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Composition-tunable $Cu_2(Ge_{1-x},Sn_x)(S_{3-y},Se_y)$ Colloidal Nanocrystals: Synthesis and Characterization

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Chemicals

Copper (II) acetylacetonate ($Cu(acac)_2$, 99.99+%), sulfur (S, 99.998%), oleylamine (OLA, 70%), acetonitrile (99.8%) and chlorobenzene (CB, 99.8%) were purchased from Aldrich. Germanium (IV) chloride ($GeCl_4$, 99.9999%), Tin (II) bromide ($SnBr_2$, 99.4%), Selenium (IV) oxide (SeO_2, 99.99%), 1-Octadecene (ODE, 90%) and 3-mercaptopropionic acid (MPA, 99%) were obtained from Alfa Aesar. Butylamine (99%), ethanol(99.7%), isopropanol (99.7%) and n-hexane (97%) were supplied by Sinopharm chemical Reagent Co., Ltd. 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) was supplied by Feiming Chemical Co., Ltd. OLA and ODE were dried under vacuum at 120 ^oC for 10 h before use.

S and Se solution. 1 M OLA-S stock solution was made by dissolving 0.64 g (20 mmol) of sulfur powder in 20 mL of OLA under argon atmosphere at 60 ^oC by stirring and held at 60 ^oC for 4 hours to yield a perfectly clear solution. 1M ODE-Se solution was prepared by dissolving 2.22 g (20 mmol) of SeO_2 in 20 mL of ODE under argon atmosphere at 150 ^oC by stirring and held at 150 ^oC for 4 hours to yield a perfectly clear solution.

Synthesis of $Cu_2(Ge_{1-x},Sn_x)S_3$ alloyed NCs. Take x=0.5 for example, typically, 261.8 mg (1 mmol) of $Cu(acac)_2$ and 69.6 mg (0.25 mmol) of $SnBr_2$ were first loaded into a flask containing 10 mL OLA. The flask was degassed by a vacuum pump for 30 min to remove water and other low-boiling point impurities at 120 ^oC. Afterwards, $GeCl_4$ (43 μL, 0.325 mmol) and 1 mL ODE were injected into this solution. The temperature was subsequently increased to 160 ^oC, followed by swift injection of 1.5 mL OLA-S solution into the flask. The reaction solution was then heated to 280 ^oC in 10 min and maintained at this temperature for 2 hours to finish the reaction. Subsequently, the solution was cooled down to 60 ^oC and then precipitated with 30 mL of isopropanol and centrifuged at 8000 rpm for 5 min. The upper yellow solution was discarded and n-hexane was added to disperse the nanocrystals. Then the product was further purified by adding a certain amount of isopropanol and centrifuging. This process was repeated for three times to yield the nanocrystal product that could be dispersed in common organic solvents such as toluene for later use.

Synthesis of $Cu_2(Ge_{0.5},Sn_{0.5})(S_{3-y},Se_y)$ alloyed NCs. The synthesis was performed under conditions almost identical to the synthesis of $Cu_2(Ge_{1-x},Sn_x)S_3$ NCs, except that the OLA-S and ODE-Se solution with corresponding ratios was used.

Fabrication of photovoltaic devices

Prior to the growth of CdS nanorods (NRs), a compact TiO_2 layer was deposited on a cleaned FTO glass substrate by dip-coating with a TiO_2 organic solution (made by titanium butoxide/diethanolamine/ absolute ethanol solution), followed by a calcination at 500 ^oC for 30 min. CdS NR arrays on TiO_2-coated FTO were then prepared according to a literature method with some modifications.[1] Briefly, 20 mL of 0.05 M $Cd(NO_3)_2$, 20 mL of 0.05 M thiourea solution and 20 mL of 0.03 M glutathione solution were mixed and loaded into a 100 mL autoclave containing a piece of TiO_2-coated FTO substrate, subsequently subjected to hydrothermal treatment at 200 ^oC for 3 h to give CdS NR arrays with length of 700~800 nm on TiO_2-coated FTO. These CdS NR arrays are employed as the n-type electron conducting materials of solar cells with $Cu_2(Ge_{1-x},Sn_x)(S_{3-y},Se_y)$ NCs as the p-type light harvester.

