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Abstract

We report the first synthesis of high-quality binary and ternary Sb2Se3-xSx nanotubes across the entire compositional range from x = 0 to 3 via a simple, low-cost, colloidal synthetic method of injection of Sb(III)-complex solution into a hot paraffin liquid containing Se, S, or a mixture thereof. In contrast to the classic rolling mechanism, the modular formation of the reported nanotubes follows a four-stage self-seeding process: (i) amorphous nanospheres, (ii) short crystalline nanotubes growing out of relatively large amorphous nanospheres, (iii) long crystalline nanotubes attached to small amorphous nanospheres, and (iv) single-crystal nanotubes. The obtained single-crystal nanotubes have tunable composition, orthorhombic phase, well-defined rectangular cross sections, and growth direction along [001], as revealed by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, and selected area electron diffraction studies. UV–vis-NIR absorption spectroscopy reveals that the optical bandgap energy of the Sb2Se3-xSx (0 ≤ x ≤ 3) nanotubes increases quadratically with the sulfur concentration x with these bandgap energies falling in the range from 1.18 to 1.63 eV at the red edge of the solar spectrum. The present study opens a new avenue to low-cost, large-scale synthesis of high quality semiconductor nanotubes with technological applications in solar energy conversion and also for a wide range of optical nanodevices operating in the near-infrared.

Main-group compounds V2VI3 (V = As, Sb, Bi; VI = S, Se, Te) materials have applications in catalytic agents, thermoelectric devices, optoelectronic devices, and infrared spectroscopy.1–3 Among these compounds, Sb2S3 and Sb2Se3 are important photoconductive semiconductors (Eg = 1.64 and 1.11 eV, respectively) that crystallize in the orthorhombic system (pbnm space group).4–6 Their useful properties (e.g., photovoltaic, photocconducting, photocatalytic, Peltier effect) make them promising candidates for important applications in diverse areas such as solar energy conversion, thermoelectric cooling, photodetector technology, thermoelectric power generation, and opto-electronics in the near-infrared region.7–8 Ternary alloys of Sb2Se3-xSx (0 < x < 3) may have composition-dependent bandgap energies, and due to disorder-induced phonon scattering processes may have lower lattice thermal conductivities and better efficiency in solar energy conversion than the binary compounds.3 Inorganic semiconducting hollow nanotubes could be advantageous in nanoscale electronics, optoelectronics, and biochemical sensing applications. However, synthesis of binary Sb2Se3, Sb2S3, and ternary Sb2Se3-xSx (0 < x < 3) nanotubes is still difficult for industrial applications; there exist great challenges to obtaining high-quality nanotubes using a simple, inexpensive, and efficient approach. Although various methods have been developed for the fabrication of one-dimensional (1D) Sb2S3 and Sb2Se3 nanostructures including nanorods, nanowires, and nanoribbons, investigations of nanotube synthesis are quite rare.10–13 In 2004, Chen’s group reported the synthesis of Sb2S3 nanotubes for the first time via the chemical vapor transport reaction.14 In 2007, Son’s group reported the synthesis of Sb2S3 nanotubes with ultrathin walls (1.5–2.0 nm) via the rolling mechanism.15 To our knowledge, no effective techniques have been reported for the synthesis of binary Sb2Se3 and ternary Sb2Se3-xSx (0 < x < 3) nanotubes.

Here we report the synthesis of single-crystal Sb2Se3-xSx nanotubes across the entire compositional range from x = 0 to 3 by a simple colloidal process involving the injection of Sb(III)-complex solution into a hot Se, S, or their mixture in paraffin liquid. This represents the first synthesis of binary Sb2Se3 nanotubes and ternary Sb–Se–S 1D nanostructures. We also discovered that the optical bandgap energy of the as-synthesized Sb2Se3-xSx (0 ≤ x ≤ 3) nanotubes increases

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As shown in Scheme 1a, the current synthetic method is modeled on the well-developed technique for colloidal synthesis of high-quality CdSe nanocrystals, which involves the injection of trioctyolphosphine (TOP)-selenium precursor into the Cd-complex solution at 250–300 °C in a high-boiling-point solvent such as trioctyolphosphine oxide (TOPO). Deng et al. modified this classic procedure by using “green” and low-cost paraffin liquid as the solvent, dissolving Se powder in paraffin liquid directly (i.e., without TOP), to synthesize zinc blende CdSe nanocrystals. This technique avoided the use of TOP for dissolving the Se powder, as TOP is a hazardous, unstable, expensive, and environmentally harmful solvent, whereas paraffin liquid \([\text{CH}_3(\text{CH}_2)_n\text{CH}_3, n = 16–22]\) is a nontoxic, environmentally friendly, inexpensive, and stable solvent with boiling points above 300 °C.

