Electronic supplementary information

Synthesis and Photoresponse of Novel Cu_2CdSnS_4 Semiconductor Nanorods†

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Experimental section

I. Chemicals

Copper monochloride (CuCl, AR), tin dichloride hydrated ($SnCl_2·2H_2O$, AR), cadmium acetate dihydrate (Cd $(CH_3COO)_2·2H_2O$, AR), carbon disulfide(CS_2, AR), 3-mercaptopropionic acid ($HSCH_2CH_2CO_2H$, 98%), hexylamine ($CH_3(CH_2)_5NH_2$, 99%) were purchased from Aladdin inc. All chemical reagents were used as received without any further purification.

II. Synthesis of Cu_2CdSnS_4 Nanorods.

1.0 mmol CuCl, 0.5 mmol $SnCl_2·2H_2O$, 0.5 mmol $Cd(CH_3COO)_2·2H_2O$ were dissolved in 12.0 mL of hexylamine by ultrasound in 50mL conical flask. 12.0 mL of hexylamine was loaded into another 50 mL conical flask. Afterwards, 1.0 mL of carbon disulfide and 1.0 mL of 3-mercaptopropionic were slowly added into the conical flask in an ice water bath, respectively. The former solution was slowly added into the later solution. Subsequently, 1.0 mL of 3-mercaptopropionic was added into the solution. After 12 h continuously vigorous stirring, the solution was transferred into 40 mL Teflon-lined stainless steel autoclave and solvothermal reaction at 140℃ for 25 min then rise to 180℃ and keep at this temperature for 2 h. Finally, the

autoclave was naturally cooled to room temperature. The nanocrystals were isolated by precipitation with 20 mL of methanol followed by centrifugation at 4000 rpm for 5 min. The purified nanocrystals were re-dispersed in chloroform for TEM and XRD measurements.

III. Characterization

The powder XRD pattern was recorded using a Bruker D8 X-ray diffractometer. Energy Disperse Spectroscopy (EDS) spectrum was obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were taken on a FEI Tecnai G2 F20 electron microscope with an accelerating voltage of 200 kV. UV-vis-NIR absorption spectrum was measured by metash UV-5200 spectrophotometer. X-ray photoelectron spectra (XPS) were measured with VG ESCALAB MK (VG Company, UK) at room temperature by using a Mg Kα X-ray source (hV=1253.6 eV) at 14 kV and 20 mA. The optoelectronic properties were carried out by spin casting 2.0 mL of concentrated nanocrystals solution in chloroform onto a glass slide (2*2cm). Annealing process was conducted at 400□in the glove-box under N_2 atmosphere in order to remove ligands and solvent. Current-voltage characteristics were tested using a Keithley 2400 source meter under AM 1.5G solar simulator (Abet inc. Sun 2000) that had an intensity of 100 mW/cm^2. The scanning voltage was tuned from -5V to 5 V.

Figure S1. Unit cell of wurtzite Cu_2CdSnS_4

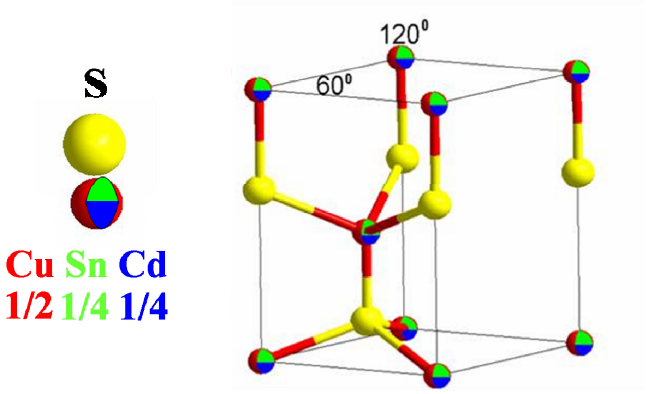

Table S1. Comparison of experimental and simulated XRD peaks for wurtzite Cu_2CdSnS_4.

hkl	Observed 2θ	Simulated 2θ	Δ2θ
100	26.472	26.479	-0.007
002	27.890	27.884	+0.006
101	29.989	29.974	+0.015
102	38.908	38.827	+0.081
110	46.731	46.736	-0.005
103	50.596	50.634	-0.038
112	55.298	55.299	-0.001

Crystal data

Formula Cu_2CdSnS_4

Crystal system Wurtzite

Space group $P6_3mc$ (No. 186)

