Synthesis, Characterization, and Catalytic Performance of Sb$_2$Se$_3$ Nanorods

Ning Hu, Marcos A. Cheney, Younes Hanifehpour, Sang Woo Joo, and Bong-Ki Min

1Key Laboratory of Biorheological Science and Technology, Ministry of Education and Key Lab of Visual Damage and Regeneration and Restoration of Chongqing, Bioengineering College, Chongqing University, Chongqing 400030, China
2University of Maryland Eastern Shore, Princess Anne, MD 21853, USA
3School of Mechanical Engineering, WCU Nano Research Center, Yeungnam University, Gyeongsan 712-749, Republic of Korea
4Center for Research Facilities, Yeungnam University, Gyeongsan 712-749, Republic of Korea

Correspondence should be addressed to Ning Hu; huning@cqu.edu.cn, Marcos A. Cheney; macheney@umes.edu, and Sang Woo Joo; swjoo1@gmail.com

Received 19 January 2017; Revised 22 March 2017; Accepted 2 April 2017; Published 4 July 2017

Abstract

Antimony selenide has many potential applications in thermoelectric, photovoltaic, and phase-change memory devices. A novel method is described for the rapid and scalable preparation of antimony selenide (Sb$_2$Se$_3$) nanorods in the presence of hydrazine hydrate and/or permanganate at 40°C. Crystalline nanorods are obtained by the addition of hydrazine hydrate in a reaction mixture of antimony acetate and/or chloride and sodium selenite in neutral and basic media, while amorphous nanoparticles are formed by the addition of KMnO$_4$ in a reaction mixture of antimony acetate/chloride and sodium selenite. The powder X-ray diffraction pattern confirms orthorhombic phase crystalline Sb$_2$Se$_3$ for the first and second reactions with lattice parameters $a = 1.120$ nm, $b = 1.128$ nm, and $c = 0.383$ nm and amorphous Sb$_2$Se$_3$ for the third reaction. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) images show the diameter of nanorods for the first and second reactions to be in the order of 100 nm to 150 nm and about 20 nm particles for the third reaction. EDX and XPS suggest that the nanorods are pure Sb$_2$Se$_3$. The UV-vis analysis indicates a bandgap of 4.14 and 4.97 eV for the crystalline and amorphous Sb$_2$Se$_3$, respectively, corresponding to a blue shift. The photocatalytic study shows that the decolorization of Rhodamine in solution by nanoparticles is slightly greater than nanorods.

1. Introduction

Structure, morphology, and composition of nanorods and nanoparticles are important parameters that give rise to their properties and thus applications. Morphological and structural changes associated with semiconducting V$_2$VI$_3$ compounds such as Sb$_2$Se$_3$ are not well understood.

The semiconducting V$_2$VI$_3$ compounds (Sb$_2$S$_3$ and Sb$_2$Se$_3$) are highly anisotropic semiconductors with a layered structure parallel to the growth direction with orthorhombic phase crystal structure, which is known to adopt a number of packing structures resulting in either trigonal prismatic or octahedral coordination of the metals within a layered matrix of chalcogens [1]. Semiconductor selenides find applications as laser materials, optical filters, sensors, and solar cells. Antimony selenide, an important member of these V$_2$VI$_3$ compounds, is a layer-structured semiconductor of orthorhombic crystal structure and exhibits good photovoltaic properties and high thermoelectric power (TEP) which allows possible applications for optical and thermoelectronic cooling devices [2–7]. Over the past two decades, many methods have been employed to prepare Sb$_2$Se$_3$ nanotubes, nanoribbons, nanowires, nanosheets, nanorods, nanobelts, nanospheres, and nanoflakes, including thermal decomposition [8, 9], complex decomposition approach [10], solvothermal reaction [11, 12], microwave irradiation [13], vacuum evaporation [14], and other chemical reaction approaches [15, 16]. However, most of the reports were focused on the preparation of Sb$_2$Se$_3$...
with reaction times much more than 10 h [17–22]. Hence, the synthesis of 1D nanomaterials in high yield via a quick process is still a challenge. In this study, antimony selenide (Sb$_2$Se$_3$) nanomaterials with uniform size and morphology are prepared by a soft hydrothermal process using hydrazine hydrate and permanganate in just 30 min. The surprising morphological and structural changes occurring in the presence of permanganate are also presented. The present route is simple, cost-effective, and reproducible.

