

## Electronic Supplementary Information

### Cu(In<sub>1-x</sub>Ga<sub>x</sub>)S<sub>2</sub> Nanocrystals and Films: Low-Temperature Synthesis with Size and Composition Control

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## Experimental details

**Synthesis.** Different precursor solutions were used for different final compositions. For CuGaS<sub>2</sub>, inside a nitrogen-filled glove box, 0.75 mmol of CuCl (99.995%, Aldrich), 0.75 mmol of GaCl<sub>3</sub> (99.999%, Aldrich) and 6 ml of oleylamine (technical grade, Fluka) were loaded in a 50 mL three-neck reaction flask with an attached condenser and a stopcock valve. The valve was closed before removing the flask from the glove box, where it was attached to a Schlenk line and placed on a heating mantle. After opening the stopcock valve and degassing three times at room temperature, the mixture was heated to 130 °C by stirring under vacuum ( $\approx$ 50 mTorr) for one hour and subsequently cooled to room temperature. The stopcock valve was closed again before moving again the flask to the glove box. 1.5 mmol of S (99.98%, Aldrich) was sonicated with 2 ml of oleylamine for 30 minutes to form an orange color solution. The resulting S source solutions were rinsed by oleylamine in the reaction flask containing the precursor solution while rapidly stirring.

Small amounts (2 mL) of the mixture solution were put in glass vials and then irradiated by X-rays for 5 minutes at room temperature without stirring. Afterwards, the solutions were added to 5 ml of toluene (anhydrous, Aldrich). Then, 5 ml of ethanol (ACS reagent grade, >99.5%, Aldrich) were also added to flocculate the particles that were then collected by centrifugation at 6000 rpm for 5 minutes. The supernatant was decanted and the dark precipitate was then re-dispersed in toluene ( $\approx$ 10 ml) forming a stable solution.

The precursor solutions for CuInS<sub>2</sub> and Cu(In<sub>1-x</sub>Ga<sub>x</sub>)S<sub>2</sub> were obtained by partly or completely replacing GaCl<sub>3</sub> with InCl<sub>3</sub> (99.999%, Aldrich), while keeping the feed molar ratio Cu/(In+Ga)/S equal to 1/1/2. The relative Ga/(Ga+In) ratio controlled the value of x.

**Characterization.** The products were systematically characterized by energy dispersive spectroscopy (EDS, with a JSM-7000 instrument), transmission electron microscopy (TEM, with a JEOL JEM-2100F instrument) and selected area electron diffraction (SAED) with an accelerating voltage of 200 kV and a Gatan UltraScan 1000 CCD camera. TEM was performed on nanocrystal films obtained by drop-casting from toluene solutions on carbon-coated 200 mesh nickel grids. The size distribution was derived with the Image-J software from measurements on  $\approx 10^3$  nanocrystals.

Powder X-ray diffraction (XRD, Rigaku D/MAX2500) patterns were recorded at room temperature. These data were collected at  $2\theta$  angles between  $20^\circ$  and  $70^\circ$  with a  $0.1^\circ$  step size and a counting time of 5 second per step. XRD samples were prepared by depositing the purified nanocrystals on low-background quartz plates. X-ray photoelectron spectroscopy (XPS, Thermo Scientific) was performed using a monochromatized Al X-ray source. The data collection was performed under vacuum ( $2.0 \times 10^{-9}$  Torr) with an electron analyzer pass energy of 160 eV.