In a typical procedure, 0.5 mmol of purified $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs were dispersed in 2 mL of CB, then mixed with 2 mL of 1-butylamine, 0.5 mL of MPA in a 10 mL vial for ligand exchange. The vial was sealed and sonicated for 45 min, then the $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs were precipitated with methanol, and re-dispersed in a mixed solvent of 2 mL of 1-butylamine, 1 mL of CB, and 200 μL of MPA. The solution was centrifuged at 8000 rpm for 3 min to precipitate any aggregations. The upper solution was filtered through a PTFE filter (pore size 200 nm). $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs film was then deposited onto CdS nanorod arrays using a layer-by-layer spin-coating method in an Ar-filled glovebox. 30 μL of $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs solution was spin-coated at 2500 rpm for 20 s, then placed on a hotplate preheated to 150 °C for 3 min. This process was repeated for 4 times, resulting in film with CdS NRs covered by $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs, onto which 15 μL of HTM solution (spiro-MeOTAD/chlorobenzene (90 mg/1mL) solution was used with added 35.8 μL LiTFSI/acetonitrile (520 mg/1 mL) and 21.8 μL TBP.) was finally spin-coated at 5500 rpm for 30 s. 120 nm of Au films were finally deposited by thermal evaporation under pressure of 6×10^{-4} Pa. The active area of the device was 0.11 cm^2. Photovoltaic measurement was recorded with an AM 1.5G Oriel solar simulator (model 92250A-1000) at an illumination intensity of 100 mW/cm^2.The current-voltage characteristics of each cell were recorded with a Keithley 2400 source meter.

Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation source (λ = 1.541 Å) operating at 40 kV and 200 mA with a scanning rate of 5°/ min in the 2θ range of 20-70° at a step size of 0.02 s. The TEM images showing the morphology of the NCs were obtained on a FEI TECNAI G^2 spirit microscope, operating at an accelerating voltage of 100 kV. HRTEM images and selective area electron diffraction (SAED) patterns were obtained with a FEI TECNAI F30 S-Twin (FEI company) with an accelerating voltage of 300 kV. Element analysis as an ensemble measurement was conducted on FEI Quanta 200F scanning electron microscope equipped with energy dispersive spectroscopy (EDS) detector. UV-Vis-NIR absorption spectra of NCs suspensions in toluene were acquired in 1 cm path length quartz cuvettes using a Cary 5000 spectrophotometer. Transient photocurrent measurements were conducted in a quartz cell under nitrogen in aqueous solution with 0.01 M $Eu(NO_3)_3$ /0.1 M KCl using an AM1.5 Xe lamp illumination. A saturated calomel electrode (SCE) was employed as the reference electrode, and a Pt foil as counter electrode. The nanocrystal film was sprayed onto FTO to form the work electrode. The photoelectrochemical response of the $Cu_2(Ge_{1-x},Sn_x)(S_{3-y},Se_y)$ nanocrystal films was obtained by varying the bias potentials from -0.6~0.2V, and the stability of the NC films was assessed by measuring the photoelectrochemical response under constant bias of -0.4 V under 20 s on/off chopped illumination.

Table S1. Comparison of experimental and simulated XRD results of cubic Cu_2SnS_3 NCs.

hkl	d_{obs}	d_{calc}	d_{obs}-d_{calc}	I	2-TH
111	3.1460	3.1419	0.0041	100	28.383
200	2.7232	2.7210	0.0022	12	32.890
220	1.9253	1.9240	0.0013	61	47.201
311	1.6402	1.6408	-0.0006	41	55.998
222	1.5708	1.5710	-0.0002	3	58.725
400	1.3610	1.3605	0.0005	9	68.970
331	1.2490	1.2485	0.0005	16	76.193
420	1.2170	1.2169	0.0001	4	78.546

Crystal date

Formula	Cu_2SnS_3
Crystal system	Cubic
Space group	F-43m (216)
Unit cell dimensions	a=b=c=5.4420 Å

Atomic coordinates

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F.**
Cu	4a	0	0	0	0.6667
Sn	4a	0	0	0	0.3333
S	4c	1/4	1/4	1/4	

Note that Cu^+, and Sn^{4+} ions occupy the same position

Table S2. Atomic composition obtained by EDS overview spectra from $Cu_2(Ge_{1-x},Sn_x)(S_{3-y},Se_y)$ NCs.

