Electronic Supplementary Information

Synthesis of Cu$_3$SnS$_4$ Nanocrystals and Nanosheets by using Cu$_{31}$S$_{16}$ as Seeds

Luoxin Yi, a,b Dan Wang,* and Mingyuan Gao* a

aInstitute of Chemistry, the Chinese Academy of Sciences, Bei Yi Jie 2, Zhong Guan Cun, Beijing 100190, China, bInstitute of Process Engineering, the Chinese Academy of Sciences, No. 1 Zhongguancun North Second Street, Beijing 100190

Experimental Section

Chemicals. Stannic chloride pentahydrate (SnCl$_4$·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$_3$SnS$_4$ 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$_4$·5H$_2$O 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$_3$SnS$_4$ Nanosheets. Cu$_3$SnS$_4$ 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$_4$·5H$_2$O. 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: orthorhombic Cu$_3$SnS$_4$, JCPDS No.36-0217.
REFERENCES: