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Colloidal synthesis and characterisation of Cu_3SbSe_3 nanocrystals†

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Electronic Supplementary Information

Experimental Details

Preparation of OLA/ DMAB/ Se solution

5 mL OLA, 7.5 mL DMAB and 6 mmol Se powder (99.9%, Aladdin) were added in a two-neck flask (50 mL) connected to a Schlenk line. Then the temperature was raised up to around 110°C under vacuum, stirring for dissolving Se powder. Keep the temperature for a few minutes, the color of mixture solution turned immediately from dark into colorless. The temperature of the OLA/ DMAB/ Se solution was held constant at 90 °C.

Synthesis of Cu_3SbSe_3 nanocrystals

2.25 mmol copper (Ⅱ) acetylacetonate (97%, Aladdin), 0.75 mmol antimony (III) acetate (99%), and 12 mL oleylamine (C-18 content 80%-90%, Aladdin) were added into a three-neck flask (100mL) connected to a Schlenk line (all chemicals are used as receives). Then the temperature was raised up to around 130°C under vacuum, stirring for degassing about an hour and purging with Ar for 3 times. All reaction conditions were kept inert to prevent the formation of the oxide. The flask was then heated to 190 °C, where 2.5 mL of 1.2 M/L solution of Se/DMAB in oleylamine were injected. After injection, the solution turns dark, and the temperature was held at 190 °C for 30 minutes. After the reaction, the mixture was cooled down to approximately 70 °C by air quenching. Then, 10 mL of toluene and 30 mL of ethanol were added into the reaction mixture and the nanocrystals were collected using centrifuge (separated into eight 15 mL centrifuge tubes) at 8000 rpm for 5 minutes. The supernatant of the centrifuged mixture was discarded. Similar step of adding 10 mL of toluene and 30 mL of ethanol and centrifuge was repeated. The supernatant was decanted again. The final precipitant was dispersed in approximately 20 mL toluene to form a stable ink solution.

Preparation for Cu_3SbSe_3 nanocrystals films

0.2-0.3 mL ink (using a toluene solution of Cu_3SbSe_3 nanocrystals) was drop-casted on soda-lime glass (SLG) with the area of 2.40 cm^2. The sample was then put in the draught cupboard so that the solvent can evaporate naturally. Consequently, a dense Cu_3SbSe_3 nanocrystals thin film was formed on the SLG. On the other hand, the Cu_3SbSe_3 nanocrystals films on the ITO glass were also prepared and the nanocrystals films were served as the working electrodes in the photoelectrochemical (PEC) test. 0.2-0.3 mL ink (using a toluene solution of Cu_3SbSe_3 nanocrystals) was drop-casted on ITO glass with the area of 1.96 cm^2. The sample was then put in the draught cupboard so that the solvent can evaporate 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 Cu_3SbSe_3 nanocrystals films.

Materials characterizations

TEM samples were prepared by dropping the diluted Cu_3SbSe_3 ink solution directly to a carbon-coated copper TEM grid (200 mesh). TEM images were obtained on a JEM-2100F field-emission microscope at a working voltage of 200 kV. Energy Dispersive X-ray spectroscopy (EDX) data were collected as an ensemble measurement in an environment scanning electron microscope (ESEM, Quanta-200 at a 20 keV accelerating voltage). XRD was performed on a X-ray diffraction system (Rigaku3014) equipped with Cu Kα radiation (λ=1.54 Å) using a dried thin film sample prepared by drop-casting the nanocrystal-ink. UV-vis-NIR spectra were collected for

Cu_3SbSe_3 nanocrystals using a Hitachi U-4100 spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed with the Spectrometer of Thermo-VG Scientific ESCALAB 250Xi. 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. The incident-photon-to-current efficiency (IPCE) plots were collected from the Cu_3SbSe_3 nanocrystals film in the light wavelength of 400-1050 nm at applied voltage of -0.65 V vs. SCE in 0.5M H_2SO_4 solution.