$Cu_2(Ge_{1-x},Sn_x)(S_{3-y},Se_y)$	Cu/Ge/Sn/S/Se molar ratio	
	In precursors	In products
Cu_2GeS_3	2.00/2.00/0.00/3.00/0.00	2.00/0.96/0.00/2.94/0.00
$Cu_2(Ge_{0.75},Sn_{0.25})S_3$	2.00/1.00/0.25/3.00/0.00	2.00/1.00/0.29/3.26/0.00
$Cu_2(Ge_{0.5},Sn_{0.5})S_3$	2.00/0.75/0.50/3.00/0.00	2.00/0.61/0.56/3.16/0.00
$Cu_2(Ge_{0.25},Sn_{0.75})S_3$	2.00/0.50/0.75/3.00/0.00	2.00/0.29/0.86/3.20/0.00
Cu_2SnS_3	2.00/0.00/1.00/3.00/0.00	2.00/0.00/0.99/3.00/0.00
$Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$	2.00/0.75/0.50/2.00/1.00	2.00/0.48/0.43/1.71/1.07
$Cu_2(Ge_{0.5},Sn_{0.5})(S,Se_2)$	2.00/0.75/0.50/1.00/2.00	2.00/0.45/0.47/0.93/2.14
$Cu_2(Ge_{0.5},Sn_{0.5})Se_3$	2.00/0.75/0.50/0.00/3.00	2.00/0.48/0.46/0.00/3.15

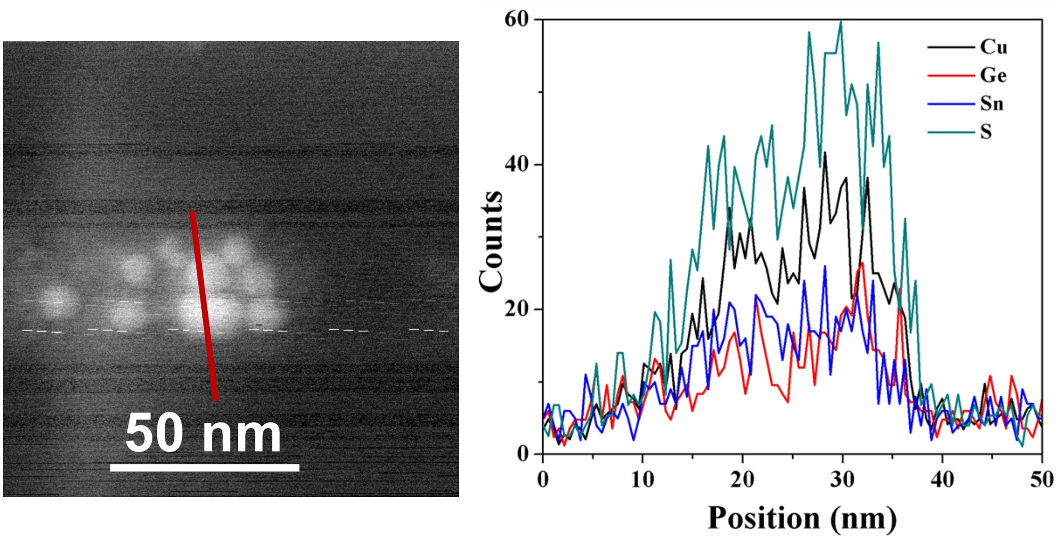

Fig. S1 STEM-EDS line scan of the $Cu_2(Ge_{0.75},Sn_{0.25})S_3$ NCs.

