Colloidal synthesis and characterizations of single-crystalline Sb_2Se_3 nanowires

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Electronic Supplementary Information

Experimental Details

Preparation of Se/DMAB/OLA solution

5 mL OLA, 7.5 mL DMAB and 6 mmol Se powder (99.9%, Aladdin) were added into a two neck round bottomed flask (50 mL) connected to a Schlenk line (Fig. S1 (a)). Then the temperature was heated up to around 110°C under vacuum with stirring to dissolve Se powder. The temperature was kept constant for a few minutes, the color of mixture solution turned immediately from dark (Fig. S1 (b)) to colorless (Fig. S1 (c)). The temperature of the Se/DMAB/OLA solution was held constant at 90 °C.

Fig. S1 The photographic image where a two necked round bottomed flask consisted of 6 mmol Se powders and 7.5 mL DMAB in 5 mL OLA (a) at room temperature, (b) at the start of the reduction reaction 110 °C, and (c) at the end of the reduction, Se/DMAB/OLA colorless solution.

Synthesis of Sb_2Se_3 nanowires

A. The use of antimony trichloride as Sb source

In a typical synthesis, 1.0 mmol of antimony trichloride ($SbCl_3$) and 10 ml of oleylamine were added into a three-neck round bottomed flask (50 ml) connected to a Schlenk line (all chemicals were used as received from suppliers without any prior arragements). The temperature was adjusted up to around 120°C under vacuum with stirring as well as degassing for about an hour and purging with Ar for 3 times. The flask was then heated to 180 °C, where 1.5 ml of 1.0 M solution of Se/DMAB in oleylamine was injected. After injection, the solution turned dark and the temperature was held at 180 °C for 30 minutes. After the reaction, the products were recovered from precipitation-dispersion cycles utilizing toluene and ethanol (1:3 v/v).

B. The use of antimony triacetate as Sb source

1.0 mmol of antimony triacetate ($Sb(CH_3COO)_3$) and 10 ml of oleylamine were added into a three-neck round bottomed flask (50 ml) connected to a Schlenk line (all chemicals were used as

received from suppliers without any prior arragements). The temperature was adjusted up to around 120°C under vacuum with stirring as well as degassing for about an hour and purging with Ar for 3 times. The flask was then heated to 190 °C, where 1.7 ml of 1.0 M solution of Se/DMAB in oleylamine was injected. After injection, the solution turned dark and the temperature was held at 190 °C for 30 minutes. After the reaction, the products were recovered from precipitation-dispersion cycles utilizing toluene and ethanol (1:3 v/v).

Preparation for Sb_2Se_3 nanowires films

0.2-0.3 mL of ink (using a toluene solution of Sb_2Se_3 nanowires) was drop-casted onto a sodalime glass (SLG) with an area of 2.40 cm^2. The sample was then put in a draught cupboard so that the solvent evaporated naturally. Consequently, a dense Sb_2Se_3 nanowires thin film was formed on the SLG. On the other hand, the Sb_2Se_3 nanowires films on an ITO glass were also prepared and the nanocrystals films were served as working electrodes in photoelectrochemical (PEC) test. 0.2-0.3 mL of ink (using a toluene solution of Sb_2Se_3 nanowires) was drop-casted onto an ITO glass with an area of 1.96 cm^2. The sample was then put into a draught cupboard so that the solvent evaporated naturally. After that, the samples were dried at 100 °C under vacuum for 8 hours to remove the ligands and to improve the conductivity of the Sb_2Se_3 nanowires films.

Materials Characterizations

The synthesized Sb_2Se_3 nanowires were characterized by transmission electron microscopy （TEM）and selected area electron diffraction (SAED) via JEM 2100F microscope. The crystal structure and chemical composition were characterized by X-ray diffraction (Riguaku 3014) and energy-desperive X-ray spectroscopy (EDAX-GENSIS60S) using a dried thin film samples prepared by drop-casting the nanocrystal-ink, respectively. The Raman spectra was taken by using a LabRAM ARAMIS spectrometer. UV-vis-NIR spectra were carried out to evaluate the optical properties of Sb_2Se_3 nanowires using UV-vis-NIR HITACHI U-4100 spectrophotometer. The photoelectrochemical characterization of the film was carried out in 0.5 M H_2SO_4 solution in a Pyrex electrolytic cell. Where the sample, a purity graphite plate, and a saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. A 300 W xenon lamp was used as light source, with the light intensity kept at 100 mW/cm^2.

