Diameter-Controlled and Surface-Modified Sb$_2$Se$_3$ Nanowires and Their Photodetector Performance

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Due to its direct and narrow band gap, high chemical stability, and high Seebeck coefficient ($1800 \text{ mVK}^{-1}$), antimony selenide (Sb$_2$Se$_3$) has many potential applications, such as in photovoltaic devices, thermoelectric devices, and solar cells. However, research on the Sb$_2$Se$_3$ materials has been limited by its low electrical conductivity in bulk state. To overcome this challenge, we suggest two kinds of nano-structured materials, namely, the diameter-controlled Sb$_2$Se$_3$ nanowires and Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires. The photocurrent response of diameter-controlled Sb$_2$Se$_3$, which depends on electrical conductivity of the material, increases non-linearly with the diameter of the nanowire. The photosensitivity factor ($K = \frac{I_{\text{light}}}{I_{\text{dark}}}$) of the intrinsic Sb$_2$Se$_3$ nanowire with diameter of 80–100 nm is highly improved ($K = 75$). Additionally, the measurement was conducted using a single nanowire under low source-drain voltage. The dark- and photocurrent of the Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowire further increased, as compared to that of the intrinsic Sb$_2$Se$_3$ nanowire, to approximately 50 and 7 times, respectively.

Group V-VI binary pnictogen chalcogenide semiconductors, typically crystallizing into a one-dimensional nanostructure in layer-structures parallel to the growth direction, have attracted a lot of attention owing to their specific properties and potential application in various fields, namely, photovoltaic, thermoelectric, and electric devices. In particular, antimony selenide (Sb$_2$Se$_3$) has promising characteristics, such as narrow band gap (approximately 1 eV), high chemical stability, and high Seebeck coefficient (1800 mVK$^{-1}$). These properties are attributable to a fast transition from amorphous to crystalline state. Despite its potential in various applications, research on the synthesis and application of the Sb$_2$Se$_3$ nanostructures has been limited by challenges, such as its low thermoelectric power factor ($\alpha^2s$), low spectral response ($R_s$), and low external quantum efficiency (EQE), which result in low electrical conductivity ($\sigma$, $10^{-6} \sim 10^{-2} \Omega^{-1}\text{m}^{-1}$) in bulk state.

Nonetheless, a few groups have synthesized and studied Sb$_2$Se$_3$ nanomaterials to improve its electrical conductivity. For example, Golberg et al. synthesized single-crystalline Sb$_2$Se$_3$ nanowires using a hydrothermal method and investigated its field emission and photoconductive properties. Single crystalline Sb$_2$Se$_3$ nanowires, synthesized for 72 h at 180$^\circ$C exhibited remarkable response to 600 nm of specific visible light with response time of 0.3 sec. However, their time-consuming synthetic process, low electrical conductivity, and low photosensitivity factor ($K = \frac{I_{\text{light}}}{I_{\text{dark}}}$) still hamper practical applications of the Sb$_2$Se$_3$ nanowires.

Here we suggest new synthetic process of single-crystal Sb$_2$Se$_3$ nanowires to overcome these challenges. Sb$_2$Se$_3$ nanowires were synthesized by injection of chemicals into hot solvent (called Hot Injection method). This is one of the most common methods to produce nano-structured materials such as Q-dots, metal alloy nanoparticles, and metal oxide nanoparticles, as size controlled nanoparticles can be easily prepared. Using this hot injection method, we could not only produce Sb$_2$Se$_3$ nanowires quickly, but could also control the diameter of the nanowires.

Using an additional process, Sb$_2$Se$_3$ nanowires decorated with Ag$_2$Se nanoparticles (Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires) were also developed. Ag$_2$Se nanoparticles increased the electrical conductivity and also improved photosensitivity of the Sb$_2$Se$_3$ nanowires.

Results

Characterization of nanowire. Figures 1a shows representative transmission electron microscopy (TEM) image of the intrinsic Sb$_2$Se$_3$ nanowires grown using the hot injection method. Individual nanowires had a diameter of...
80–100 nm, and a typical length of several micrometers. A high-resolution TEM image and corresponding electron diffraction pattern of the nanowires, as shown in Figure 1(b), revealed that as-synthesized nanowire is single crystal without any detectable crystal defect. The powder X-ray diffraction (XRD) pattern of the intrinsic Sb$_2$Se$_3$ nanowires had five prominent peaks, which were indexed to the (120), (230), (221), (240), and (061) planes, corresponding to the orthorhombic crystal structure of Sb$_2$Se$_3$ with Pmma space group (Figure 1 c).

Diameter of nanowires is a critical factor, especially in semiconductor nanowires, as their electronic properties strongly depend on diameter of the wire. For instance, GaN nanowires showed various photocurrent responses between 1 nA and 100 μA according to their diameter$^{38}$. In our study, the diameter of Sb$_2$Se$_3$ nanowires could be controlled. Figure 2 shows transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of various diameter of Sb$_2$Se$_3$ nanowires, which were controlled by altering the precursor and surfactant ratio. Oleic acid was used as the surfactant in our study. Generally, high concentration of surfactant results in smaller sizes, including diameter, thickness, and length. Three diameter of nanowires were obtained, which were 200–300 nm, 80–100 nm, and 50 nm, with precursor and surfactant ratios of 1:2, 1:4, and 1:20, respectively. An increase in oleic acid resulted in narrow diameter Sb$_2$Se$_3$ nanowires. In addition, SEM images, which correlated well with the TEM images, confirmed that the nanowires synthesized had smooth surfaces.