Taking Sb2Se3 nanotubes for an example, the synthesis involves the injection of Sb(III)-2-ethylhexanoic acid (EHA) complex into the Se-paraffin liquid solution at the temperature of 220 °C (for the experimental details see Supporting Information). Immediately after injection, the color of the mixed solution turned from yellow to gray black, indicating the formation of Sb2Se3 species. Serial aliquots were taken at different intervals for monitoring the kinetics of nanotube formation, and the resulting solid products were purified and imaged with scanning electron microscopy (SEM), as shown in Figure 1a, Figures S1 and S2 (see Supporting Information). In the initial stage, depicted in Figure 1a (5 s), noncrystalline and homogeneous nanospheres with diameters \(\sim 180 \text{ nm}\) were obtained at 5 s reaction; no crystalline nanostructures or nanotubes were observed at this stage, as revealed by the X-ray diffraction (XRD) patterns in Figure 1d. In the second stage, there appeared a small amount of short nanotubes growing on the surface of each nanosphere with crystalline peaks showing up in the XRD pattern at 15 s reaction. By the third stage, relatively long nanotubes had emerged with only a small residue of the original amorphous nanosphere still remaining at 60 s reaction. Finally, in the fourth stage, there were uniform nanotubes only (i.e., no amorphous spheres) at 180 s reaction. Transmission electron microscopy (TEM) images shown in Figure S3 (see Supporting Information) are consistent with our SEM results. The TEM images in Figure 1a (180 s) and Figure S1 (see Supporting Information) reveal that the end product contains a large quantity of uniform 1D Sb2Se3 nanotubes with lengths of \(\sim 1 \mu\text{m}\) and diameter of \(\sim 100 \text{ nm}\). Closer inspection reveals the product to have a hollow cuboidal morphology with a well-defined rectangular cross-section; see Figure 1b,c. Typical nanotubes are \(\sim 100 \text{ nm}\) wide, \(\sim 80 \text{ nm}\) thick, and have wall thickness \(\sim 10 \text{ nm}\).

On the basis of the above observations, we performed a simple mass calculation to study the transformation process from nanospheres to nanotubes. The volume of a solid nanosphere is give by

\[
V = \frac{4\pi}{3} \times \left(\frac{d}{2}\right)^3
\]  

(1)

Assuming a diameter \(D = 180 \text{ nm}\), the volume of a single nanosphere will be \(3.1 \times 10^6 \text{ nm}^3\). For a Sb2Se3 nanotube, the volume could be calculated using

\[
V = L \times \left[ H \times D - (H - 2d) \times (D - 2d) \right]
\]  

(2)

Here \(L = 1000 \text{ nm}\), \(H = 100 \text{ nm}\), \(D = 80 \text{ nm}\), and \(d = 10 \text{ nm}\). The volume of a single Sb2Se3 nanotube is thus found to be \(3.2 \times 10^5 \text{ nm}^3\). Supposing the equal densities for the amorphous Sb2Se3 nanospheres and crystalline Sb2Se3 nanotubes, the masses of the solid amorphous Sb2Se3 nanospheres and hollow crystalline Sb2Se3 nanotubes should be nearly identical. Thus, the above simple calculation strongly supports our postulated transformation of a single solid amor-
phous Sb₂Se₃ nanosphere to a single hollow crystalline Sb₂Se₃ nanotube.

In addition, our UV–vis-NIR absorption spectra obtained as function of reaction time show that the absorption onset does not shift much (∼0.05 eV) during the transformation process from amorphous nanosphere to single-crystal nanotubes as shown in Figure S2f,g (see Supporting Information), whereas the XRD patterns obtained after different reaction times show the increasing crystallinity of the product (see Figure 1d).

The above results clearly indicate that the formation of nanotubes follows a four-stage, self-seeding process as shown in Scheme 1b: (i) formation of amorphous nanospheres that act as sacrificial reservoirs for Sb₂Se₃ nanotubes; (ii) growth of short nanotubes out of relatively large nanospheres; (iii) long nanotubes attached to small residual nanospheres; and (iv) complete nanotubes with no nanospheres attached. To further verify the growth mechanism, we performed the control experiment with double precursor Sb(III) and Se concentrations, while keeping the other experimental parameters the same. As shown in Figure S4 (see Supporting Information), the TEM images of the Sb₂Se₃ products harvested at different intervals demonstrated that the larger sized nanotubes (∼250 nm in diameter, ∼5 µm in length) were grown from larger sized nanospheres (∼700 nm in diameter); the well-defined four-stage self-seeding growth process is consistent with the observations from the lower precursor concentrations. It is expected that the sizes of the nanotubes could be further tuned by changing the reaction parameters such as the concentration of the precursors and reaction temperature. We believe that the formation of Sb₂Se₃ nanotubes was via the preferential formation of the crystalline Sb₂Se₃ species on the surface of the amorphous nanospheres. As soon as the crystalline species were grown, mass transport to the growing region in one end of the nanotubes would lead to depletion of the amorphous nanospheres as the sacrificial reservoirs in another end and eventually resulted in the formation of the well-defined nanotubes.

