

Electronic Supplementary Material (ESI) for Chemical Communications.

This journal is © The Royal Society of Chemistry 2014

## Electronic Supporting Information

### Scalable synthesis of cubic $\text{Cu}_{1.4}\text{S}$ nanoparticles with long-term stability by laser ablation of salt powder

Y. Zhou, H. Liu, J. Yang, J. Mao, C. K. Dong, T. Ling and X. W. Du\*

Institute of New-Energy Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

#### Contents

Experimental Section

page S2

Supporting Figures

page S2

## Experimental Section

**Materials.** Copper acetylacetonate powder ( $\text{Cu}(\text{acac})_2$ , 97% in purity), copper acetate powder ( $\text{Cu}(\text{ac})_2$ , 97% in purity), dimethyl trisulfide (DMTS, 99% in purity), thioacetamide (TAA, 98% in purity) and oleic acid (OA, 99% in purity) were purchased from J&K Chemical. Ethanol (analytical grade), chloroform (analytical grade); dimethylformamide (analytical grade) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. Lead acetate testing paper was purchased from Shanghai SSS Reagent Co., LTD.

**Synthesis of  $\text{Cu}_{1.4}\text{S}$  Nanoparticles.** 0.03 g  $\text{Cu}(\text{acac})_2$  (about 0.1 mmol) was dispersed in 3 ml ethanol with 6  $\mu\text{L}$  DMTS and 9  $\mu\text{L}$  OA. 10 ml centrifugal tube was applied as reaction vessel. The dispersion was irradiated by a nanosecond pulsed Nd:YAG laser (Beamtech, Dawa-350) with a pulse width of 7 ns, wavelength 532 nm and power density  $4 \times 10^7 \text{ W cm}^{-2}$  for 30 min. The whole synthetic process was conducted under ambient conditions without gas protection. Then the product was centrifuged at 15000 rpm for 30 min, washed with ethanol and chloroform in sequence, and then dissolved in DMF. In a control experiment, 0.024 g  $\text{Cu}(\text{ac})_2$  and 0.003 g TAA served as copper and sulfur source, respectively, and the other synthetic procedure and parameters are same with the DMTS system.

**Synthesis of CuS nanostructures.** 0.3 g  $\text{Cu}(\text{acac})_2$  (about 1 mmol) was dissolved in 30 ml ethanol with 60  $\mu\text{L}$  DMTS and 90  $\mu\text{L}$  OA. Then the mixture was heated in a 50 mL reaction vessel at 473 K for 1 hour. The product was centrifuged at 15000 rpm for 10 min, then washed with ethanol for several times. In another experiment, 0.24 g  $\text{Cu}(\text{ac})_2$  and 0.03 g TAA were used as copper and sulfur source, the preparation was conducted under the same conditions described above.

**Characterization.** The morphology of products was observed by using a field-emission scanning electron microscope (FESEM; Hitachi S-4800). The product size, distribution and composition were measured by using a FEI Technai G2 F20 transmission electron microscope (TEM) equipped with a field-emission gun and an Oxford INCA energy-dispersive X-ray spectroscopy (EDS) module. The phase structure was investigated by using a Bruker D8 advance X-ray diffractometer (XRD). The UV-Vis-NIR absorption spectra were measured with a Hitachi U-4100 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) spectra were collected on a K-Alpha XPS spectrometer (ThermoFisher Scientific).

## Supporting Figures

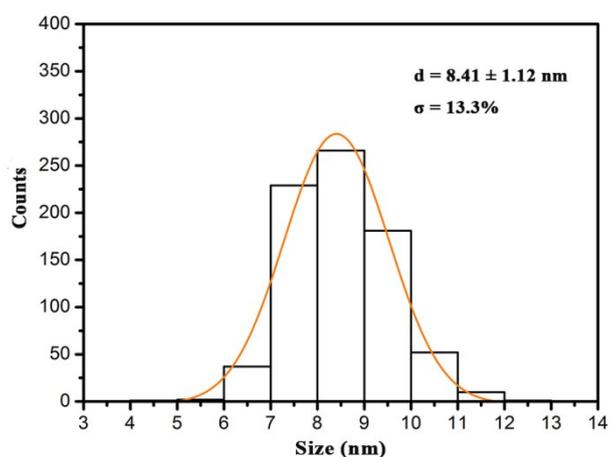


Figure S1. The size distribution of cubic  $\text{Cu}_{1.4}\text{S}$  nanoparticles obtained from TEM images