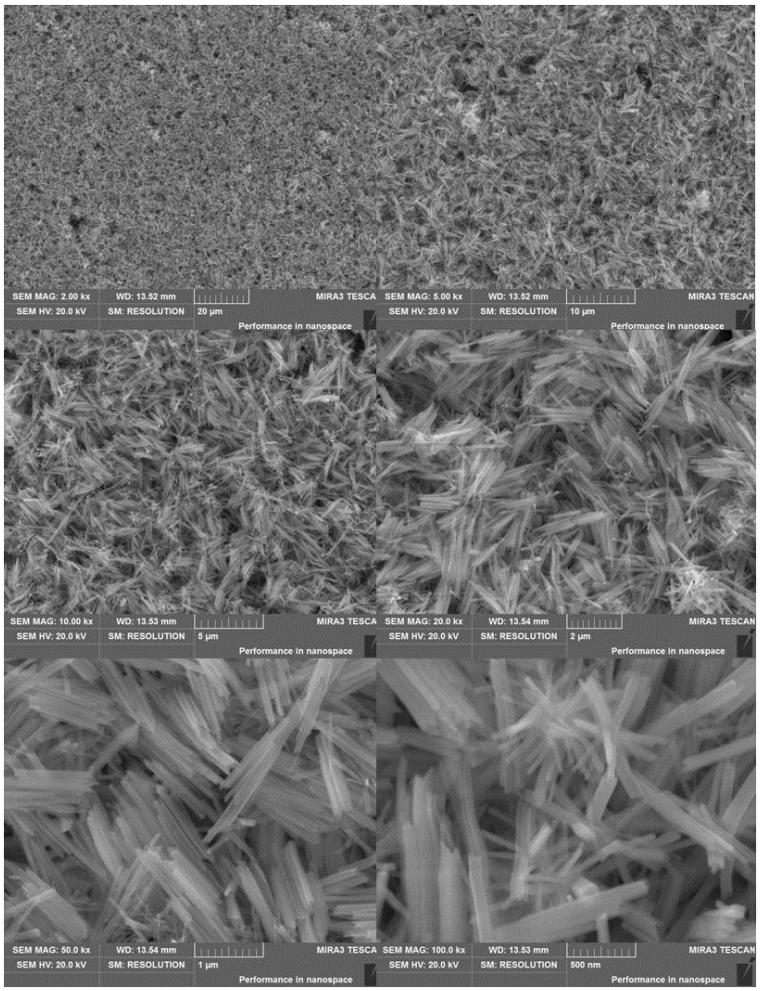

Fig. S2 Additional SEM images for synthesized Sb_2Se_3 nanowires at different magnitudes.

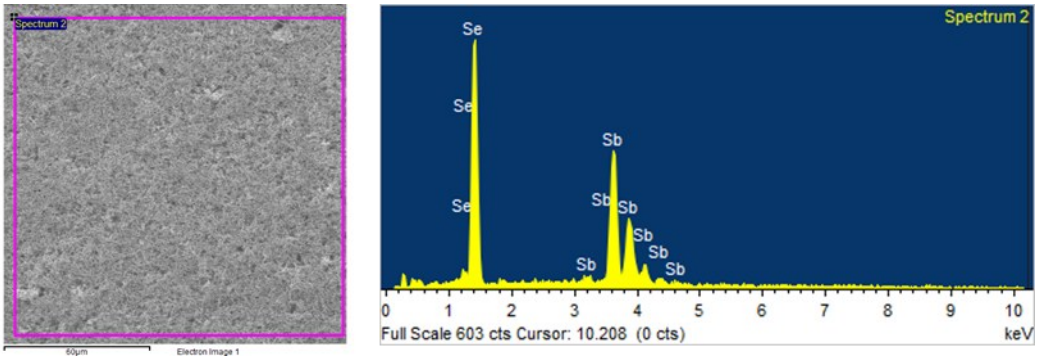

Fig. S3 Representative energy dispersive X-ray spectroscopy spectrum for Sb_2Se_3 nanowires and the quantitative analysis

The sample used for determining the quantitative composition of Sb_2Se_3 film by EDX was prepared by dropping the concentrated dispersion of Sb_2Se_3 nanocrystal-ink onto the soda-lime glass substrate. In order to get average composition of synthesized nanocrystals, 3 different area of nanocrystal film were examined. The average composition of synthesized nanocrystal is

$Sb_{2.00}Se_{2.88}$.