2. Experimental Section

2.1. Synthesis. All chemicals were of analytical grade and were used as received. All glassware were acid-cleaned, and the ultrapure water was devoid of any trace of organics. The synthesis of Sb$_2$Se$_3$ is performed by a new redox method using antimony acetate and/or chloride salts, sodium selenide, hydrazine hydrate (N$_2$H$_4$·H$_2$O), and/or permanganate in neutral and basic aqueous solution, respectively. For the first reaction, Sb(CH$_3$COO)$_3$ (0.227 g, 0.750 mmol) and Na$_2$SeO$_4$ (0.259 g, 1.49 mmol) were weighted independently and then placed together into a 50 mL volumetric flask followed by the addition of 25 mL of pure water at room temperature. It is important to dissolve all the salts simultaneously via sonication to obtain the results desired. After the salts were completely dissolved, 3 mL of 80% hydrazine hydrate and NaOH (0.01 mol, pH = 10) is added dropwise to the solution followed by dilution to the 50 mL mark with pure water and then placed in a sonicator bath at 40°C for 40 min. After the addition of hydrazine, the solution turned turbid, and a white/beige precipitate appeared, which rapidly settled down, leaving a colorless solution. The solids are separated by filtration (Whatman filter paper) and washed with ethanol and pure water, followed by air drying at room temperature for characterization. The first reaction is summarized as

$$2\text{Sb(}\text{CH}_3\text{COO)}_3\text{(aq) + 3Na}_2\text{SeO}_4\text{(aq) + N}_2\text{H}_4\cdot\text{H}_2\text{O + 6Na}^+ + 6\text{CH}_3\text{COO}^- + \text{NH}_3 \rightarrow \text{Sb}_2\text{Se}_3\text{(s) + N}_2 + \text{H}_2\text{O + 6Na}^+}$$  \hspace{1cm} (1)

Note that we run the above reaction in the absence of NaOH as well. Since there were no noticeable differences in the color of the product with and without NaOH, we proceeded to change the salt type of the reaction. The only difference observed was in the amount of solids produced which were more in the presence of NaOH.

For the second reaction, the above process was repeated, except that SbCl$_3$ was used in place of Sb(CH$_3$COO)$_3$, with no NaOH, to study the effect of salt type and pH on the reaction. In this case, the solids produced are black:

$$2\text{SbCl}_3\text{(aq) + 3Na}_2\text{SeO}_4\text{(aq) + N}_2\text{H}_4 \rightarrow \text{Sb}_2\text{Se}_3\text{(s) + N}_2 + \text{H}_2\text{O + 6Na}^+ + 6\text{Cl}^- + \text{NH}_3}$$  \hspace{1cm} (2)

For the third reaction, the above process (reaction 1) is also repeated with minor changes; SbCl$_3$ is used in place of Sb(CH$_3$COO)$_3$; KMnO$_4$ is used together with hydrazine and NH$_3$ in place of NaOH. The pH of this mixture was around 10. The solids produced are a mixture of reddish brown and black in color:

$$2\text{SbCl}_3\text{(aq) + 3Na}_2\text{SeO}_4\text{(aq) + N}_2\text{H}_4 + \text{MnO}_4^- \rightarrow \text{Sb}_2\text{Se}_3\text{(s) / Sb}_2\text{Se}_3\text{Mn}_3\text{Se}_3 + \text{MnO}_2\text{(s) + N}_2 + 6\text{Cl}^- + 6\text{Na}^+ + \text{NH}_3}$$  \hspace{1cm} (3)

The pH of the permanganate solution was near neutral and unstable (reacts with water). The addition of NH$_3$ (weak base) made the solution basic and stable. At this pH, the permanganate solution is purple and stable and the manganese is mostly Mn(VII).

2.2. Characterization Techniques. The Sb$_2$Se$_3$ solids produced were characterized by X-ray powder diffraction (XRD) using a PANalytical X'Pert PRO X-ray diffractometer with a Cu-K$_\alpha$ radiation (40 KV, 30 mA), and a Pixcell solid state detector. The samples were prepared on glass sample holder. The patterns were recorded at room temperature with step sizes of 0.02°.

