Supplementary Materials

Synthesis, characterization, and surface-enhanced Raman scattering of near infrared absorbing Cu_3SbS_3 nanocrystals

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EXPERIMENTAL SECTION

Synthesis and purification of Cu_3SbS_3 NCs. The synthesis was carried out in a glass manifold under an argon atmosphere. In a typical synthesis, CuCl (3 mmol), $SbCl_3$ (1 mmol), oleylamine (OLA, 20 mL), glycerol (GLY, 20 mL), and a Teflon-coated stir bar were loaded into a 50-mL three-neck flask. The flask was fixed in a magnetic heating mantle, equipped with a thermocouple and a PID temperature controller through a neck of the flask to control the solution temperature. The flask was purged off air and water by Ar through another neck and a condenser tube was settled in the third neck as the gas outlet. Subsequently, the precursor solution was heated to 90 °C and maintained at this temperature for 30 min under stirring. The temperature was then increased to 140 °C, and 3 mmol S powders were added to the

reaction flask, which was maintained at 140 °C for 60 min. The temperature was then increased to 240 °C and maintained at this temperature for 60 min. Finally, the flask was cooled to 50 °C. Then, the black solution was separated into two 50 mL centrifuge tubes and 25 mL ethanol was added to each tube. The mixture was centrifuged at 10000 rpm for 3 min. The supernatant was discarded. Then, 25 mL ethanol was added to each tube and centrifuged again. The final precipitate was dispersed in 20 mL tetrachlorethylene.

For the scale-up synthesis, CuCl (15 mmol), $SbCl_3$ (5 mmol), oleylamine (OLA, 100 mL), glycerol (GLY, 100 mL), and a Teflon-coated stir bar were loaded into a 250-mL three-neck flask, then 15 mmol S powders were added, while the other conditions were the same as the normal synthesis above.

Characterization. The size and morphology of the Cu_3SbS_3 NCs were studied by TEM and high-resolution TEM (HRTEM, KEM-2010). Several drops of the NC dispersion were applied on TEM grids. 0.2 mL well-dispersed NC solution was spin-coated on Si substrate at 2000 rpm for scanning electron microscopy (SEM) imaging. The stoichiometry of the NCs was analyzed by an Oxford INCA energy dispersive spectrometer (EDS) equipped on TEM. The crystallinity was characterized by powder X-ray diffraction (XRD, Philips X'pert pro). NC powders were put on Pt sample stage for temperature-dependent XRD test in the vacuum (5×10^{-5} mbar). The testing temperature ran from 25 °C to 400 °C with a rate of 10 °C/min and stabilized for 5 min. Optical absorption spectra were obtained using a UV-vis-NIR spectrometer (Shimadzu SolidSpec-3700) with an integrating sphere. The measurement was taken

for films on SLG (soda-lime glass) substrate. X-ray photoelectron spectroscopy (XPS) analysis was performed with the Spectrometer of Thermo-VG Scientific ESCALAB 250. Cyclic voltammetry (CV) analysis was conducted on an electrochemical workstation (Zahner IM6ex) using spray-coated NC film (area: 0.5 cm^2) on FTO substrate as the working electrode. The reference electrode was $Ag/AgNO_3$ electrode, the counter electrode was platinum plate, and the electrolyte was 0.1 M Tetrabutylammonium hexafluorophosphate in acetonitrile. For SERS measurements, the as-prepared spin-coated Cu_3SbS_3 NC film on Si substrate was cut into several pieces and immersed into 1×10^{-5} M, 1×10^{-6} M and 1×10^{-7} M R6G aqueous solutions separately for 30 min each. The films were then rinsed thoroughly with deionized water and finally dried in N_2. The Raman spectra were recorded at room temperature on a microscopic confocal Raman spectrometer (Renishaw inVia Reflex spectrometer) using a laser beam with 514 nm excitation wavelength. The data integration for each measurement was 1 s.

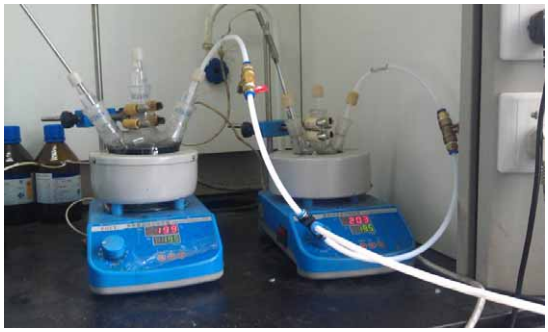

Figure S1. Scale-up synthesis equipment for Cu_3SbS_3 NCs.