In somewhat similar fashion, Xia’s group has demonstrated the synthesis of Te nanotubes by directly nucleating and growing from aqueous orthotelluric acid solution. In their growth mechanism, Te nanotubes could be preferentially grown at the circumferential edges of the crystalline cylindrical Te solid seeds via control the concentration of the Te in bulk solution. Then, the mass transport to the growing regions would lead to depletion of the Te in the center cylindrical solid seeds and result in the formation of the nanotubes with hollow interiors. Also, Ding’s group has demonstrated the formation of TiO₂ nanotubes through CeO₂ colloid-seeded deposition process in solution. Contrastively, there is a classic rolling mechanism for the growth of inorganic nanotubes, which was derived from the successful synthesis of nanotubes of carbon and other inorganic materials with layered structures in their bulk crystals. Nevertheless, our synthetic technique demonstrates the first formation of V₃V₃ nanotubes through a self-seeding process in solution. Our synthetic method is modular, and we have extended it to the synthesis of single-crystal Sb₂S₃ and Sb₂Se₃ nanotubes with rectangular cross-section.

Figure 2a and Figure S5 (see Supporting Information) show the X-ray diffraction (XRD) patterns of seven different Sb₂Se₃-S₃ (0 ≤ x ≤ 3) nanotubes with their precursor sulfur concentration x indicated; (b) (230) and (211) XRD peaks of the same nanotubes as in panel a; (c) lattice constants a (green), b (blue), and c (red), derived from XRD diffraction peaks and HRTEM images, plotted as functions of precursor sulfur concentration x.

![Figure 2](image-url)

**Figure 2.** (a) From bottom to top, XRD patterns of the Sb₂Se₃-S₃ (0 ≤ x ≤ 3) nanotubes with their precursor sulfur concentration x indicated; (b) (230) and (211) XRD peaks of the same nanotubes as in panel a; (c) lattice constants a (green), b (blue), and c (red), derived from XRD diffraction peaks and HRTEM images, plotted as functions of precursor sulfur concentration x.
position. The above results indicate that alloyed Sb$_2$Se$_{3-x}$S$_x$ nanotubes with modulated compositions between Sb$_2$Se$_3$ and Sb$_2$S$_3$ could be obtained during this simple colloidal synthesis process.

The scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) patterns in Figure 3, Figures S1, S6, and S7 (see Supporting Information) reveal that the end product contains a large quantity of Sb$_2$Se$_x$ nanotubes (normalized with the Sb peak intensity), the Si signals are from the silicon substrate, while the C signals are possibly from the trace organic materials such as paraffin liquid, 2-ethylhexanoic acid, or oleylamine; (i) sulfur concentration $x$ measured directly from the EDS spectra plotted versus the nominal precursor sulfur concentration $x$.

As seen in Figure 5, the high-resolution TEM (HRTEM) images of a series of individual nanotubes show the typical lattice spacings of about 0.82 nm and a length up to 1 µm. The microstructure of an individual Sb$_2$Se$_3$ nanotube shown in Figure 4b reveals the well-defined hollowing nanotube structure feature, consistent with the structural information gleaned from SEM images. The obvious lattice spacings of about 0.827 nm corresponds to (110) planes spacings of orthorhombic phase Sb$_2$Se$_3$ (JCPDS Card No. 72-1184). The selected area electron diffraction (SAED) pattern (inset Figure 4b) is a spot pattern, revealing that the nanotube is a single crystal. In addition, the SAED pattern indicated that the nanotube grows along the [001] direction as marked with an arrow shown in Figure 4b. Figure 4 shows that the obtained nanotubes are of high quality and free from dislocation and stacking faults.

As shown in Figure S8 (see Supporting Information), the HRTEM image of single Sb$_2$Se$_{2.6}$S$_{0.4}$ nanotube indicates that the typical lattice spacings are about 0.804 and 0.387 nm, corresponding to (110) and (001) planes spacings of orthorhombic phase, respectively. The HRTEM image also demonstrates that the nanotubes grows along the [001] direction as indicated with an arrow. These results revealed that all the nanotubes are of high quality.