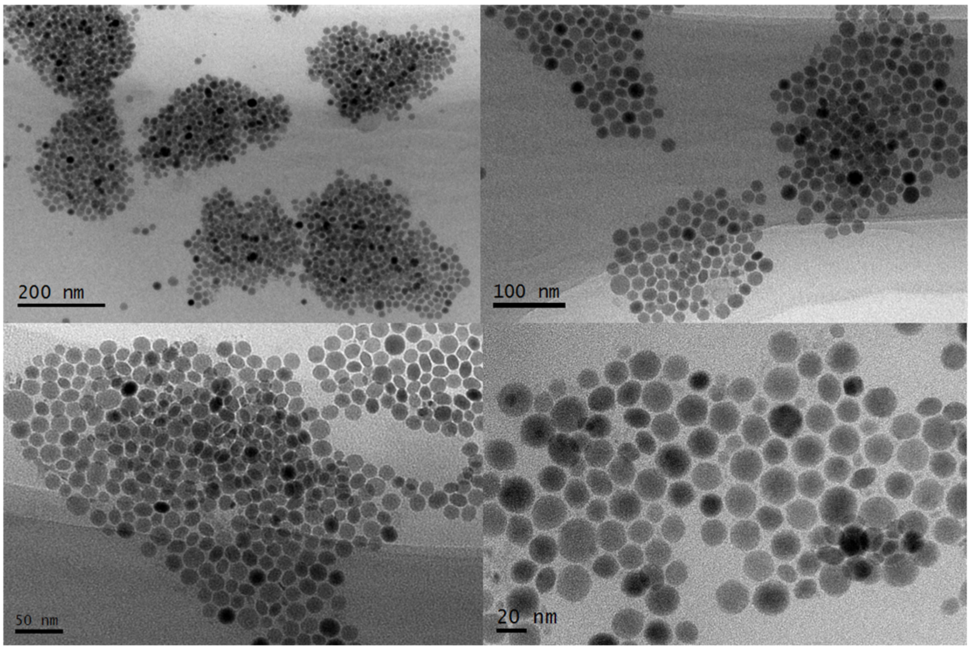

Fig. S1 Additional TEM images for synthesized Cu_3SbSe_3 nanocrystals at different magnitudes.

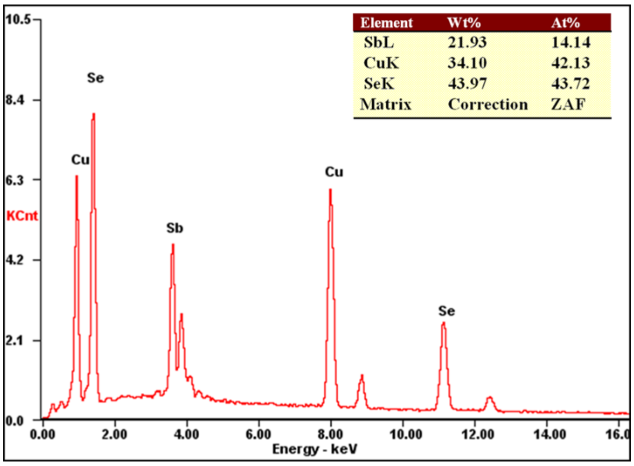

Fig. S2 Representative energy dispersive X-ray spectroscopy spectrum for Cu_3SbSe_3 nanocrystals and the quantitative analysis

The sample used for determining the quantitative composition of Cu_3SbSe_3 film by EDX was prepared by dropping the concentrated dispersion of Cu_3SbSe_3 nanocrystal-ink onto the soda-lime glass substrate. In order to get average composition of synthesized nanocrystals, 10 different area of nanocrystal film were examined. The average composition of synthesized nanocrystal is $Cu_{2.98}SbSe_{3.09}$.