Unit cell dimensions $a = b = 3.8847$ Å, $c = 6.3926$ Å

Atomic coordinates

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**
S	2b	1/3	2/3	0
Sn	2b	1/3	2/3	0.3752
Cd	2b	1/3	2/3	0.3752
Cu	2b	1/3	2/3	0.3752

Note that Cu^+, Cd^{2+}, and Sn^{4+} ions occupy the same position, and the occupancy possibilities of Cu^+, Cd^{2+}, and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

Figure S2. EDS spectrum of wurtzite Cu_2CdSnS_4 nanorods

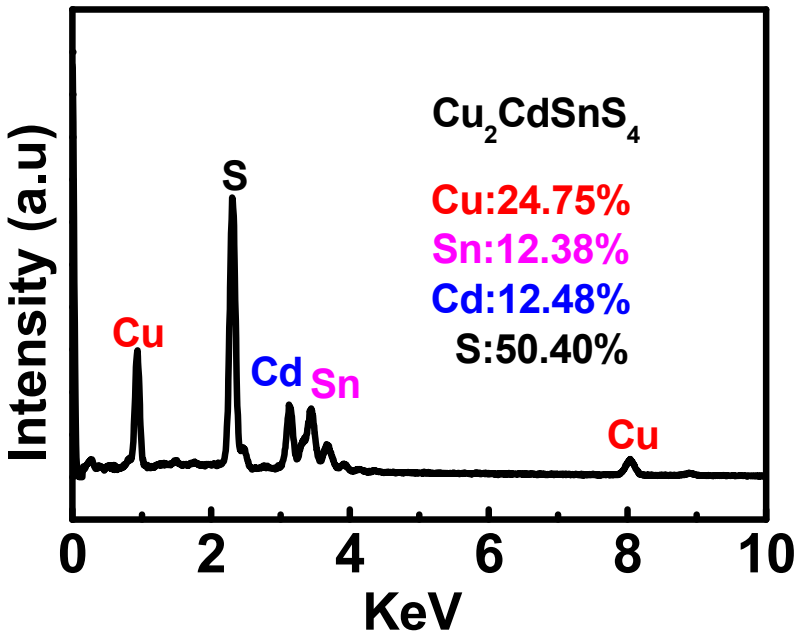

Figure S3. TEM image of wurtzite Cu_2CdSnS_4 nanorods with low density

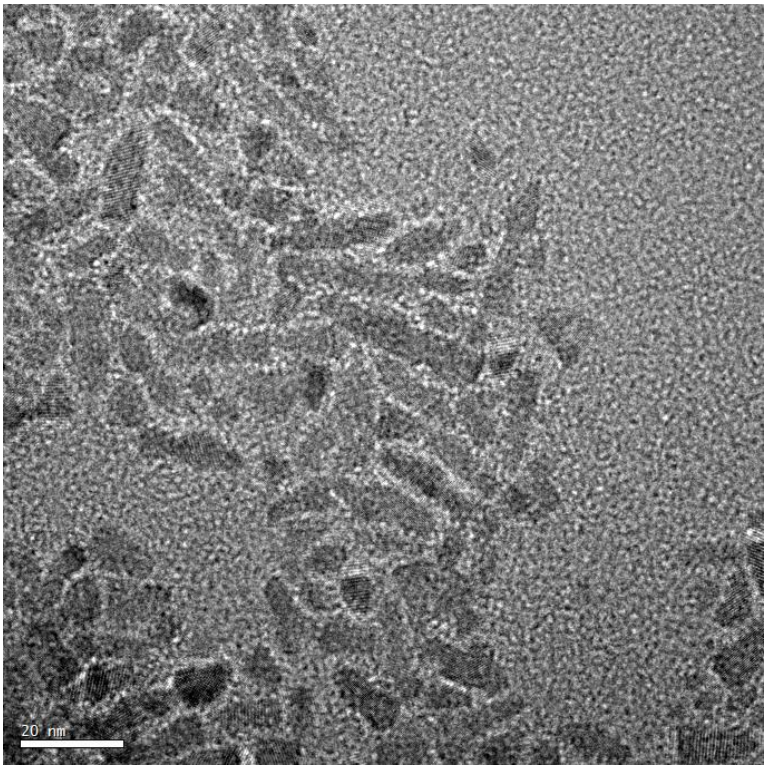

Figure S4. Size distribution of wurtzite Cu_2CdSnS_4 nanorods (a: length distribution; b: diameter distribution)