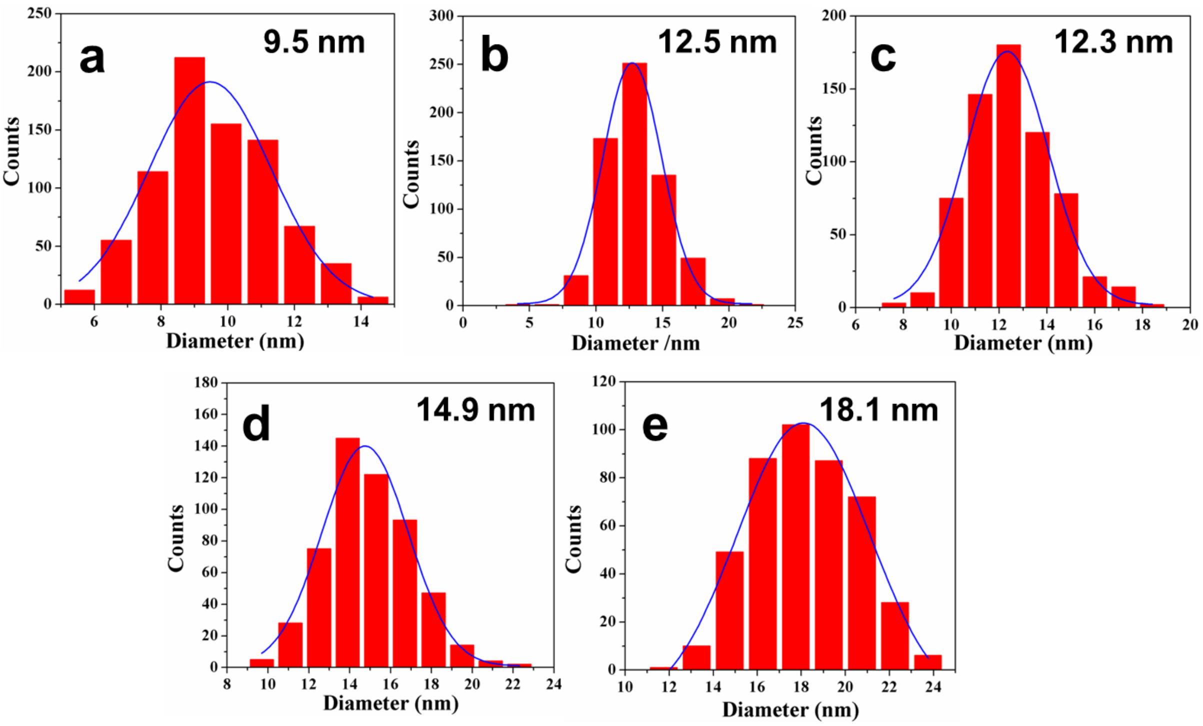

Fig. S2 Particle size distributions of a) Cu_2GeS_3, b) $Cu_2(Ge_{0.75},Sn_{0.25})S_3$, c) $Cu_2(Ge_{0.5},Sn_{0.5})S_3$, d) $Cu_2(Ge_{0.25},Sn_{0.75})S_3$ and e) Cu_2SnS_3.

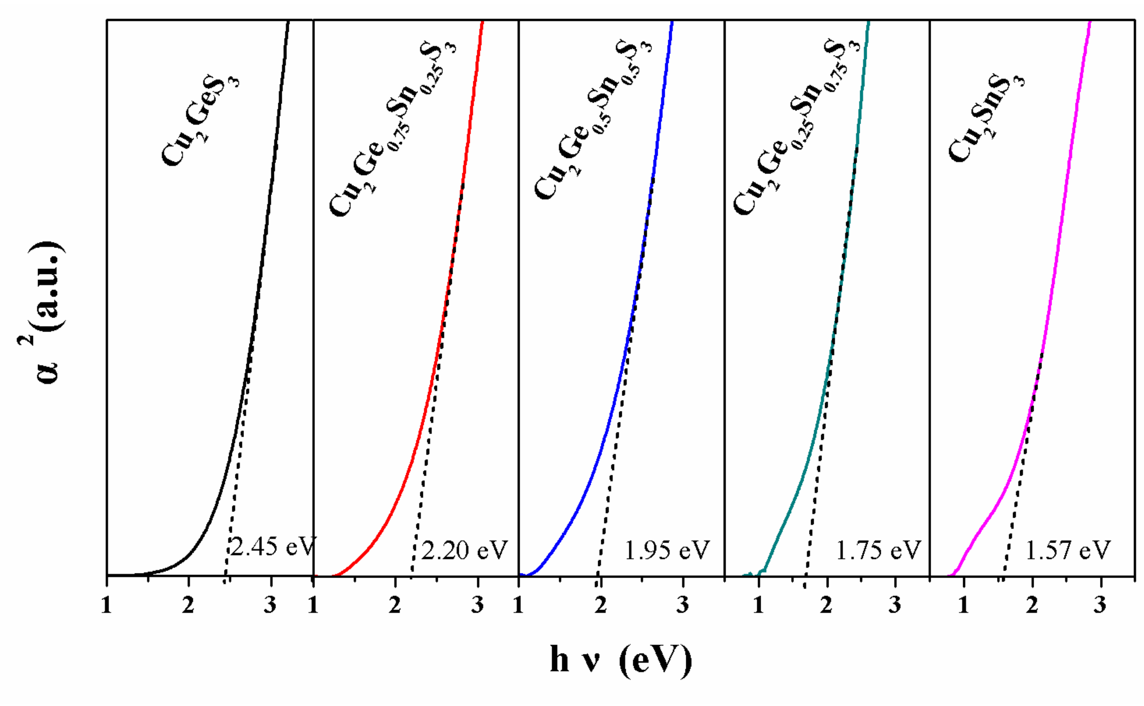

Fig. S3 Band gaps of the $Cu_2(Ge_{1-x},Sn_x)S_3$ NCs with various Sn/(Ge+Sn) ratios ($0 \leq x \leq 1$) derived from UV-vis absorption spectra.

