

Electronic Supplementary Information

Fabrication of Single Crystal CuGaS₂ Nanorods by X-ray Irradiation

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Experimental details

Synthesis.

In a nitrogen-filled glove box, 0.75 mmol of CuCl (99.995%, Aldrich), 0.75 mmol of GaCl₃ (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 in the vials. The resulting S source solutions were rinsed by oleylamine in the reaction flask containing the Cu and Ga 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 2, 4, or 6 minutes at room temperature without stirring. After irradiation, 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 (~10 ml) forming a stable solution.

To synthesize Cu(In_{1-x}Ga_x)S₂ nanocrystals, a similar procedure was followed using 0.525 mmol of InCl₃ and 0.225 mmol of GaCl₃ as the precursor solution.

Characterization.

The products were 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 nanocrystals drop-cast from toluene dispersions on carbon-coated 200 mesh nickel TEM grids. The size distribution was derived with the Image-J software from measurements on 3000 nanocrystals.

Powder X-ray diffraction (XRD, Rigaku D/MAX2500) patterns were recorded at room temperature. These data were collected at angles 2θ between 20 and 70° with a step size of 0.1° 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 using a pass energy of 160 eV in a 2.0×10^{-9} Torr pressure chamber. UV-VIS-NIR (ultraviolet-visible-near infrared) absorption spectra were obtained with a Varian Cary 500 spectrophotometer using toluene-dispersed nanocrystals.

The hard X-rays for irradiation were generated at the BL01A beamline of the National Synchrotron Radiation Research Center (NSRRC) with an electron storage ring current of either 300 or 360 mA. The photon energy distribution was centered at 10-15 keV and the dose rate was 5.1 ± 0.9 kGy s^{-1} as determined by a Fricke dosimeter with an estimated G-value of 13.¹

For transport studies, the samples were prepared on a quartz glass with interdigitated platinum electrodes as described by Sargent *et al.*² Current-voltage characteristics were acquired using a source meter (Keithley 2400 SourceMeter) with or without illumination with AM 1.5 simulated sunlight at 100 mW cm^{-2} in the

voltage bias range 0~5 V.

(1) C. J. Liu, C. H. Wang, C. C. Chien, T. Y. Yang, S. T. Chen, W. H. Leng, C. F. Lee, K. H. Lee, Y. Hwu, Y. C. Lee, C. L. Cheng, C. S. Yang, Y. J. Chen, J. H. Je and G. Margaritondo, *Nanotechnology*, 2008, **19**, 295104.

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

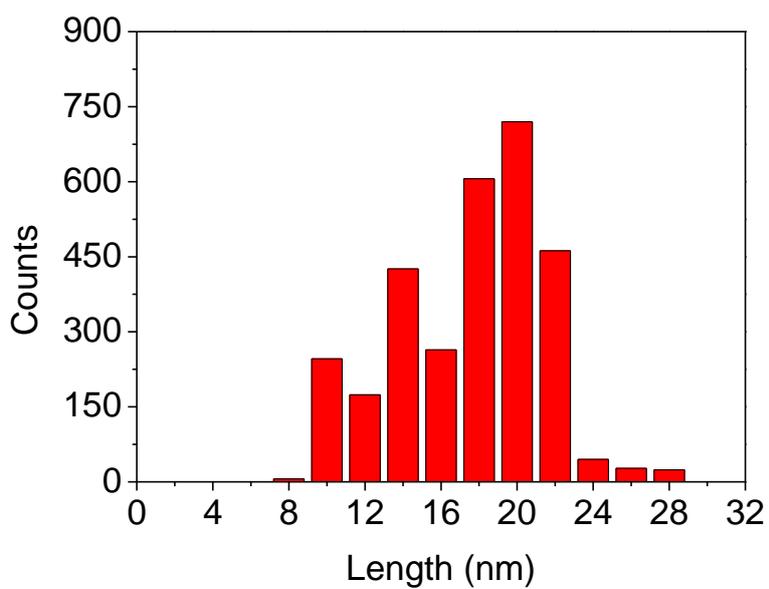
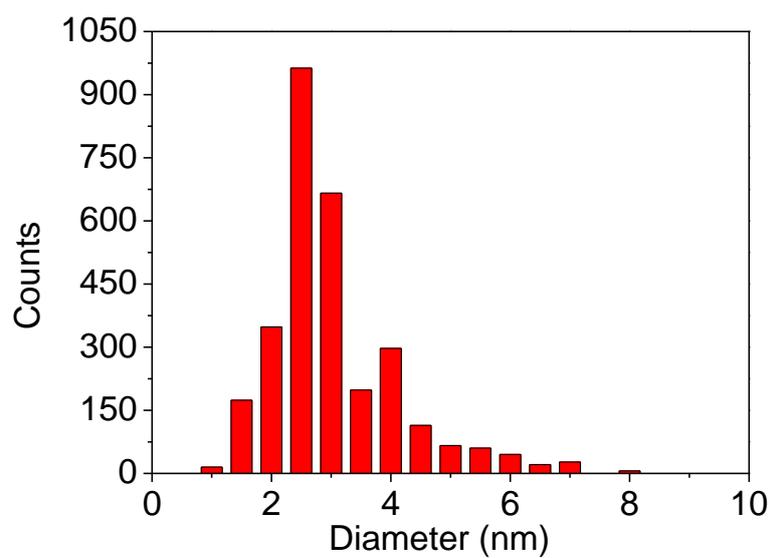