Surface structure and morphology of the sample were obtained with the aid of a Field Emission Scanning Electron Microscope (FESEM, Hitachi S-4200, Japan). The samples for FESEM analysis were prepared by suspending about 3 mg of the solid Sb$_2$Se$_3$ oxide in 1 mL of isopropanol. After the isopropanol was evaporated, the dry solid was placed on a double-sided black tape and then coated with sputtered platinum thin film prior to FESEM imaging.

Transmission electron microscopy (TEM) images were obtained with a Tecnai G$^2$ F20 S-Twin TEM instrument. The TEM operates at 200 KV using a field emission gun in Schottky mode as an electron source. The samples for TEM analysis were prepared by placing 3 mg of the air-dried solid Sb$_2$Se$_3$ in 10 mL of 2-propanol and sonication for 5 min for homogeneity. The holey carbon copper grid is dipped into the sonicated solution for a few seconds and then air-dried in the dark before analysis. UV-vis absorptions were carried out using a Shimadzu 160A (Japan) spectrophotometer. Photocatalytic performance of the Sb$_2$Se$_3$(s) rods and Sb$_2$Se$_3$(s) particles was evaluated by monitoring the decolorization of Rhodamine B in aqueous solution. The catalytic reaction is carried out in a 30 mL glass vial, which contained 10 mL of the Rh B (0.05 mM) dye solution and 15 mg of Sb$_2$Se$_3$ rods and/or Sb$_2$Se$_3$(s) particles. The mixture was allowed to react at 25°C under stirring. After reaction, the suspension was centrifuged and filtered and the supernatant analyzed using a UV-vis spectrometer (Shimadzu 160A UV, Japan). The efficiency of the catalysts is determined by difference in concentration of RhB between the initial and final readings at $\lambda_{max}$ = 501 nm.
to the following redox reactions:

\[
\begin{align*}
N_2H_4 + OH^- &\rightarrow N_2 + 4H_2O + 4e^- \quad E^0 = 1.15 \text{ V} \quad (4) \\
Sb^{3+} + 3e^- &\rightarrow Sb \quad E^0 = 0.20 \quad (5) \\
Se + 2e^- &\rightarrow Se^{2-} \quad E^0 = -0.66 \quad (6)
\end{align*}
\]

In our experiments, Sb(CH$_3$COO)$_3$ and SeO$_3^{2-}$ are used to react in molar ratios. The temperature of 40°C was chosen because at this temperature a balance is maintained between minimum input of energy (more cost-effective) and a good product yield.

3.2. X-Ray Powder Diffraction, EDX, and XPS. The phases formed by the new method described above are characterized by XRD. Figure 1 shows the XRD patterns of ((a) and (b)) the crystalline nanorods of Sb$_2$Se$_3$ produced using Sb(CH$_3$COO)$_3$ and/or SbCl$_3$, Na$_2$SeO$_3$, and N$_2$H$_4$·H$_2$O with OH$^-$ (reaction (1)) and without OH$^-$ (reaction (2)) at 40°C and sonication for 40 min. These graphs indicate that the profile parameters of the diffraction peaks of the two types of Sb$_2$Se$_3$ produced by reactions (1) and (2) are very similar. The intensity of the peaks indicates that the samples are not highly crystalline. All peaks in Figures 1(a) and 1(b) can be indexed to an orthorhombic phase with lattice parameters: \(a = 1.122 \text{ nm, } b = 1.1182 \text{ nm, and } c = 0.384 \text{ nm with}