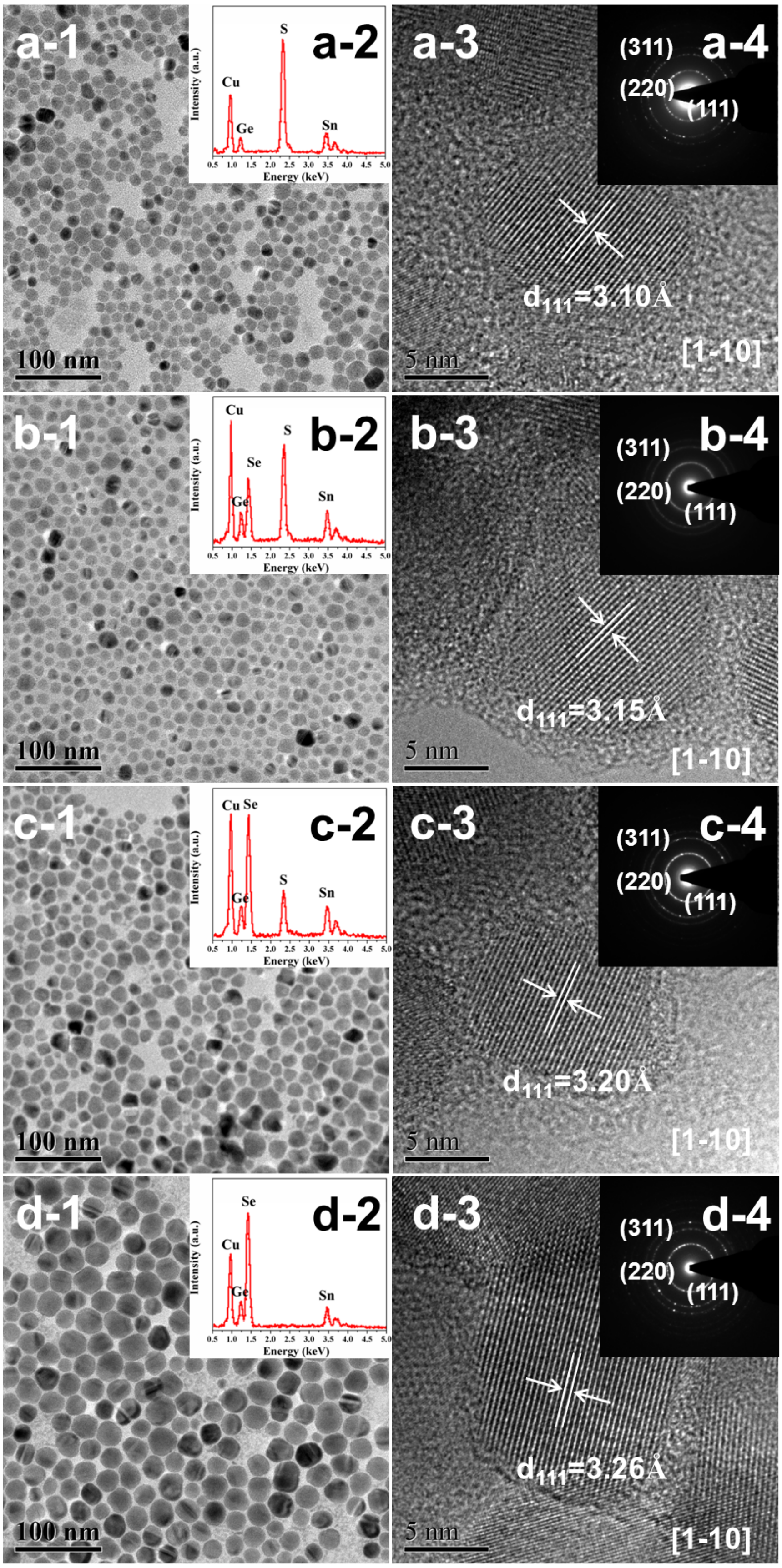

Fig. S4 TEM analysis of the $Cu_2(Ge_{0.5},Sn_{0.5})(S_{3-y},Se_y)$ (0≤ y ≤3) NCs. a), b), c), and d) denote respectively the samples $Cu_2(Ge_{0.5},Sn_{0.5})S_3$, $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$, $Cu_2(Ge_{0.5}Sn_{0.5})(S,Se_2)$, and $Cu_2(Ge_{0.5}Sn_{0.5})Se_3$ NCs. 1, 2, 3, and 4 represent the corresponding low magnification TEM images, EDS spectra, HRTEM images and SAED patterns for these samples.