Figure S1. Size distribution of our nanorods. Data based on manual count of 3000 nanorods from TEM images.

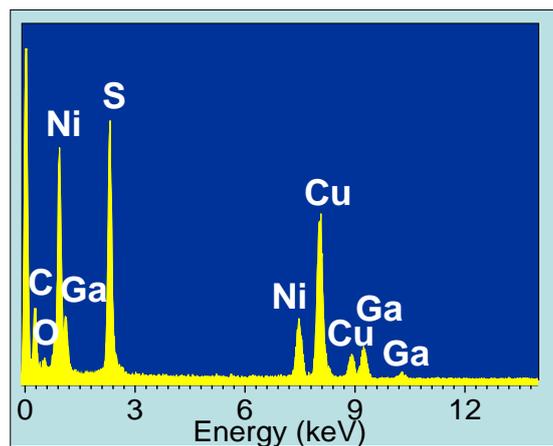


Figure S2. EDS of CuGaS₂ nanorods synthesized by 2 minutes of X-ray irradiation

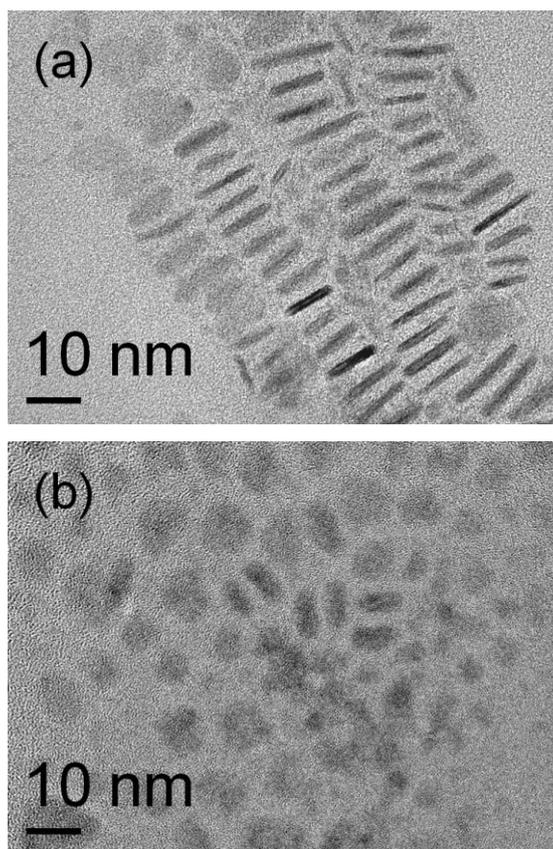


Figure S3. TEM images of CuGaS₂ nanocrystals synthesized with (a) 4 minutes and (b) 6 minutes of irradiation.

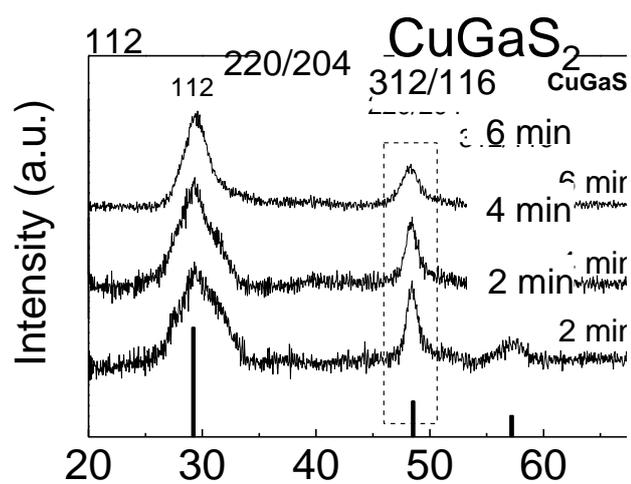


Figure S4. XRD of CuGaS₂ nanocrystals synthesized with 2, 4, and 6 minutes of irradiation.