The element composition and purity of these nano-materials were analyzed using EDXS. Figure 2(a) depicts typical EDX spectra recorded for the crystalline nanorods sample showing the presence of the elements Sb and Se. Interestingly, for the third reaction (not shown), the EDX pattern confirms the presence of Sb/Se and Mn as impurity for the Sb$_2$Se$_3$ particles, suggesting that MnO$_4^{2-}$ changed the crystallinity of the sample. Figure 2(b) shows a typical XPS survey spectrum of the as-prepared Sb$_2$Se$_3$ nanorods synthesized in the presence of hydrazine hydrate (reactions (1) and (2)) at 40°C and sonication for 40 min and suggests that the nanorods are composed of pure Sb and Se. The high resolution spectrum shown in Figures 2(b) and 2(c) indicates that the binding energies for Sb3d and Se3d in Sb$_2$Se$_3$ agree well with the published data [16].
3.3. SEM, TEM, and HRTEM Studies. The nanostructures of both crystalline and poorly crystalline Sb$_2$Se$_3$ are studied using SEM, TEM, and HRTEM imaging. Figure 3 shows the SEM images of rods obtained for nanosized nanocrystalline and poorly crystalline Sb$_2$Se$_3$. For the crystalline samples (first and second reactions), (cf. Figures 3(a)–3(d)), the images show rods with orthorhombic shapes with lengths of about 100 nm to about 2 μm. Furthermore, the rods from the first reaction (cf. Figures 3(a) and 3(b)) appear thicker (0.1 μm) than the ones from the second reaction (0.05 μm) (cf. Figures 3(c) and 3(d)). We attribute this effect to the OH$^-$ used in the first reaction (pH 10). At this solution pH, the production of solids is very fast, making the nanorods thicker. At near neutral pH, the production of solids is slower and this plus the salt type influences the size of the nanorods appearing thinner. The exact role of N$_2$H$_4$ in the formation of nanostructures is not known. We speculate that the role of N$_2$H$_4$ is both a reducing agent and a coordinator for the formation of the rod-like morphology. For the poorly crystalline sample (third reaction) (cf. Figures 3(e) and 3(f)), the images depict particles with bead-like shape with size of less than 20 nm that bundle together to form aggregates. In this reaction, it can be seen that the acetate and Cl$^-$ (from SbCl$_3$) clearly affect the structure and morphology of the particles obtained, particularly when MnO$_4^-$ is present. The effect of acetate is currently under investigation.

The TEM images shown in Figures 4(a)–4(f) display the crystal structure of the as-prepared Sb$_2$Se$_3$ nanorods (from the first and second reactions) and confirm the particle size of about 100 to 2 μm observed in the SEM images. The First Fourier Transform (FFT) patterns of the nanorods obtained from the first and second reactions is indeed crystalline in nature with a growth direction. The SEM and TEM images also show that the products of the first and second reactions consist of mixtures of large (cf. Figure 4(a)) and small (cf. Figure 4(d)) nanorods, both of which appear faceted, with rectangular cross sections. Some of the rods in Figure 4(a) have stripes perpendicular to the nanorod axis. We speculate this to be a physical effect most likely due to local bending since the TEM images did not show any noticeable atomic disregistry across the glide plane.

The TEM and HRTEM images of the poorly crystalline Sb$_2$Se$_3$ are shown in Figures 4(g)–4(i). The TEM images display the bead-like distribution obtained for the light-colored Sb$_2$Se$_3$ particles with size of less than 20 nm. Some of these particles appear to bundle together to form nanoaggregates of about 100 nm. The SAED pattern (inset in Figure 4(i))
The XRD patterns and the TEM images confirm the structures of Sb$_2$Se$_3$ nanorods and suggest that the preferred ratio of Sb to Se is the one from the second reaction in which hydrazine hydrate was used in near neutral solution (cf. Figure 2(c)). We note that the redox-assisted formation of nanorods, in our system, is different from the chalcogenide nanoparticles formation by sheet rolling [23] and cation exchange reactions [24]. This “redox-assisted” synthesis of nanorods may permit the independent control of nanostructure composition and morphology by means of judiciously selecting counter ions for Sb(III) and hydrazine and MnO$_4^-$ dose in the synthesis. The exact role of permanganate in reaction (3) is not known but we speculate that the acetate and Cl$^-$ ions from Sb(III) play a more important role than was expected. It is clear that this may be the case in the third reaction where structural and morphological changes are induced by MnO$_4^-$ by either incorporation of Mn into the lattice and/or coprecipitation of Mn during synthesis. Furthermore, the redox-stimulated shape evolution may supports this observation as it indicates that there is no growth direction and suggests what appears as poorly crystalline to amorphous phase of Sb$_2$Se$_3$.