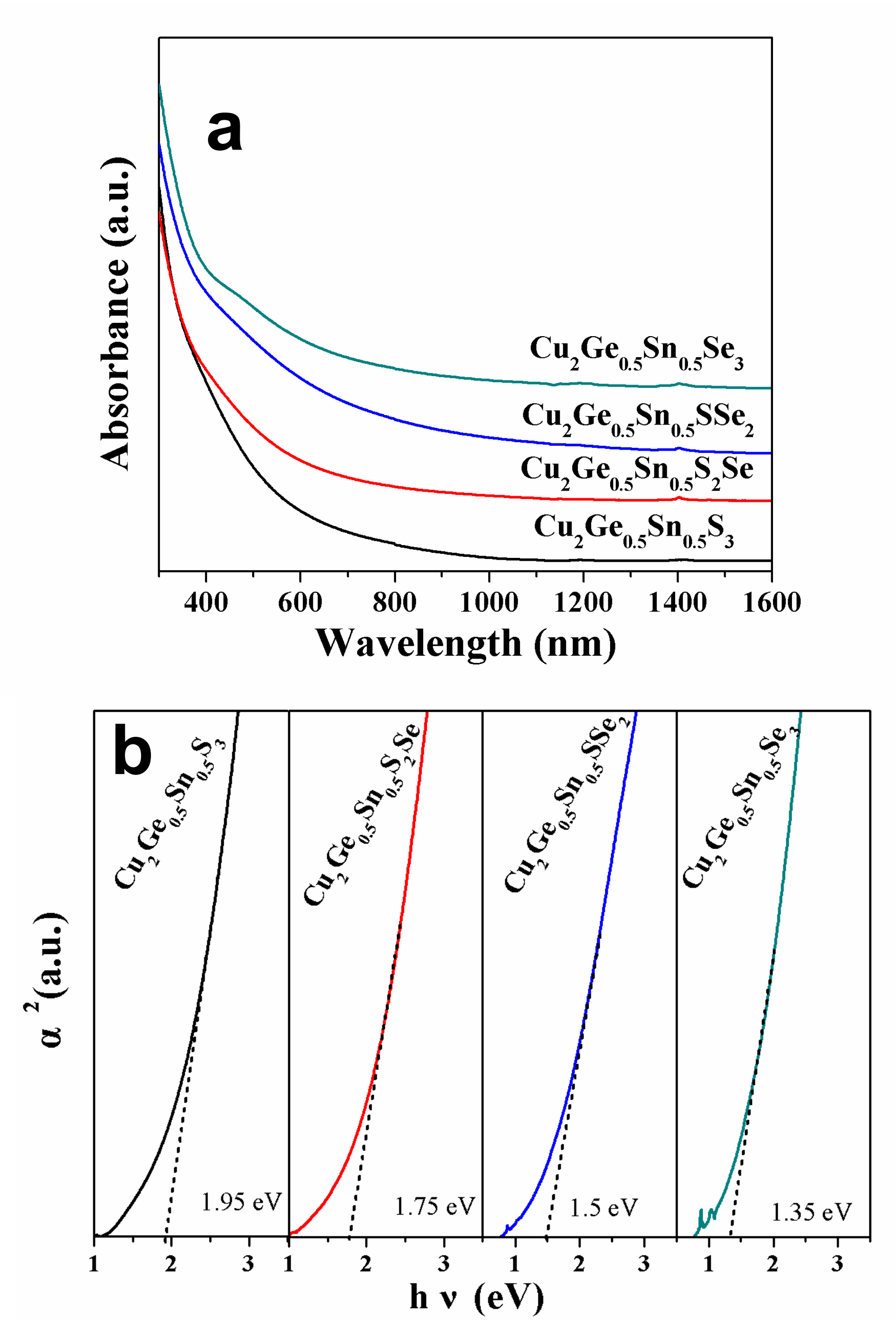

Fig. S5 a) UV-vis-NIR absorption spectra for the $Cu_2(Ge_{0.5},Sn_{0.5})(S_{3-y},Se_y)$ NCs with various Se/S ratios ($0 \leq y \leq 3$), b) Band gaps of the $Cu_2(Ge_{0.5},Sn_{0.5})(S_{1-y},Se_y)$ NCs with various Se/(S+Se) ratios ($0 \leq y \leq 3$) derived from UV-vis absorption spectra.