To improve the electrical conductivity of Sb$_2$Se$_3$ nanowires, silver precursor (AgNO$_3$) was added to the nanowire solution and nanowires decorated with silver nanoparticles were expected. However, we obtained Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires. Nonetheless, Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires were also expected to have better conductivity and photosensitivity than bare Sb$_2$Se$_3$ nanowires. Figure 3a clearly shows that each Ag$_2$Se nanoparticle was incorporated onto the Sb$_2$Se$_3$ nanowires. The high-resolution scanning TEM (HR-STEM) image of the Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires shows that Ag$_2$Se nanoparticles and Sb$_2$Se$_3$ nanowire have different lattice structures and a visible interface (Figure 3b). The HR-STEM image further supports on the synthesis of high crystallinity Ag$_2$Se nanoparticles and Sb$_2$Se$_3$ nanowires. The d spacing is 2.58 Å and 1.98 Å, which is agrees well with the distance of the [121] lattice plane of Ag$_2$Se and [002] lattice plane of Sb$_2$Se$_3$, respectively. Additionally, the unblemished nanowire surface was convincing evidence that selenium of the Ag$_2$Se nanoparticles originated from excess selenium precursor in the reaction mixture. To confirm the origin of selenium, we removed excess selenium precursor from the reaction mixture and added Ag precursors. We could not obtain the Ag$_2$Se decorated Sb$_2$Se$_3$ nanowires with this reaction condition. The powder X-ray diffraction (XRD) pattern of the Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires shows that all diffraction patterns can be indexed to the peaks of Ag$_2$Se(JCPDS 71-2410) and Sb$_2$Se$_3$(JCPDS 15-0861) without any visible peak from impurities (Figure 1c).

To find the optimum reaction condition, especially the reaction temperature, the same reaction was conducted at different temperatures. The optimum temperature of the reaction was found to be 100 °C. When the temperature was increased above 150 °C, the Ag precursor was sufficiently activated to oxidize the as-synthesized Sb$_2$Se$_3$ nanowires and resulted in Ag$_2$Se nanoparticle-decorated Sb$_2$Se$_3$ nanowires (150 °C, Supporting Information Figures S1a...
and, S1b) and more dissolved nanowires (200°C, Supporting Information Figure S1d and, S1e). The reactivity of the silver precursor decreased at 80°C and no reaction occurred. Extremely high reaction temperature at above 300°C resulted in Ag nanoparticles and a trace of Ag$_2$Se nanoparticles (Supporting Information Figure S1f and, S1g).

The selenium and silver ratio in the reaction mixture had also a significant effect on the surface morphology of the nanowires. As the amount of Ag increased, more nanoparticles attached to the surface of the nanowires, which then turned coarse. SEM images in Supporting Information Figure S2 show the surface change from bare Sb$_2$Se$_3$, 200/1, 100/1, and 50/1 ratios of Se/Ag, respectively.

Interestingly, the size of Ag$_2$Se nanoparticles on the Sb$_2$Se$_3$ nanowires could be also controlled by the diameter of the Sb$_2$Se$_3$ nanowires. An increase in the diameter of Sb$_2$Se$_3$ nanowires resulted in larger Ag$_2$Se nanoparticles. The reason was unclear, however, it can be postulated that larger curvature formed from the increase in diameter of the nanowires allowed the Ag$_2$Se nanoparticles to attach more easily onto the nanowire surface and also allowed for larger sized nanoparticles to be formed. Detailed TEM image of Ag$_2$Se nanoparticles on nanowire surface can be found in the Supporting Information Figure S3.

In order to investigate the elemental distribution in the Ag$_2$Se-decorated Sb$_2$Se$_3$ nanowires, scanning electron microscopy (SEM) and mapping analysis were performed. SEM mapping images of Se, Ag, and Sb elements are shown in Figure 4. Se atoms were distributed evenly in both, the wire and dot positions. Ag distribution was restricted to the specific areas corresponding to the positions of Ag$_2$Se nanoparticles on the Sb$_2$Se$_3$ nanowires. Ag atoms were found in the nanowire positions, the reason was not clear. EDX-STEM elemental analysis was performed to confirm the results. The O$_2$-labeled areas in Supporting Information Figure S4, shows that the dot areas were composed of Ag and Se elements, while Sb and Se elements were found in the nanowire region.

Measurement of Photo-device. Photocurrent responses of individual nanowires using 655nm irradiation were measured under ambient conditions at room temperature. Figures 5a and b are the schematic illustration and SEM image, respectively, of a single nanowire device. To fabricate the nanowire device, the nanowires are spin-coated using nanowire/hexane solution and SiO$_2$/Si substrate, after which, identical parallel electrode patterns with channel length of 4 µm were randomly positioned using the conventional lithography technique. The electrical
properties were measured either before or after scanning a single nanowire device using SEM.