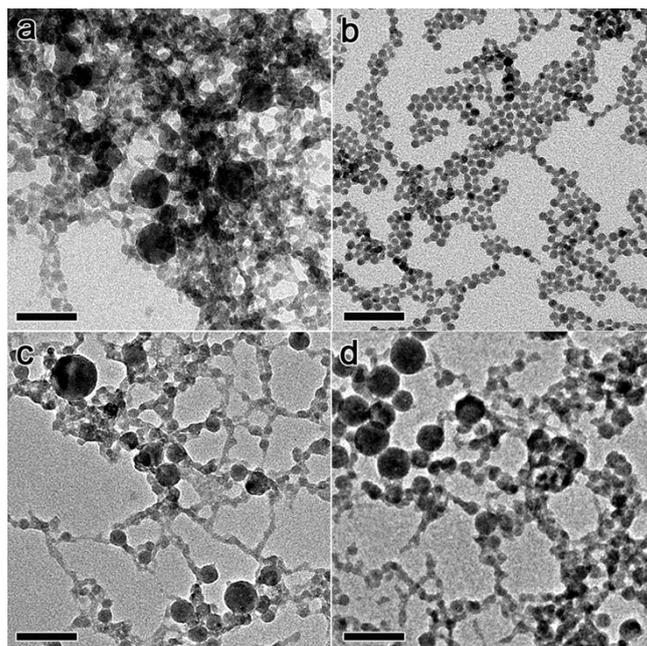


Figure S2. The products obtained with different concentration of OA. (a) 0%, (b) 0.01%, (c) 0.05%, (d) 0.1%. Scale bars represent 50 nm.

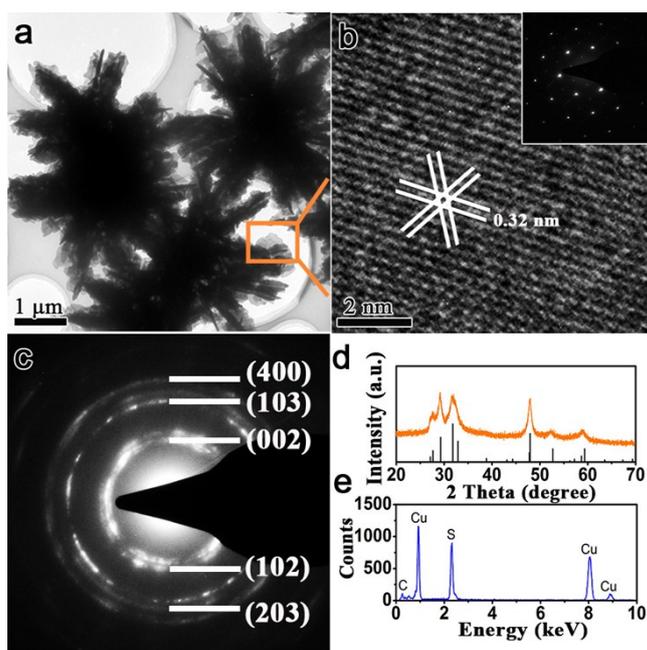


Figure S3. Characterizations on the CuS product by solvothermal synthesis. (a) TEM image, (b) HRTEM image, the inset is SEAD pattern form a single branch, (c) selected area electron diffraction pattern.(d) XRD pattern,(e) energy dispersive spectrum.



Figure S4. Optical image of the  $\text{Pb}(\text{ac})_2$  paper after being put on the opening of the cuvette for 30 seconds during LAL synthesis.

