Electronic Supplementary Information

Synthesis of Cu_3SnS_4 Nanocrystals and Nanosheets by using $Cu_{31}S_{16}$ as Seeds

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Experimental Section

Chemicals. Stannic chloride pentahydrate ($SnCl_4 \cdot 5HO$, 99%) and copper (II) acetylacetonate ($Cu(acac)_2$, 97%) were purchased from Shanghai Jingchun Chemical Company; n-dodecanethiol (98%) was obtained from Shanghai Chemical Company. Other solvents such as ethanol and dichloromethane were analytical grade and used as received.

Synthesis of Cu_3SnS_4 Nanocrystals. 0.262 g (1.00 mmol) of $Cu(acac)_2$ powder was firstly dispersed in 30 mL dodecanethiol at room temperature with the aid of magnetic stirring. Then the resultant solution was heated up to 200 °C and maintained at this temperature during the following synthesis. In the meantime, 10 mL dodecanethiol stock solution containing 0.175 g (0.50 mmol) of $SnCl_4 \cdot 5H_2O$ was prepared and divided into three equal portions which were intermittently injected into the hot $Cu(acac)_2$-dodecanethiol solution at 200 °C by 1 h interval. The first portion was injected after the $Cu(acac)_2$-dodecanethiol solution had been refluxed for 1 h. After the all three portions were injected, the reaction system was kept refluxing for 4 h. Aliquots were extracted every hour to monitor the particle growth and crystalline phase transformation. Among them, $Cu_{31}S_{16}$, sample 1, and sample 2 were extracted right before the following injection of $SnCl_4$ stock solution.

Synthesis of Cu_3SnS_4 Nanosheets. Cu_3SnS_4 nanosheets were synthesized by refluxing 30 mL dodecanethiol solution containing 0.262 g (1.00 mmol) of $Cu(acac)_2$ and 0.175 g (0.50 mmol) of $SnCl_4 \cdot 5H_2O$. The reaction lasted for 10 h. In between different aliquots were extracted.

Characterizations. Transmission electron microscopy images and selected area electron diffraction patterns were recorded on a JEM-100CXII electron microscope operating at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) images were taken on FEI Tecnai 20 working at an accelerating voltage of 200 kV. Powder X-ray diffraction was taken with a RigakuD/Max-2500 diffractometer under Cu-Kα1 radiation (λ = 1.54056Å) to investigate the crystalline structure of the resultant nanomaterials. The Cu and Sn contents were determined by the inductively coupled plasma optical emission spectrometer (ICP-OES) method using an inductively coupled plasma atomic emission spectrometer (ICP-2000) produced by Jiangsu Skyray Instrument Co., Ltd. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 220i-XL photoelectron spectrometer from VG Scientific using 300WMg KR radiation (1253.6 eV) for investigating the binding state of Sn, Cu and S apart from providing the quantification information on the atomic ratio.

XPS analysis of Sample 6 obtained via synthetic route 1. The characteristic peaks at 932.0 eV and 951.8 eV with a peak splitting of 19.8 eV in the XPS spectra of copper suggest that copper element mainly occur in mono-valent state. The peaks located at 486.0 and 494.4 eV with a peak splitting of 8.4 eV in the XPS spectrum of tin indicate that tin mainly occur as Sn (IV).[S1] The S2p peak located at around 162.1 eV indicated that S(II) occur as metal sulfide. Detailed results are provided in Figure S1.

TEM and XRD results of the nanosheets obtained via synthetic route 2. Figure S2 shows the TEM image and XRD pattern of nanosheets obtained by 48 min and 5 h, respectively.

HR-TEM of the nanosheets obtained via synthetic route 2. Figure S3 shows the HR-TEM images of single nanosheets obtained by 48 min.

SAED of the nanosheets obtained via synthetic route 2. Figure S4 shows the SAED patterns of single nanosheets obtained by 48 min and 5 h, respectively.

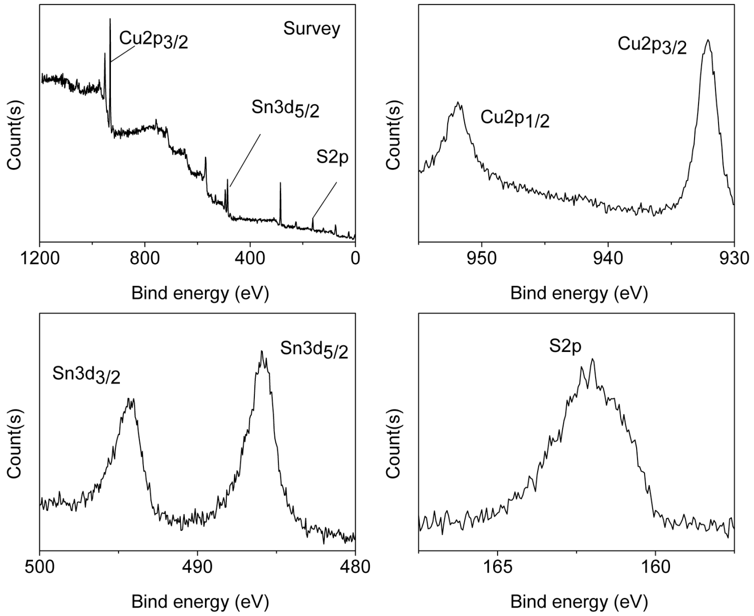

Figure S1. XPS spectra of three constituent elements in Sample 6.

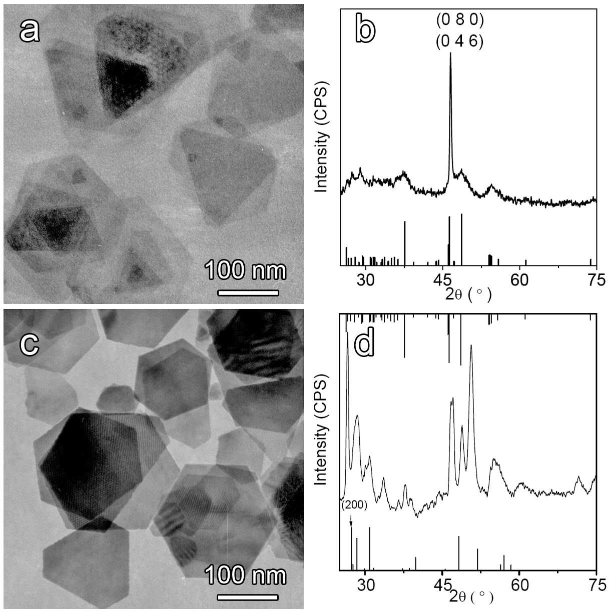

Figure S2. TEM image and XRD pattern of the nanosheets obtained via synthetic route 2 by 48 min (a, b) and 5 h (c, d), respectively. Bottom of frame b: monoclinic $Cu_{31}S_{16}$, JCPDS No.23-0959; bottom of frame d: orthorhomebic Cu_3SnS_4, JCPDS No.36-0217.

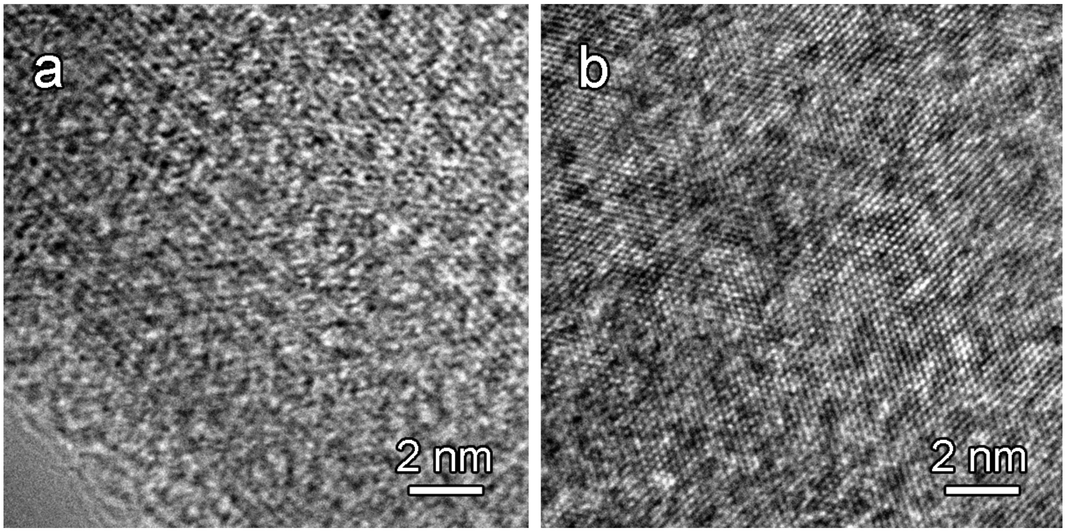

Figure S3. HR-TEM images of single nanosheets obtained via synthetic route 2 by 48 min, recorded from edge area (a) and central area (b), respectively.

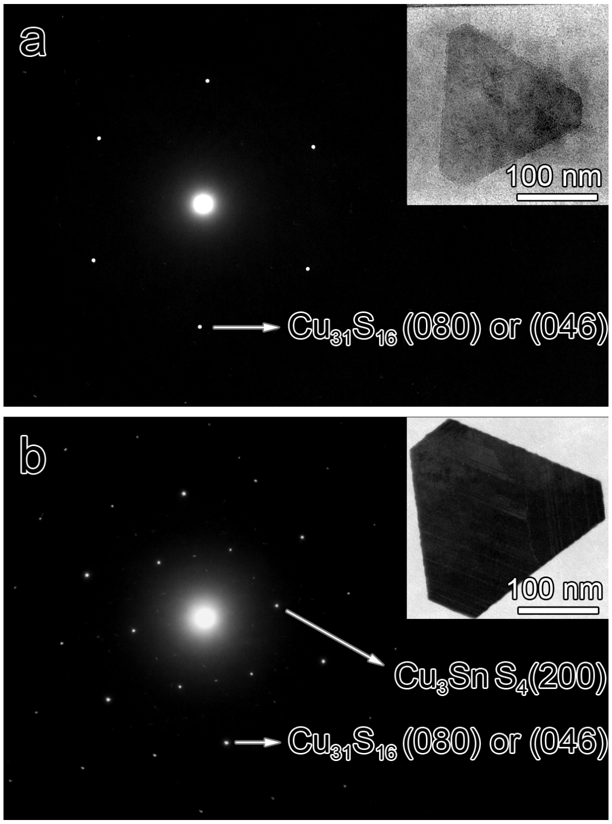

Figure S4. SAED of single nanosheets obtained via synthetic route 2 by 48 min (a) and 5 h (b), respectively. Inset: TEM images of the corresponding single nanosheets.

REFERENCES:

S1. Y. J. Xiong, Y. Xie, G. A. Du and H. L. Su, *Inorg. Chem.*, 2002, **41**, 2953.