Supporting Information

Selective Production of $CuSbS_2$, Cu_3SbS_3, and Cu_3SbS_4 Nanoparticles using a Hot Injection Protocol

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Experimental Methods

Fabrication of particulate films on an ITO-coated glass (ITO/glass) substrate

Cu-Sb-S nanoparticles were accumulated on an ITO/glass substrate with a sheet resistance of 10 Ω cm^{-2} using the previously reported layer-by layer deposition technique[1] with some modifications. Cu-Sb-S nanoparticles dispersed in toluene (*ca.* 1 wt%) were coated on the ITO/glass substrate by the spin casting technique. Then the sample was dipped in an ethanol solution containing 10 mmol dm^{-3} 1,2-ethanedithiol. By repeating these deposition procedures several times, the desired accumulation of Cu-Sb-S nanoparticles was obtained. After each deposition, the film was washed with deionized water and dried under an Ar gas flow.

Characterizations

Crystal structures of the nanoparticles were determined by X-ray diffraction (XRD) using a Rigaku Mini Flex X-ray diffractometer with Cu Kα radiation (30 kV, 15 mA) and Ni filter. Transmission electron microscopy (TEM) images were taken on a Hitachi H-9000NAR instrument operated at 200 kV. Particle size distribution was determined from the corresponding TEM image by measuring the sizes of more than 200 particles. Atomic compositions were examined by using a Hitachi TM3000 scanning electron microscope equipped with a SwiftED3000 energy dispersive X-ray spectrometer (EDX). Photoabsorption spectra of the nanoparticles dispersed in toluene were measured using a Hitachi U-4100 spectrophotometer. The photoelectrochemical properties of particulate films deposited on the ITO/glass substrate were measured by linear sweep voltammetry (LSV) in an aqueous solution containing 0.10 mol dm^{-3} $Eu(NO_3)_3$ (pH 4.0) as an electron acceptor. A Pt wire and an Ag/AgCl electrode in saturated KCl served as the counter electrode and reference electrode, respectively. Transient photocurrents were obtained by scanning applied potentials with a scan rate of 10 mV s^{-1} under chopped illumination of simulated AM 1.5 solar irradiation from an Asahi Spectra HAL320 solar simulator. A Solartron SI1280B electrochemical measurement unit was employed to obtain voltammograms. Photocurrent onsets were measured by the lock-in technique using an NF LI5630 digital lock-in amplifier connected to a Hokuto Denko HB-151 potentio-galvanostat. Sample electrodes were irradiated by chopping at 10 Hz of light of simulated AM 1.5 solar irradiation from the above solar simulator.

Reference

1 E. J. D. Klem, H. Shukla, S. Hinds, D. D. MacNeil, L. Levina and E. H. Sargent, *Appl. Phys. Lett.*, 2008, **92**, 212105.

Table S1. Parameters for fabrication of Cu-Sb-S nanoparticles with different crystalline phases.

nanoparticle	$CuSbS_2$	Cu_3SbS_4	Cu_3SbS_4
sulfur source	elemental sulfur (1.0 mmol)	elemental sulfur (2.0 mmol)	bis(trimethylsilyl) sulfide (2.0 mmol)
solvent for sulfur source	oleylamine (3.0 cm^3)	oleylamine (3.0 cm^3)	1-octadecene (3.0 cm^3)
Cu source	CuCl (0.45 mmol)	CuCl (0.45 mmol)	CuCl (0.45 mmol)
Sb source	$SbCl_3$ (0.45 mmol)	$SbCl_3$ (0.45 mmol)	$SbCl_3$ (0.45 mmol)
solvent for metallic precursor	oleylamine (7.0 cm^3)	oleylamine (7.0 cm^3)	oleylamine (7.0 cm^3)
reaction temperature / duration	260 °C / 5 min	200 °C / 10 min	240 °C / 1 min then 150 °C / 30 min

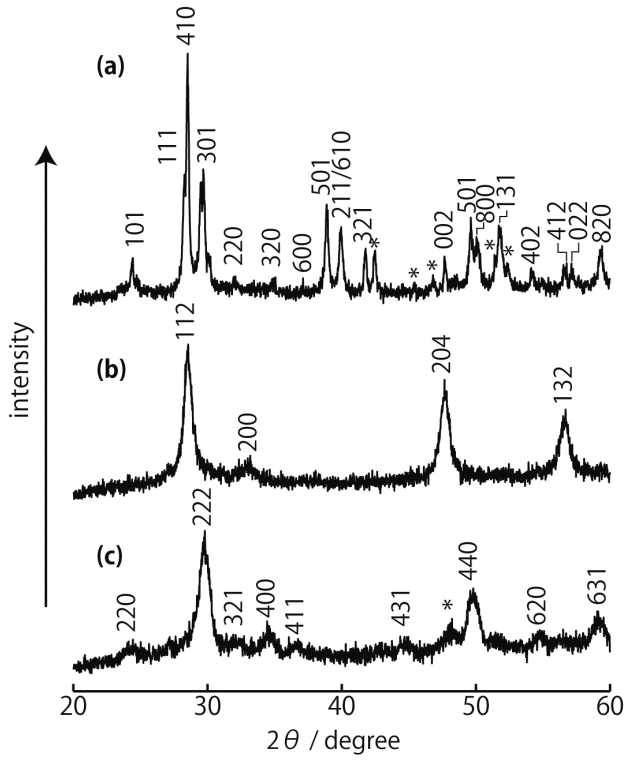

Fig. S1. XRD patterns of (a) $CuSbS_2$, (b) Cu_3SbS_4 and (c) Cu_3SbS_3 nanoparticles.