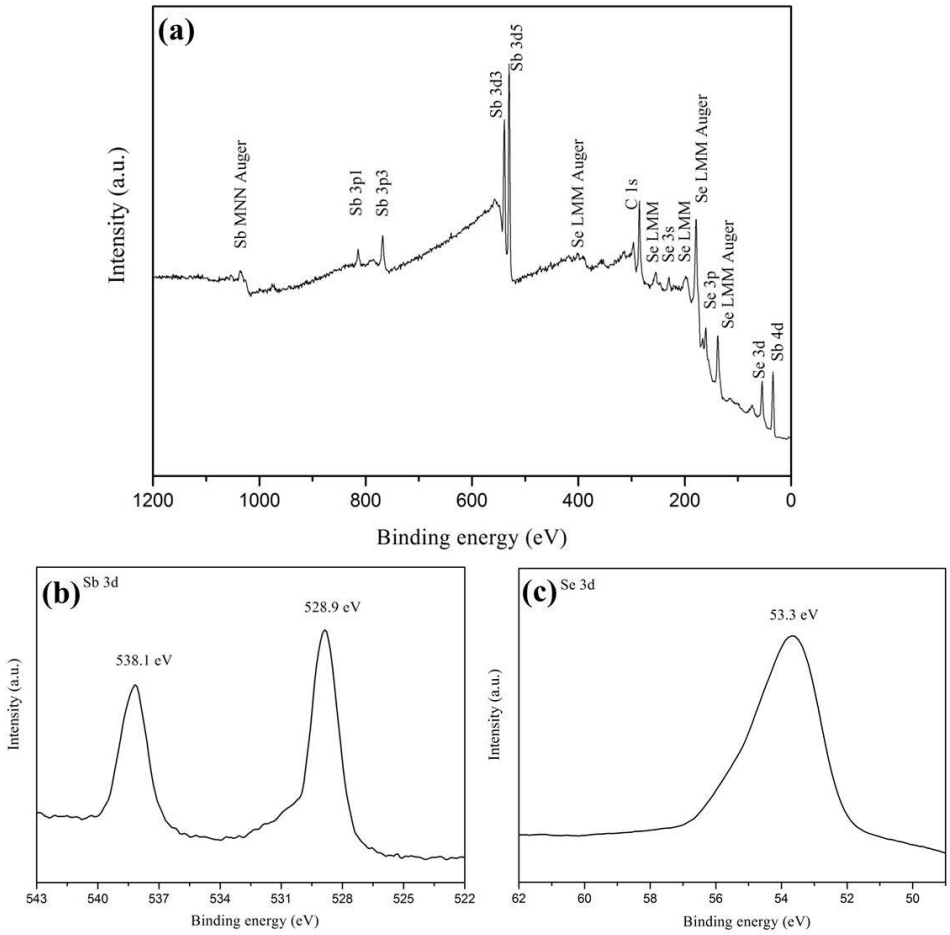

Fig. S4 XPS spectra of as-synthesized Sb_2Se_3 nanowires. (a) The comprehensive scanning spectrum, (b) Sb 3d spectrum, and (c) Se 3d spectrum.