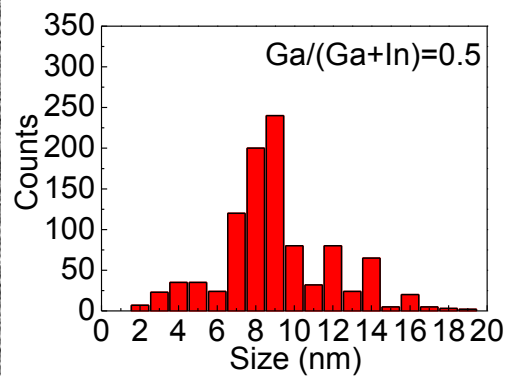
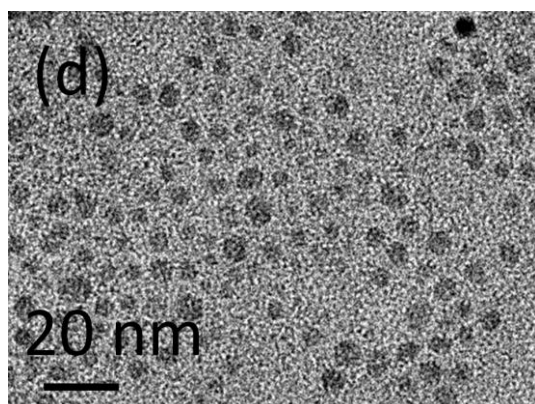
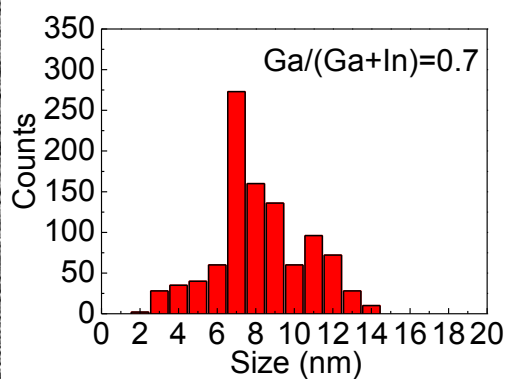
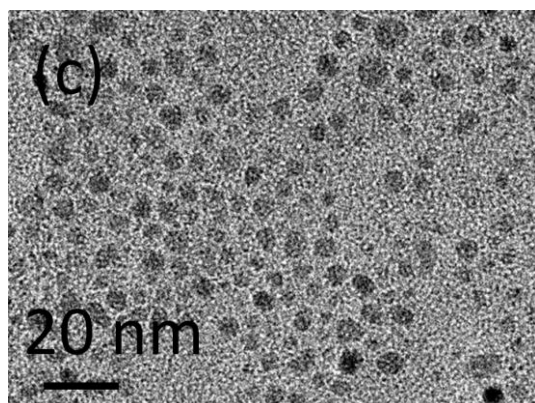
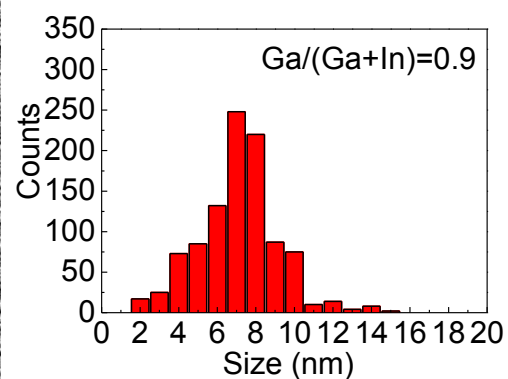
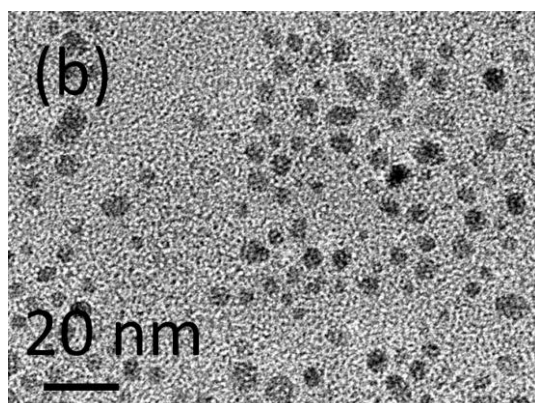
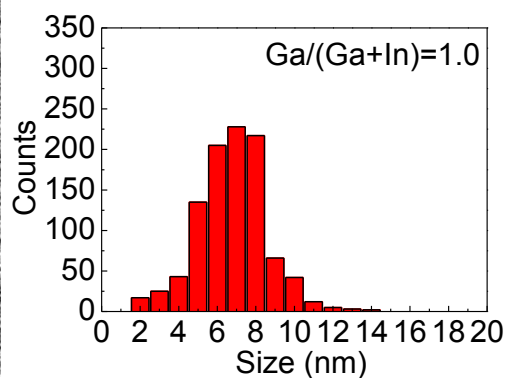
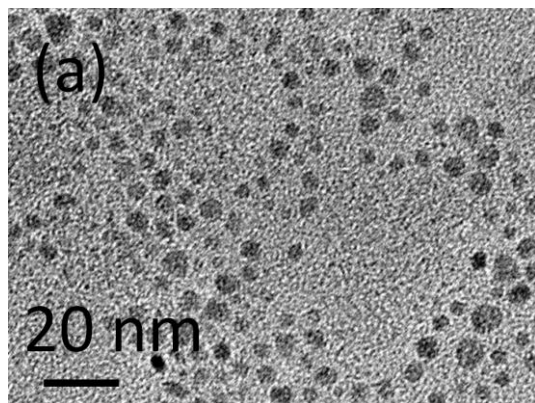
UV-VIS-NIR (ultraviolet-visible-near infrared) absorption spectra were obtained with a Varian Cary 500 spectrophotometer using nanocrystals in toluene solutions. For transport studies, the samples were prepared on a quartz glass with interdigitated gold electrodes as described by Sargent et al.<sup>1</sup> I-V characteristics were acquired using a source meter (Keithley 2400 SourceMeter) with or without illumination with AM 1.5 simulated sunlight at  $100 \text{ mW cm}^{-2}$  in the voltage bias range 0~5 V.