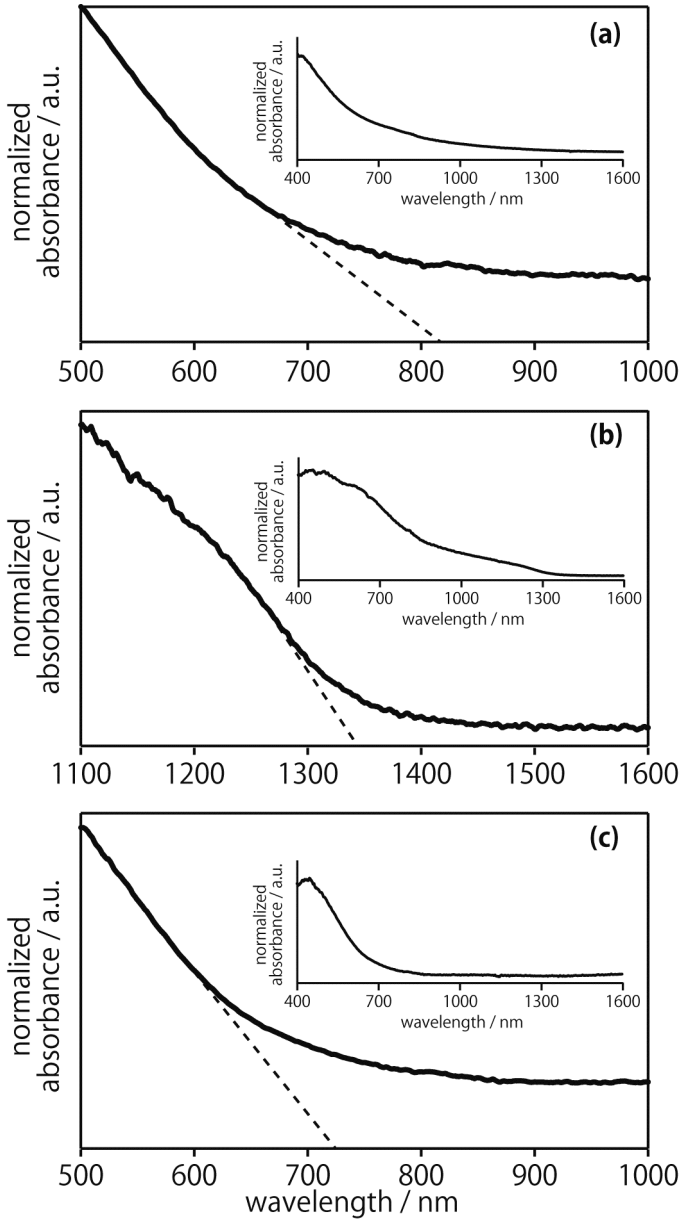

Fig. S2. Photoabsorption spectra of (a) $CuSbS_2$, (b) Cu_3SbS_4 and (c) Cu_3SbS_3 nanoparticles dispersed in toluene.

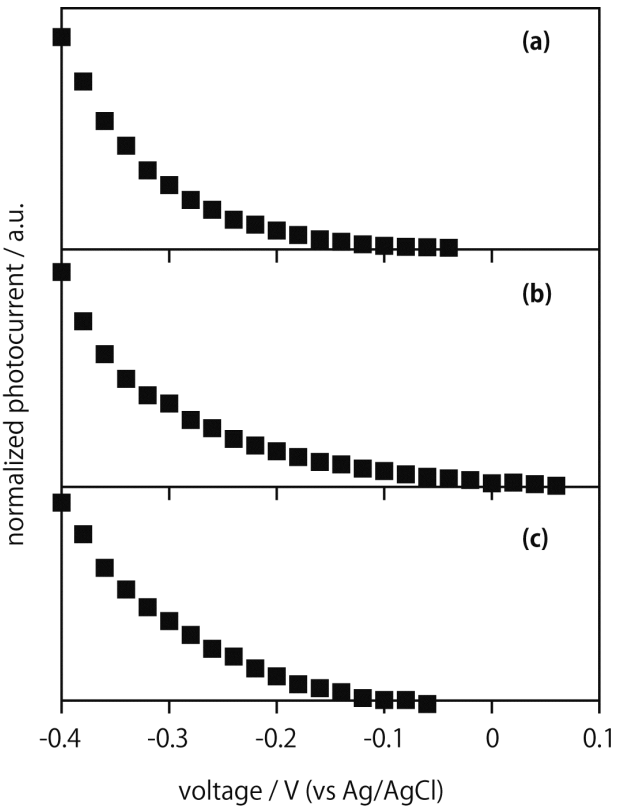

Fig. S3. Photocurrent onsets of (a) $CuSbS_2$, (b) Cu_3SbS_4 and (c) Cu_3SbS_3 particulate films deposited on an ITO/glass substrate.