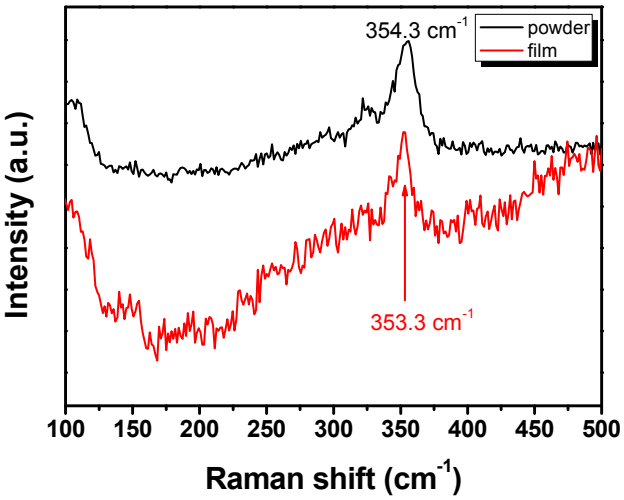

Figure S2. Raman spectra of Cu_3SbS_3 NCs.

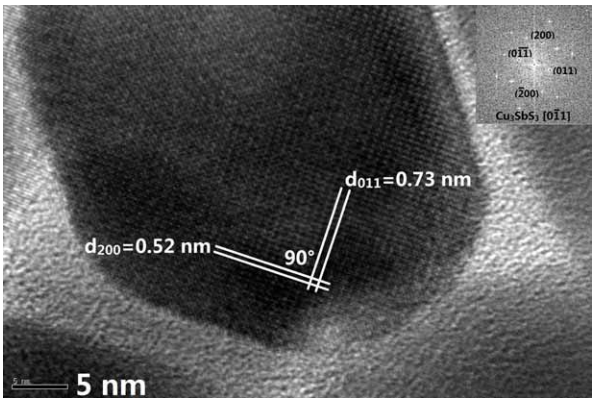

Figure S3. HRTEM image of a Cu_3SbS_3 NC and its FFT.

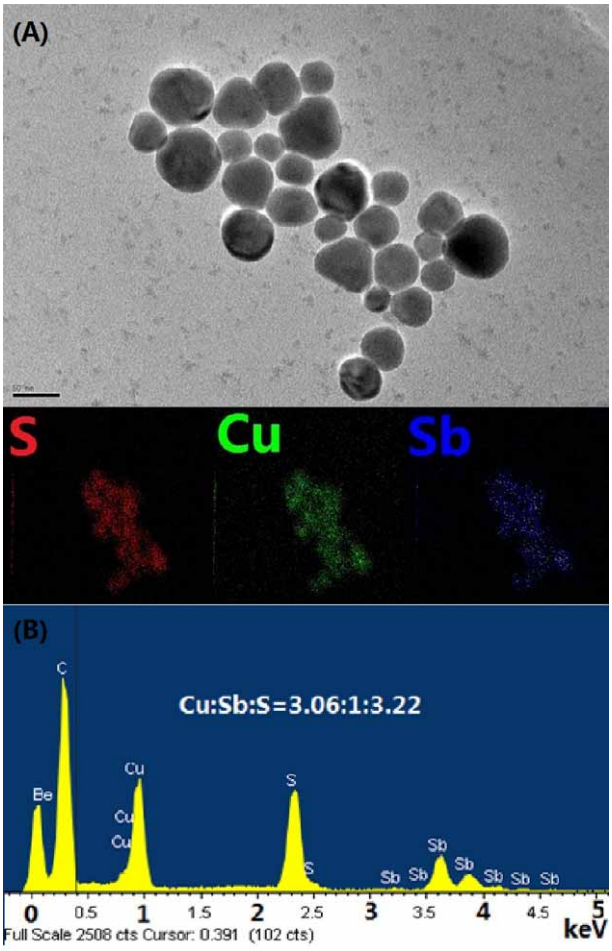

Figure S4. (A) TEM image of Cu_3SbS_3 NCs and the elemental mapping. (B) EDS spectrum of the NCs.