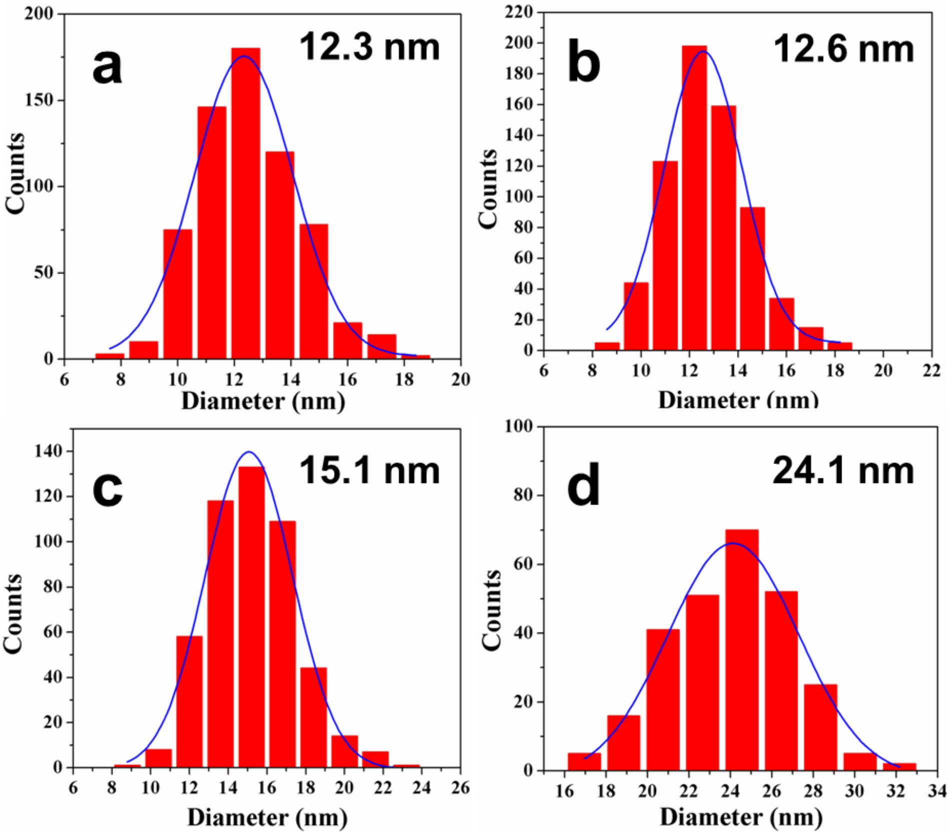

Fig. S6 Particle size distributions of a) $Cu_2(Ge_{0.5},Sn_{0.5})S_3$, b) $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$, c) $Cu_2(Ge_{0.5},Sn_{0.5})(S,Se_2)$, and d) $Cu_2(Ge_{0.5},Sn_{0.5})Se_3$.