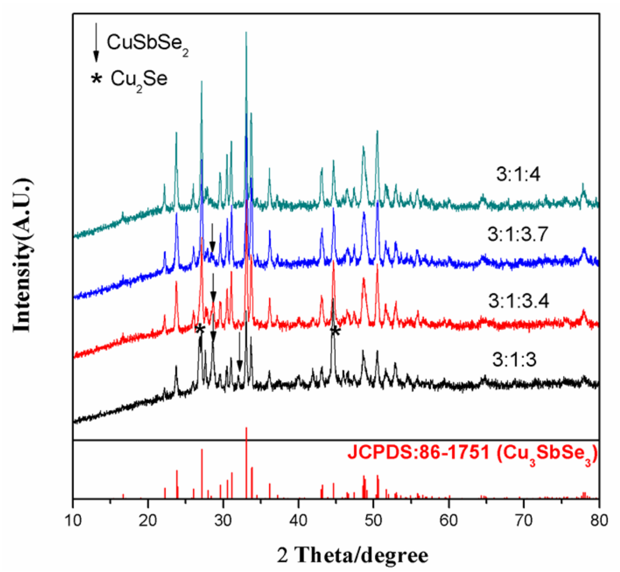

Fig. S3 XRD patterns for synthesized product at different ratios of precursors (Cu: Sb: Se) 190 °C for 30 min.

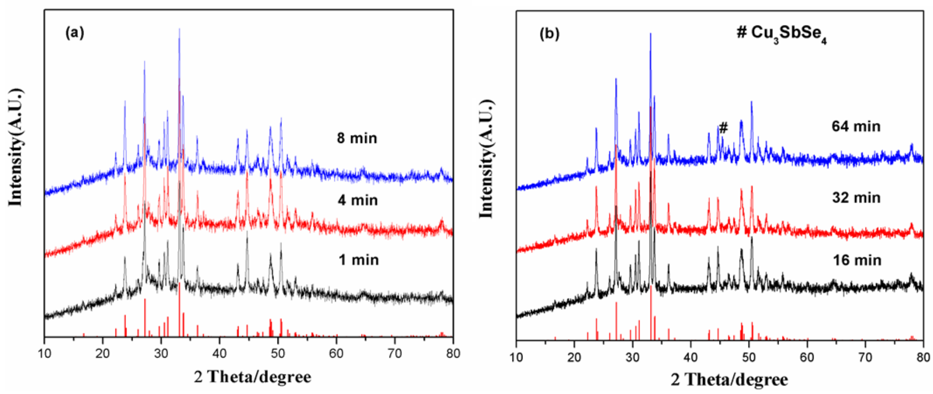

Fig. S4 XRD patterns for synthesized product at different time 190 °C with Cu: Sb: Se ratio is 3: 1: 4.

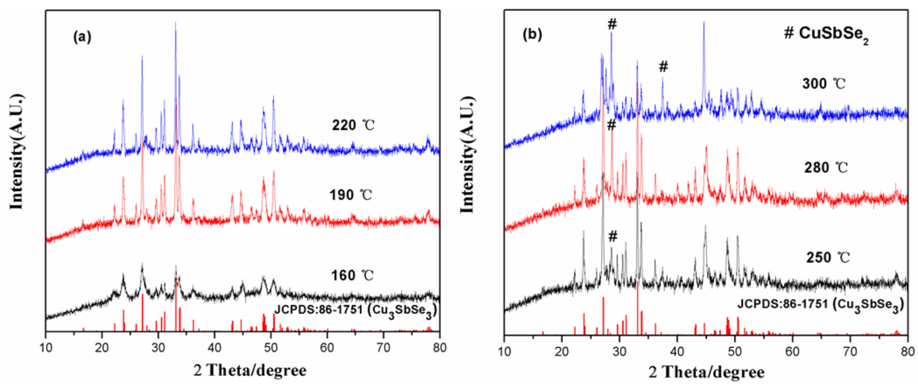

Fig. S5 XRD patterns for synthesized product at different temperature for 30 min when Cu: Sb: Se ratio is 3: 1: 4.