Analysis of optical absorption spectra is one of the most effective tools for understanding and/or engineering the band structure and energy gaps of semiconductor materials. The optical absorption experiments reported in Figure 6a were carried out to determine the band gap energies of our nanotube samples. For direct band gap semiconductors, the

![Figure 4.](image-url)
optical absorption near the band edge follows the formula:

\[ \alpha \nu = A (\nu - E_g)^{1/2} \]

where \( \alpha \), \( \nu \), and \( E_g \) are the absorption coefficient, optical frequency, and band gap energy, respectively, while \( A \) is a constant. The \( E_g \) can thus be estimated from a plot of \((\alpha \nu)^2\) versus the photon energy \((\nu)\). The estimated band gaps for our various samples were found to be 1.63, 1.48, 1.33, 1.29, 1.25, 1.21, and 1.18 eV; see Figure 6b. The band gap \( E_g \) is thus seen to increase from 1.18 eV for \( \text{Sb}_2\text{Se}_3 \) to 1.63 eV for \( \text{Sb}_2\text{S}_3 \) as the concentration of S increases in the \( \text{Sb}_2\text{Se}_3-x\text{S}_x \) series.

The dependence of the optical transition energy on composition \((x)\) was found to fit a quadratic equation as shown in Figure 6c and characterized by the following relation

\[ E_g(x) = 0.0344x^2 + 0.0481x + 1.18 \text{ eV} \]  \( (4) \)

The fitted values of the bandgap energy obtained in our measurements are in good agreement with the previously reported values from 1D \( \text{Sb}_2\text{S}_3 \) and \( \text{Sb}_2\text{Se}_3 \) nanostruc-

Figure 5. HRTEM images and their indexed fast Fourier transforms (FFTs) of \( \text{Sb}_2\text{Se}_3-x\text{S}_x \) \((0 \leq x \leq 3)\) nanotubes, labeled with the corresponding precursor sulfur concentration \( x \). All scale bars are 1 nm.

Figure 6. (a) UV−vis-NIR absorption spectra of \( \text{Sb}_2\text{Se}_3-x\text{S}_x \) \((0 \leq x \leq 3)\) nanotubes at room temperature. (b) Plots of \((\alpha \nu)^2\) vs the photon energy \((\nu)\) reveal the band-gaps of \( \text{Sb}_2\text{Se}_3-x\text{S}_x \) nanotube samples as 1.63, 1.48, 1.33, 1.29, 1.25, 1.21, and 1.18 eV for \( x = 3.0, 2.3, 1.5, 1.2, 1.0, 0.4, \) and 0, respectively. (c) The band gap energy plotted versus the sulfur concentration \( x \) (nominal precursor sulfur concentration \( x \)); the solid curve is a quadratic fit to the measured values of the band gap energy extracted from the absorption spectra in panel b.

\[ E_g(x) = 0.0344x^2 + 0.0481x + 1.18 \text{ eV} \]  \( (4) \)

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The experimental values of nanotube bandgaps are near the optimum value for photovoltaic conversion, suggesting that these nanotubes may be promising for applications in solar energy and for a wide range of optical nanodevices operating in the near-infrared range. Further work to explore their structures, optical properties, and technological applications is currently underway.

Conclusions. Using a simple and low-cost colloidal synthetic technique involving the injection of Sb(III)-complex source solution into a hot paraffin liquid containing Se, S, or a mixture thereof, we have demonstrated the capability of tuning the composition and the energy gap of single-crystal binary and ternary Sb$_2$Se$_3$, Sb$_2$S$_3$ (0 ≤ x ≤ 3) nanotubes having rectangular cross sections across the entire composition range. The modular formation of these nanotubes follows a four-stage self-seeding process: (i) amorphous nanospheres, (ii) short crystalline nanotubes growing out of relatively large amorphous nanospheres, (iii) long crystalline nanotubes attached to small amorphous nanospheres, and (iv) single-crystal nanotubes. We have demonstrated the smooth dependence of the bandgap on composition from Sb$_2$Se$_3$ to Sb$_2$S$_3$ in the near-infrared region from 1.18 to 1.63 eV. The estimated band-gaps of our nanotubes are at the red edge of the solar spectrum, thus suggesting that these nanotubes may hold promise for solar energy conversion as well as for novel opto-electronics applications. By the suitable choice of sources and/or synthetic parameters, it is reasonable to expect that the present methods can be extended to the synthesis of other semiconductor nanotubes as well.

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Supporting Information Available: Additional synthesis and characterization details, SEM and TEM images, EDS patterns, UV–vis-NIR absorption spectra, size distribution histograms, and XRD patterns of the samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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