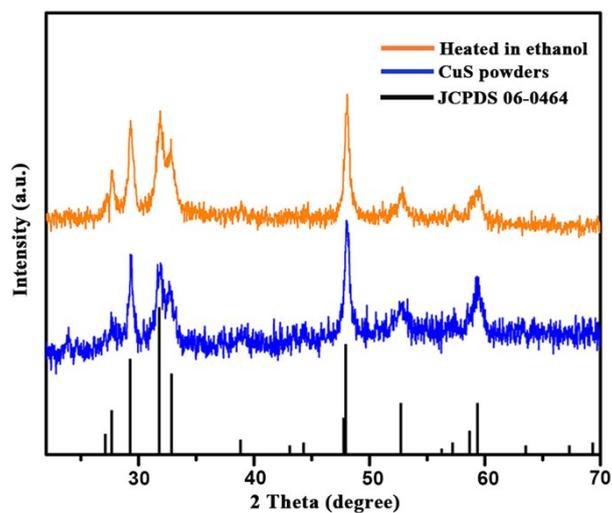


Figure S5. XRD patterns of CuS powder before and after and heated in ethanol at 473 K for 1 hour.

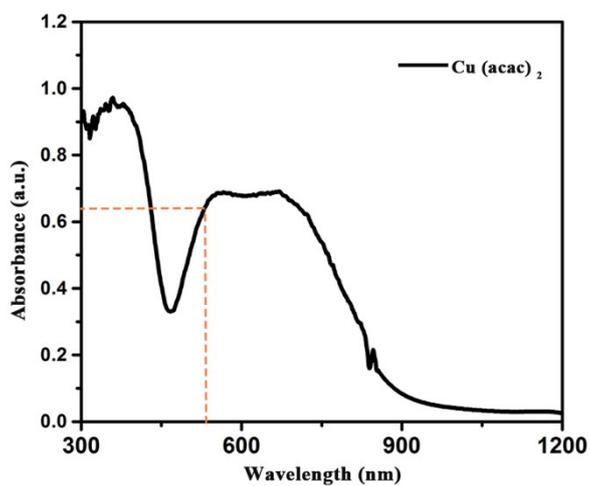


Figure S6. The UV-Vis absorption of  $\text{Cu}(\text{acac})_2$  raw material.

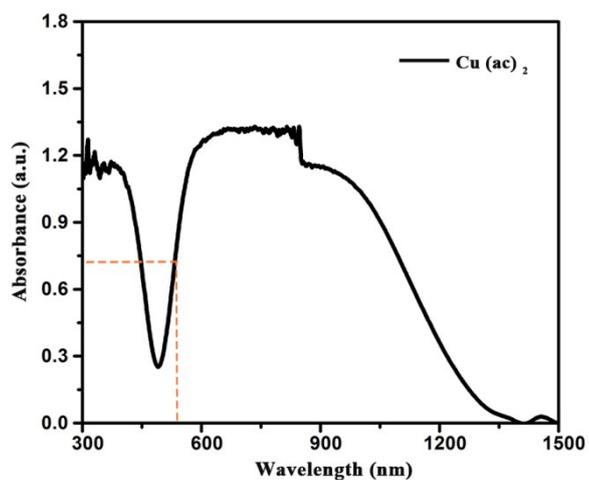


Figure S7. The absorption spectrum of  $\text{Cu}(\text{ac})_2$  powder .

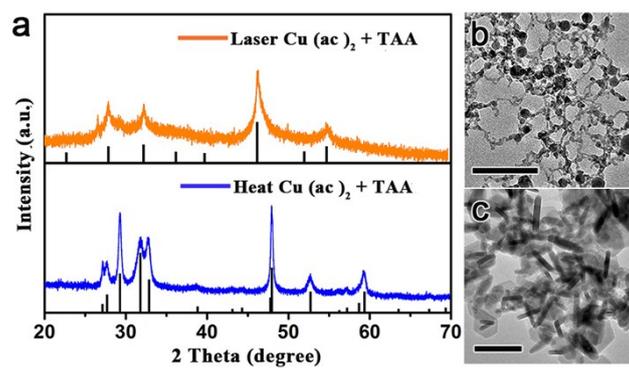


Figure S8. characterizations on the products by LAL and solvothermal synthesis in Cu(ac)<sub>2</sub> and TAA system. (a) XRD patterns of the products by LAL and solvothermal synthesizes, (b) TEM image of the product by LAL synthesis, (c) TEM image of the product by solvothermal synthesis.

**End ESI**