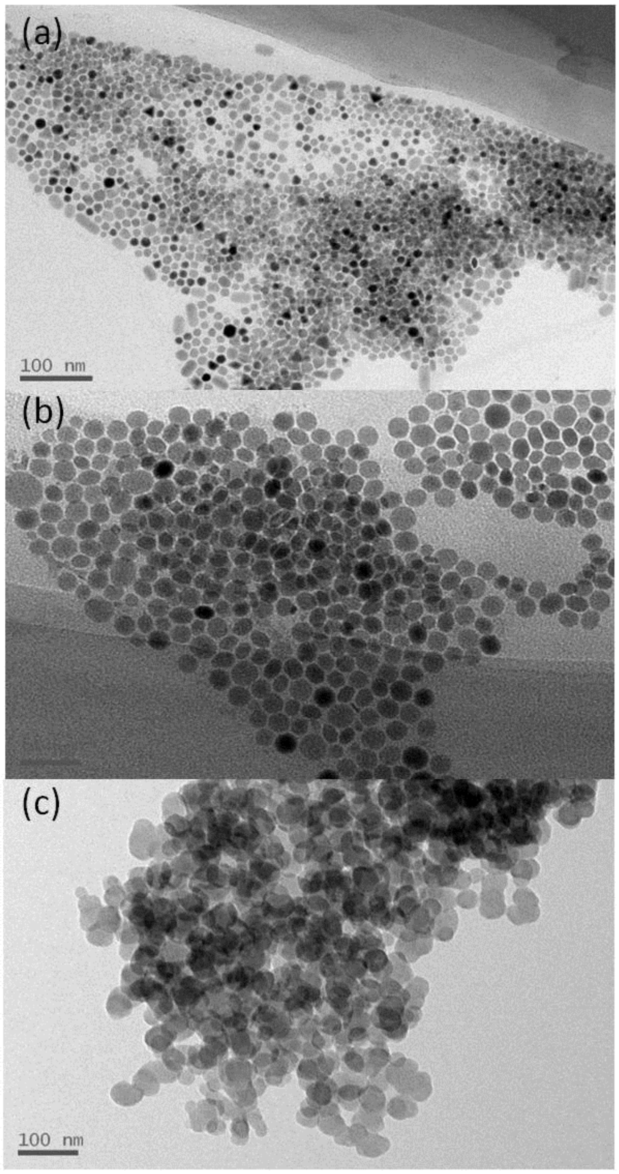

Fig. S6 TEM image for synthesized product at different temperature for 30 min when Cu: Sb: Se ratio is 3: 1: 4. (a) 160 °C, (b) 190 °C, (c) 220 °C.

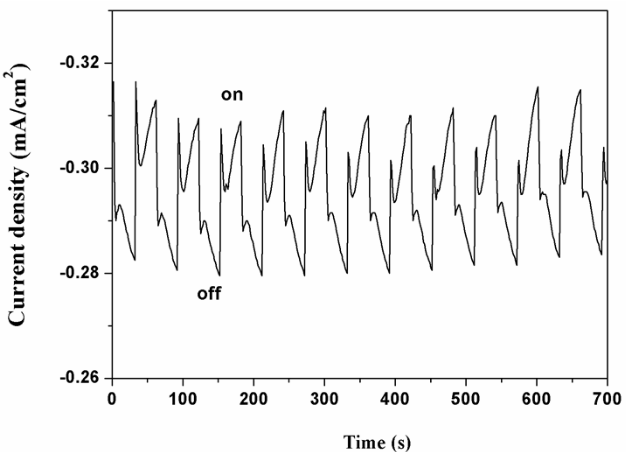

Fig. S7 The transient photocurrent spectrum for the obtained CASe films at -0.65 V vs. SCE