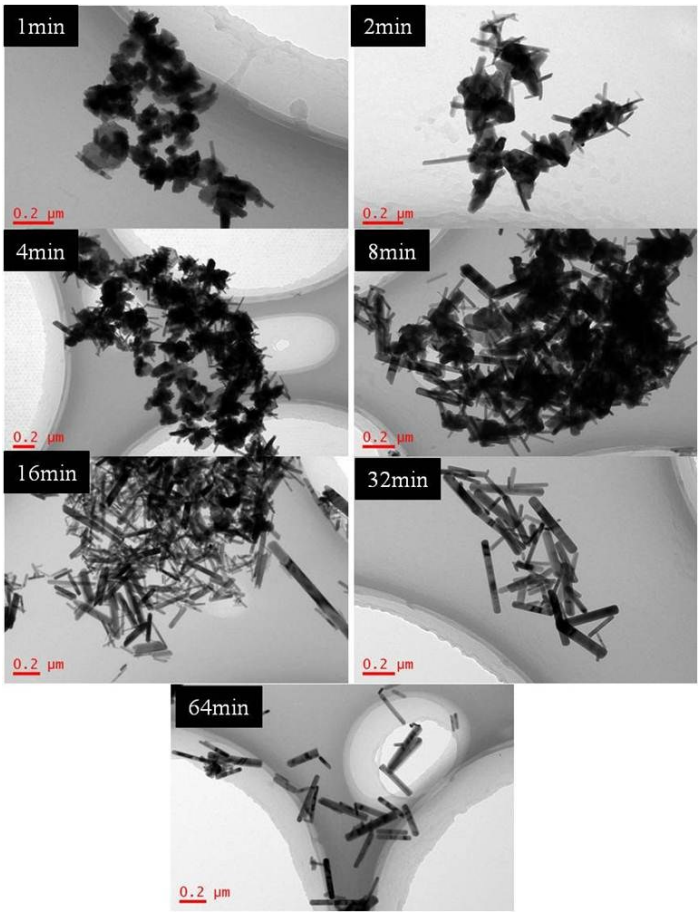

Fig. S5 TEM images for each aliquots taken out at different time (a) 1min, (b) 2min, (c) 4min, (d) 8min, (e) 16min, (f) 32min, (g) 64min.

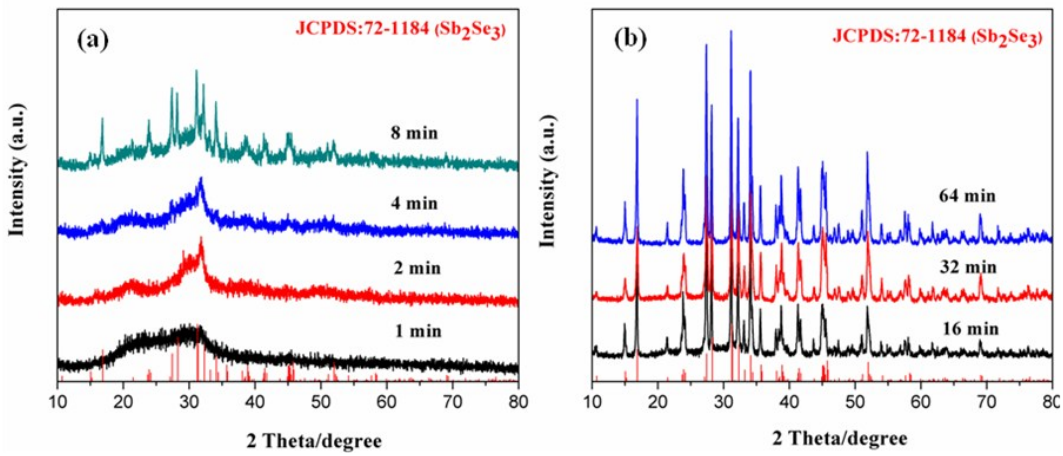

Fig. S6 XRD spectra of each aliquots taken out at different time.

