few of the rods were thicker, with diameters of 400–500 nm. Bright spots in the SAED pattern of an individual rod show the single crystallinity of these rods and can be indexed as shown in figure 6(d). It can be concluded that these submicron rods had preferential growth direction along the (001) direction, which was consistent with the XRD result.

Nonionic, anionic and cationic surfactants, such as polyethylene glycol (PEG-2000), sodium dodecyl sulfo-nate (SDS), sodium dodecyl benzene sulfonate (SDBS), cetyltrimethyl ammonium bromide (CTAB) and polyvinyl pyrrolidone (PVP, K-30), were added to the reaction system in an attempt to minimize and make the products more uniform. However, no significant difference in morphology was seen. Meanwhile, the reaction was slowed on the addition of some surfactants. For example, when PVP was added, the reaction time should be prolonged to 4.5 h to complete the synthesis. This might be due to the protective adsorption of the surfactant onto the reduced Sb colloid particles.

The difference in morphology between Sb₂Se₃, Sb₂Te₃ and Bi₂Te₃, which were synthesized under similar conditions, is reasonably suggested to result from the difference between their crystal structures. Sb₂Te₃ and Bi₂Te₃ have similar intrinsic anisotropic layered crystal structures [36], in which every 15 layers stacked along the c axis and present the combination of three hexagonal layer stacks of composition in which each set consists of five atoms (Te₁–Sb(Bi)–Te₂–Sb(Bi)–Te₁). Between two adjacent Te₁ layers, there are van der Waals bonds, while all others are covalent bonds. This special bonding structure leads
Figure 7. (a) The diffuse reflectance spectrum of as-prepared Sb$_2$Se$_3$ submicron rods; (b) the absorbance spectrum corresponding to (a); (c) the plot corresponding to (b), from which the bandgap ($E_g$) can be derived to be 1.16 eV.

3.3. Optical property of as-prepared Sb$_2$Se$_3$

Figures 7(a) and (b) show the UV–vis diffuse reflectance spectrum and the corresponding absorbance spectrum of as-prepared Sb$_2$Se$_3$ rods. Based on these data, and according to the following formula:

\[ \alpha = \sqrt{h\nu - E_g} / h\nu \]  \hspace{1cm} (6)

where $h\nu$ is the corresponding phonon energy and $\alpha$ is the absorbance coefficient, we made a $(ah\nu)^2 \sim h\nu$ plot (figure 7(c)), from which the bandgap ($E_g$) can be derived to be 1.16 eV. This value is near the optimum value for photovoltaic conversion, suggesting that Sb$_2$Se$_3$ submicron rods may be very promising for applications in solar energy and photoelectronics [28]. Our results are similar to those reported in [25, 28].

4. Conclusions

A new microwave-assisted chemical method was developed to synthesize orthorhombic Sb$_2$Se$_3$ rods with diameters of 100–200 nm and 1D preferential growth along the (001) direction from antimony sodium tartrate and Se powder. The reaction mechanism was studied in detail in comparison with those of Bi$_2$Te$_3$ and Sb$_2$Te$_3$, and was found to be based on the polyol reducing process. The morphology of Sb$_2$Se$_3$ is mainly determined by its inherent anisotropic crystal structure. The differences in the properties of the elements (Bi and Sb, Se and Te) and the crystal structures of the compounds result in the differences in the synthesis mechanisms and the morphologies of Sb$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$. As-prepared Sb$_2$Se$_3$ has a suitable bandgap value (1.16 eV) for applications in photovoltaic conversion.

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