Figure 5c shows the I–V curves of a single Sb$_2$Se$_3$ nanowire device with a diameter of 100 nm measured under dark as well as in presence of 655 nm illumination (15 mW·cm$^{-2}$). Photo-response properties were measured when the light was turned on and off, at 10 sec intervals (Figure 5d). From the I–V curve, the electrical conductivity of the 100 nm diameter Sb$_2$Se$_3$ single nanowire in dark condition was $7.6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ which was similar to the bulk Sb$_2$Se$_3$.

Electrical conductivity of the Sb$_2$Se$_3$ nanowire increased under the 655 nm irradiation condition. At 3 V bias, the current under dark conditions was 450 pA, which increased to 34 nA with illumination. The photosensitivity factor, K was defined as $K = \frac{I_{\text{light}}}{I_{\text{dark}}}$, where $I_{\text{light}}$ and $I_{\text{dark}}$ correspond to current measured with a 655 nm laser turned on and off, respectively. The K factor of the intrinsic Sb$_2$Se$_3$ nanowire was found to be 75, which was comparable to previous results$^{22}$ (where K value was 15, with power density of 1.68 mWcm$^{-2}$, under 615 nm illumination). However, the conductivity was 3 times the previous result. The Sb$_2$Se$_3$ nanowires used in this study, which were generated using the hot injection method were expected to be more resistant to oxidation and contained fewer surface defects (e.g. dangling bonds) than hydrothermally grown Sb$_2$Se$_3$ nanowire due to passivating ligands. Moreover, we used relatively thick (Ti (20 nm)/Au (100 nm)) metal electrodes with very slow deposition rates (1 $\mu\text{A} \cdot \text{sec}$) and a thermal evaporator, which we presumed would allow for better Ohmic contact between the nanowire and the metal electrode.

As shown in Figure 6, time responses of three different diameters of the Sb$_2$Se$_3$ nanowire (100 nm, 200 nm, and 400 nm) are also compared. When the Sb$_2$Se$_3$ wires are irradiated using same light source (655 nm, 6.5 mW·cm$^{-2}$) photocurrent response increased with the diameter and the ratio of the magnitude of the photocurrent response in 100, 200, and 400 nm wires were 1, 7, and 21, respectively.

The photocurrent in the nanowire for a given photon energy can be expressed as$^{40}$
In addition, the power absorbed in the photoconductor (P_{abs}) and the photoconductive gain (G) can be expressed as

\[ P_{abs} = \eta \times P_{opt} = \eta \times I_0 A \]  

\[ G = \frac{\tau}{\tau_t} \]  

Where, \( P_{opt} \) is the incident optical power, \( I_0 \) is the illumination intensity, \( A (= \pi dL/2) \) is the exposed surface area of the nanowire, and \( \tau_t \) is the carrier transit time of the nanowire.

In bulk Sb\(_2\)Se\(_3\) material, the increase in photocurrent is proportional to the nanowire surface area (1:2:4 for 100 nm:200 nm:400 nm) due to light absorption. However, in the Sb\(_2\)Se\(_3\) nanowire, the increase in photocurrent was greater than the light absorbed, probably because of the increase in photoconductive gain due to the nanowire structure. In semiconductor nanowires, a depletion space charge layer forms due to the surface state and Fermi-level pinning, which allows for physical separation of the electron and the hole within the nanowire. (Supporting Information Figure S5) Until the critical diameter of the nanowire is reached, the depletion layer remains fully depleted and the recombination barrier increases. This may prolong the life of photo-generated carriers and may further increase the photocurrent as the nanowire diameter increases. 

(Figure 6) Time-dependent photocurrent response of the Sb\(_2\)Se\(_3\) nanowires with 3 different diameter. (100 nm (blue), 200 nm (red) and 400 nm (black)). Light incidence is 655 nm (5.6 mWcm\(^{-2}\)) pulsed light with a period of 30 s. Applied voltage is 3 V.

(Figure 7a) shows the I–V curves of a device fabricated using Ag\(_2\)Se-decorated Sb\(_2\)Se\(_3\) single nanowire with 100 nm diameter, measured both in dark and under 655 nm illumination (15 mW cm\(^{-2}\)). The photo-response property of the Ag\(_2\)Se-decorated nanowire was also measured when the light was turned on and off at 10 sec intervals (Figure 7b). Compared with the pure Sb\(_2\)Se\(_3\) nanowires of similar size (100 nm diameter) but without Ag\(_2\)Se decoration, the current under dark conditions increased approximately 50 times (from 450 pA to 22.8 nA at 3 V) and photocurrent increased approximately 7 times (from 34 nA to 228 nA at 3 V). The K factor of Ag\(_2\)Se-decorated Sb\(_2\)Se\(_3\) nanowires was 10. The addition of Ag\(_2\)Se
obtained in dark conditions was 450 pA, which increased to 34 nA.