Figure 3: SEM images of ((a) and (b)) large crystalline Sb$_2$Se$_3$ nanorods (reaction (1)), ((c) and (d)) small crystalline Sb$_2$Se$_3$ nanorods (reaction (2)), and ((e) and (f)) poorly crystalline Sb$_2$Se$_3$ nanoparticles (at two different magnifications) prepared using hydrazine hydrate and MnO$_4^-$ at 40$^\circ$C and sonication for 40 min.
Figure 4: ((a), (b), and (c)) TEM and HRTEM images of the large crystalline Sb$_2$Se$_3$ nanorods (at three different magnifications); ((d), (e), and (f)) TEM and HRTEM images of the small crystalline Sb$_2$Se$_3$ nanorods; ((g), (h), and (i)) TEM and HRTEM image of the poorly crystalline Sb$_2$Se$_3$ nanoparticles. The insets in (c), (f), and (i) correspond to the FFT's and SAED patterns of a single Sb$_2$Se$_3$ nanorod and nanoparticle.

The UV-vis absorption spectrum of the crystalline and amorphous Sb$_2$Se$_3$ samples is shown in Figure 5. The spectrum of the crystalline samples shows an absorption maximum of 750 nm for reaction (1) and 760 nm for reaction (2), while the poorly crystalline samples show a maximum of 730 nm with corresponding band gaps of 1.65, 1.63, and 1.70 eV, respectively. This observation suggests a red shift
Figure 5: UV absorption patterns of the crystalline ((a) red and (b) green lines) Sb$_2$Se$_3$ nanorods and poorly crystalline ((c) blue line) Sb$_2$Se$_3$ nanoparticles.

Figure 6: UV-vis absorbance spectra of RhB in solution after exposure to Sb$_2$Se$_3$ nanoparticles, in the presence of natural light, for 0, 2, and 4 h, respectively.

compared to the bulk sample consistent with common knowledge that the smaller the size of the particle, the higher the band gap. A solar cell under construction in our laboratory showed potential when Sb$_2$Se$_3$ was paired with CdS.

The efficiency of the semiconductor nanoparticles and nanorods with different band gap to function as photocatalyst was measured using RhB as a model organic pollutant in the presence of natural light. Figure 6 shows the UV absorption spectra of RhB in solution at different time intervals (0, 2, and 4 h) for nanoparticles (since decolorization of RhB by nanoparticles was slightly higher than nanorods; only results for nanoparticles are shown). In 2 h, about 50% of the RhB is decolorized followed by a 75% decolorization in 4 h. The photodecolorization of RhB by semiconductor nanoparticles may be explained by an adsorption-oxidation-desorption mechanism where oxygen accepts an electron forming a superoxide radical anion. These can react with water to form highly reactive hydroxyl radicals.

4. Conclusion

A new method using hydrazine hydrate and permanganate was developed to prepare Sb$_2$Se$_3$ nanorods and nanoparticles with uniform size and morphology. The use of hydrazine hydrate in basic solution (in the presence of selenite and antimony acetate) channels the reaction towards the production of large rod-like Sb$_2$Se$_3$ nanocrystals, while the use of hydrazine hydrate in near neutral solution (in the presence of selenite and antimony chloride) channels the reaction in the direction of producing small rod-like Sb$_2$Se$_3$ nanocrystals. The use of permanganate, hydrazine, Sb(CH$_3$COO)$_3$, and selenite produces Sb$_2$Se$_3$ nanocrystals with Mn as an impurity. One attractive feature for our system is that it is simple, cost-effective, and reproducible. Large scale production would depend on what is desired. For large nanorods, the first reaction is recommended, while for fine nanorods, the second reaction is best. The photocatalytic study demonstrated that semiconductor nanoparticles are more effective in the decolorization of RhB via possibly free radical formation. Antimony selenide nanoparticles may find potential application not only in thermoelectric, photovoltaic, and phase-change memory devices but also as catalyst for the transformation of organic pollutants.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the National Research Foundation of Korea (Grant NRF-2015-002423).

References


[19] D. B. Wang, C. X. Song, X. Fu, and X. Li, “Growth of one-dimensional Sb\textsubscript{2}Se\textsubscript{3} and Sb\textsubscript{2}Se\textsubscript{3} crystals with straw-tied like architectures,” Journal of Crystal Growth, vol. 28, p. 611, 2005.


Submit your manuscripts at https://www.hindawi.com