The hard X-ray source was a high brightness superconducting wavelength shifter at the BL01A beam line of the 1.5 GeV with 360 mA storage ring at National Synchrotron Radiation Research Center (NSRRC, Taiwan). We used a “white” (unmonochromatized) beam with no optical elements except one set of beryllium and

Kepton windows. A slit system produced a transversal beam section of  $13 \times 9 \text{ mm}^2$ . The calculated X-ray photon flux absorbed by the precursor solutions was centered at  $\approx 12.5 \text{ keV}$  and ranged in photon energy from  $6.5\sim 30 \text{ keV}$ . The delivered dose rate absorbed by the precursor solution was  $4.1 \pm 0.6 \text{ kGy s}^{-1}$  as measured with a Fricke dosimeter ( $0.8\text{N H}_2\text{SO}_4$ ) with an estimated  $G(\text{Fe}^+)$  value of  $13.^2$

(1) J. Tang, S. Hinds, S. O. Kelley, and E. H. Sargent, *Chem. Mater.*, 2008, **20**, 6906.

(2) C. H. Wang, C. J. Liu, C. L. Wang, C. C. Chien, Y. Hwu, R. S. Liu, C. S. Yang, J. H. Je, H. M. Lin, G. Margaritondo, *Appl. Phys. A*, 2009, **97**, 295.



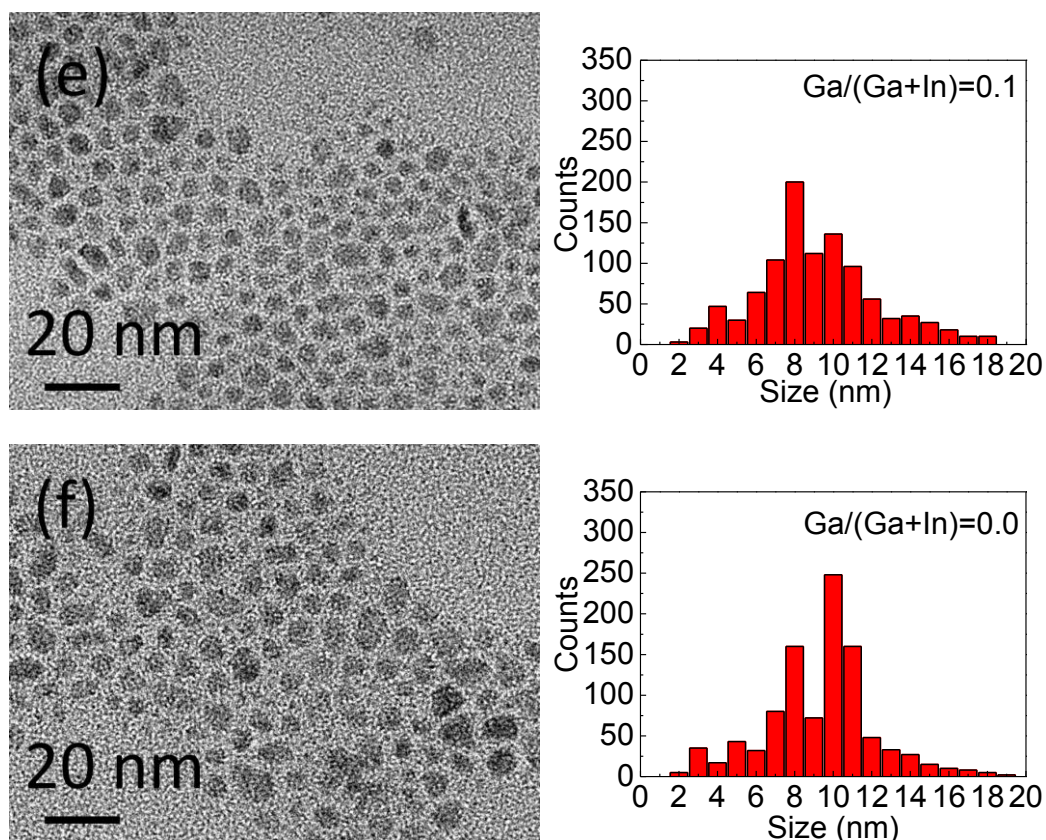


Figure S1. Typical TEM images of the Cu(In<sub>1-x</sub>Ga<sub>x</sub>)S<sub>2</sub> nanocrystals, corresponding to (a) 1.0, (b) 0.9, (c) 0.7, (d) 0.5, (e) 0.1, and (f) 0.0 Ga/(Ga+In) molar ratio and the corresponding size distribution histogram. Data based on manual counts of  $\approx 10^3$  nanocrystals in TEM images.