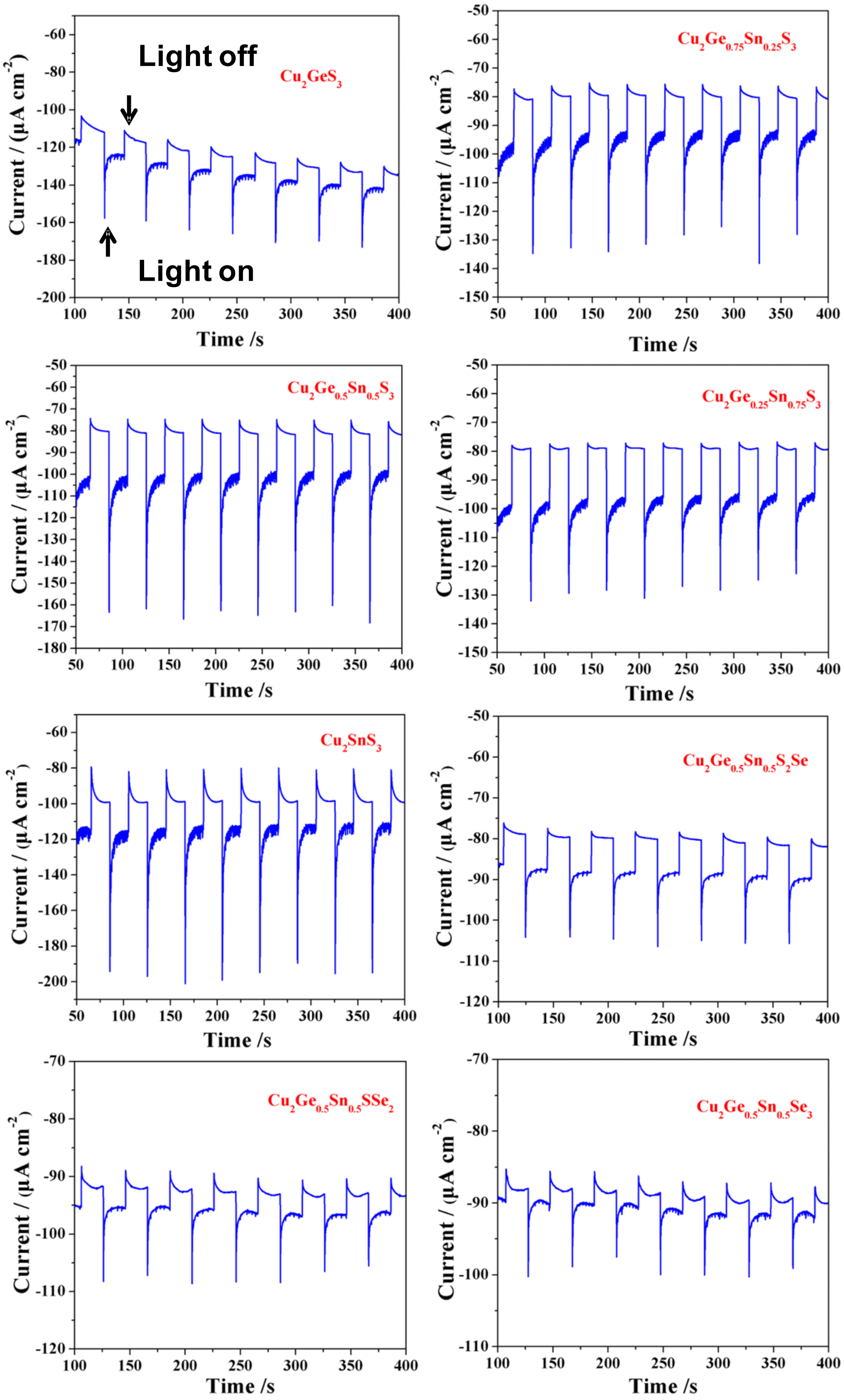

Fig. S7 Transient photocurrent response of the $Cu_2(Ge_{1-x},Sn_x)(S_{3-y}Se_y)$ NCs under constant bias of -0.4V.

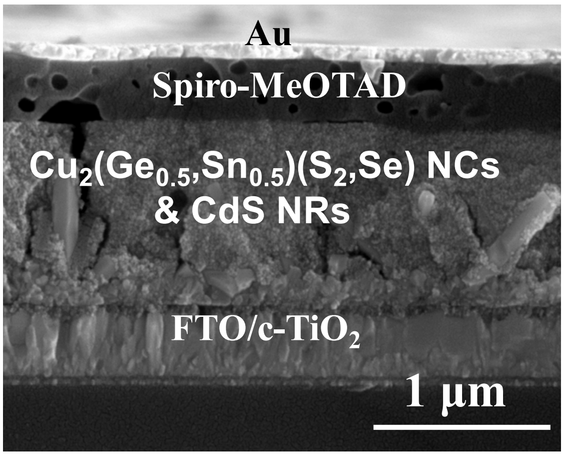

Fig. S8 SEM cross-sectional image of the $Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs-based solar cell with the configuration of FTO/c-TiO_2/CdS NRs/$Cu_2(Ge_{0.5},Sn_{0.5})(S_2,Se)$ NCs/Spiro-MeOTAD/Au.

[1] C. Yang, S. Liu, M. Li, X. Wang, J. Zhu, R. Chong, D. Yang, W.-H. Zhang, C. Li, *J. Colloid Interface Sci.,* **2013**, *393*, 58.