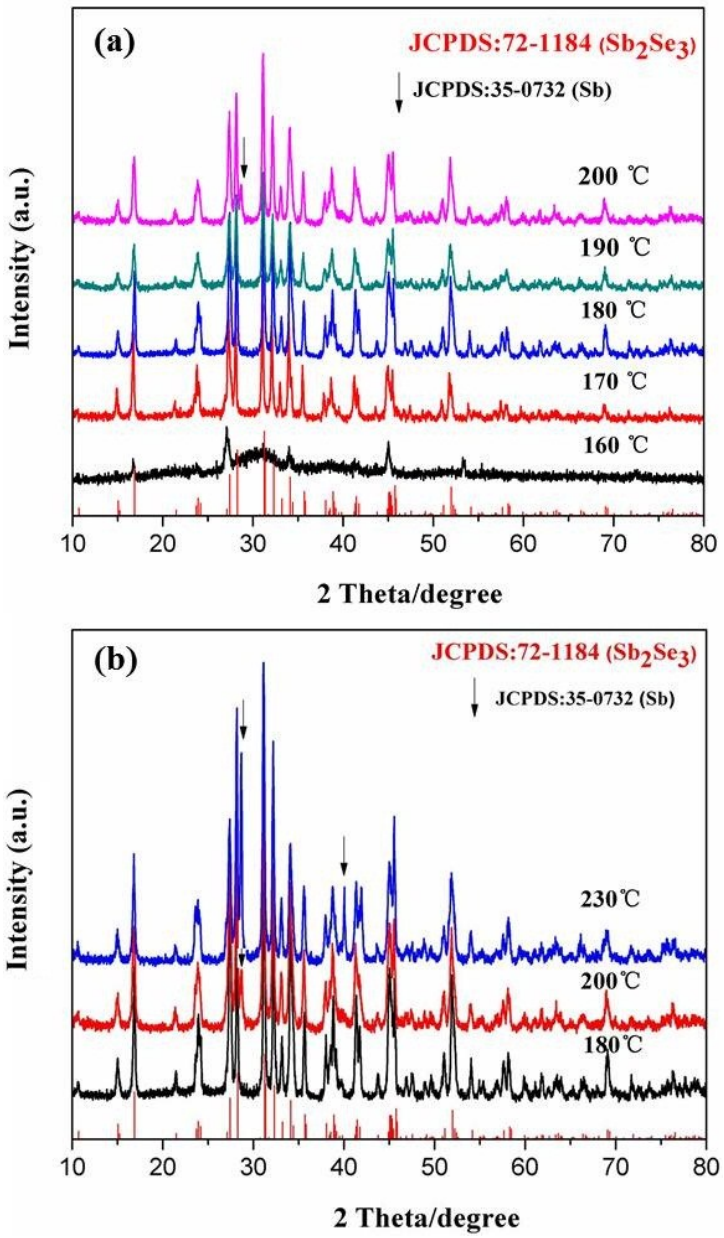

Fig. S7 XRD patterns for synthesized product at different temperature for 30 min using antimony chloride as the Sb source.

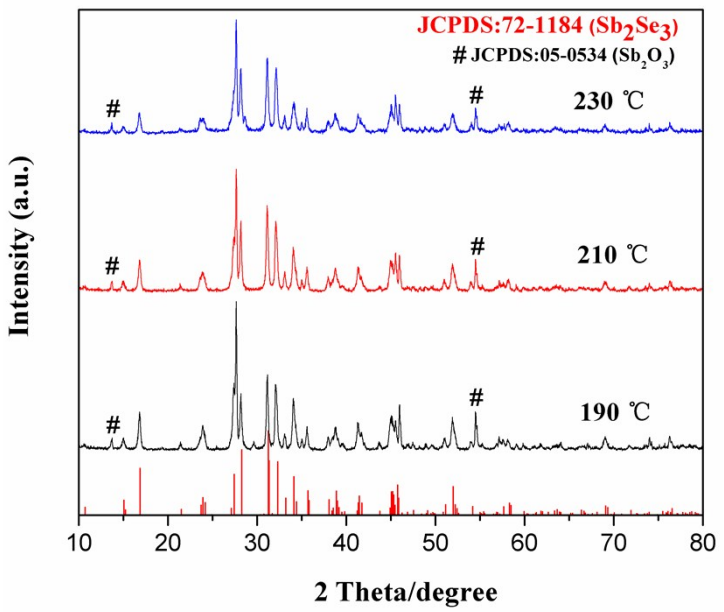

Fig. S8 XRD patterns for synthesized product at different temperature for 30 min using antimony triacetate as the Sb source (Sb:Se=1:1.5).

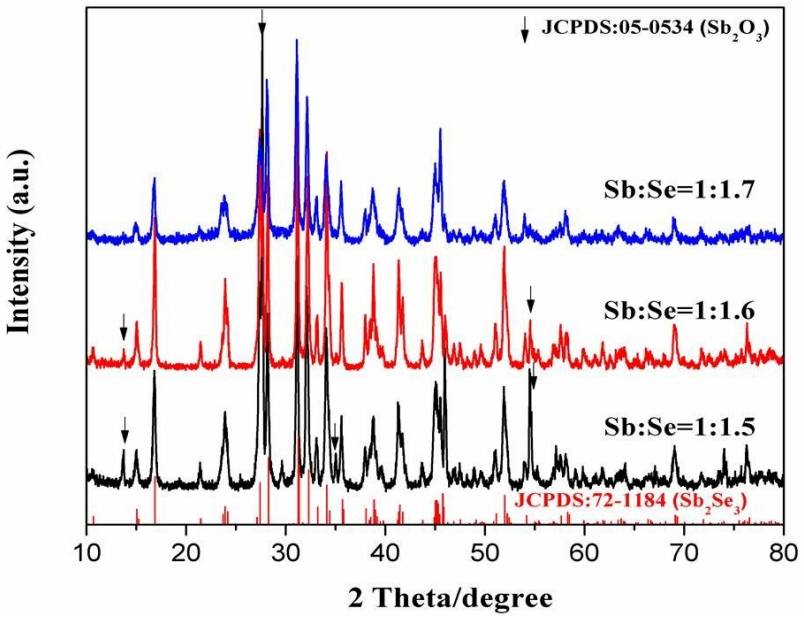

Fig. S9 XRD patterns for synthesized product at different ratios of precursors (Sb: Se) 190 °C for 30 min using antimony triacetate as the Sb source.