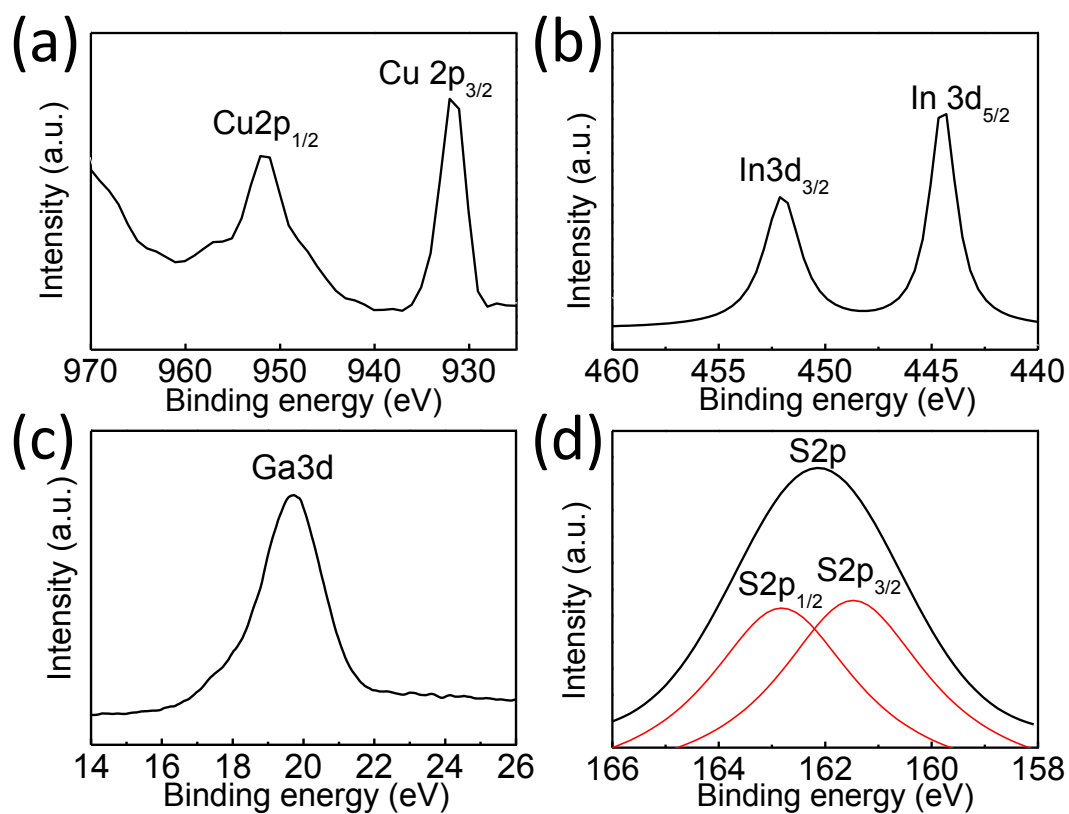


Figure S2. XPS spectra of  $\text{Cu}(\text{In}_{0.73}\text{Ga}_{0.27})\text{S}_2$  nanocrystals: (a) Cu 2p, (b) In 3d, (c) Ga 3d and (d) S 2p peaks

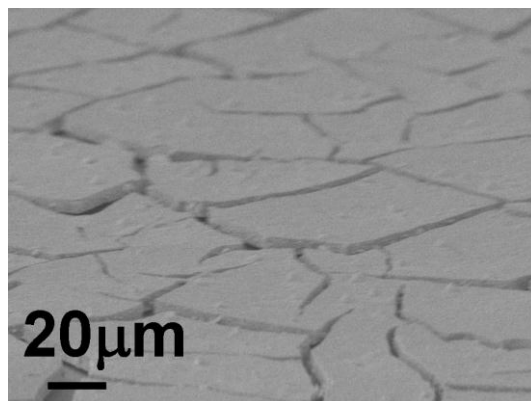


Figure S3. SEM image of a  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$  nanocrystal film obtained with multiple dropping steps: cracks are clearly visible.