

**$\text{Cu}_2\text{Ge}(\text{S}_{3-x}\text{Se}_x)$  Colloidal Nanocrystals: Synthesis, Characterization, and Composition-dependent Band Gap Engineering**

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## Experimental Section

**Chemicals.** Copper (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ , 99.99+%), sulfur (S, 99.998%), oleylamine (OLA, 70%) and Chlorobenzene (CB, 99.8%) were purchased from Aldrich. Germanium (IV) chloride ( $\text{GeCl}_4$ , 99.9999%), selenium (Se, 99.99%) and 3-mercaptopropionic acid (MPA, 99%) were obtained from Alfa Aesar.

**S and Se solution.** 1M 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 120 °C by stirring and held at 200 °C for 5 hours to yield a perfectly clear solution, while 1M OLA-Se solution was prepared by the same process except that the temperature was kept at 180 °C.

**Synthesis of  $\text{Cu}_2\text{GeS}_3$  nanocrystals.** In a typical synthesis, 261.8 mg (1 mmol) of  $\text{Cu}(\text{acac})_2$  was 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 125 °C. Afterwards,  $\text{GeCl}_4$  (214 mg, 1 mmol) was injected into this solution. The temperature was subsequently increased to 160 °C, followed by swift injection of 2 ml OLA-S/Se solution into the flask. The reaction solution was then heated to 280 °C in 10min and maintained at this temperature for 2 hours to finish the reaction. Subsequently, the solution was cooled down to 60 °C and then precipitated with 30 mL of ethanol and centrifuged at 8000 rpm for 5 min. The upper yellow solution was discarded and toluene 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  $\text{Cu}_2\text{GeS}_{(3-x)\text{Se}_x}$  alloyed NCs and pure  $\text{Cu}_2\text{GeSe}_3$  NCs.** The synthesis was performed under conditions almost identical to the synthesis of  $\text{Cu}_2\text{GeS}_3$  NCs, except that the OLA-S and OLA-Se solution with corresponding ratios was used.

### Fabrication of photovoltaic devices.

A dense  $\text{TiO}_2$  layer was first deposited on a cleaned FTO glass substrate by dip-coating with a  $\text{TiO}_2$  organic solution (made by titanium butoxide/diethanolamine/ absolute ethanol solution), followed by a sintering at 500 °C for 30 min.<sup>[1]</sup> CdS nanorod arrays on  $\text{TiO}_2$ -coated FTO were then prepared according to the reported process<sup>[2]</sup>. Briefly, a mixture solution of cadmium nitrate, thiourea, and glutathione with

a molar ratio of 1:1:0.6 was loaded into a 100 mL autoclave containing a piece of TiO<sub>2</sub>-coated FTO substrate, subsequently subject to hydrothermal treatment at 200 °C for 3.5 h. CdS nanorod arrays with length of ~700 nm and diameter of ~ 100nm were thus obtained. These CdS nanorod arrays are employed as the n-type electron conducting materials of solar cells with Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs as light harvester. 2mL of 1-butylamine , 0.5 mL of MPA, 2mL of CB and 1mmol Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs were mixed in a 20 mL vial for ligand exchange. The vial was sealed and sonicated for 45 min, then the Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs were precipitated with methanol, and re-dispersed in a mixed solvent of 2 mL of 1-butylamine , 1mL of CB and 50 μ L of MPA. The solution was centrifuged at 8000 rpm for 5 min to precipitate any aggregations. The upper solution was filtered through a PTFE filter (pore size 220 nm). Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs film was deposited onto CdS nanorod arrays using a layer-by-layer spin-coating method in ambient atmosphere. 100 μ L of Cu<sub>2</sub>Ge(S<sub>2</sub>Se) solution was spun at 2000 rpm for 20 s, then placed on a hotplate preheated to 150 ° C for 3min. This process was repeated for 8 times. The resulting samples were pumped overnight in the antechamber of glove box before being transferred to the evaporation chamber. 10 nm of MoO<sub>3</sub> and 80 nm of Au films were then deposited sequentially at  $2 \times 10^{-4}$  Pa with a metal mask with area of 11.34 mm<sup>2</sup>. Current density-voltage (J-V) data were measured using a Keithley 2420 source-meter, and the illumination intensity was 100 mW cm<sup>-2</sup> (AM 1.5G Oriel solar simulator).

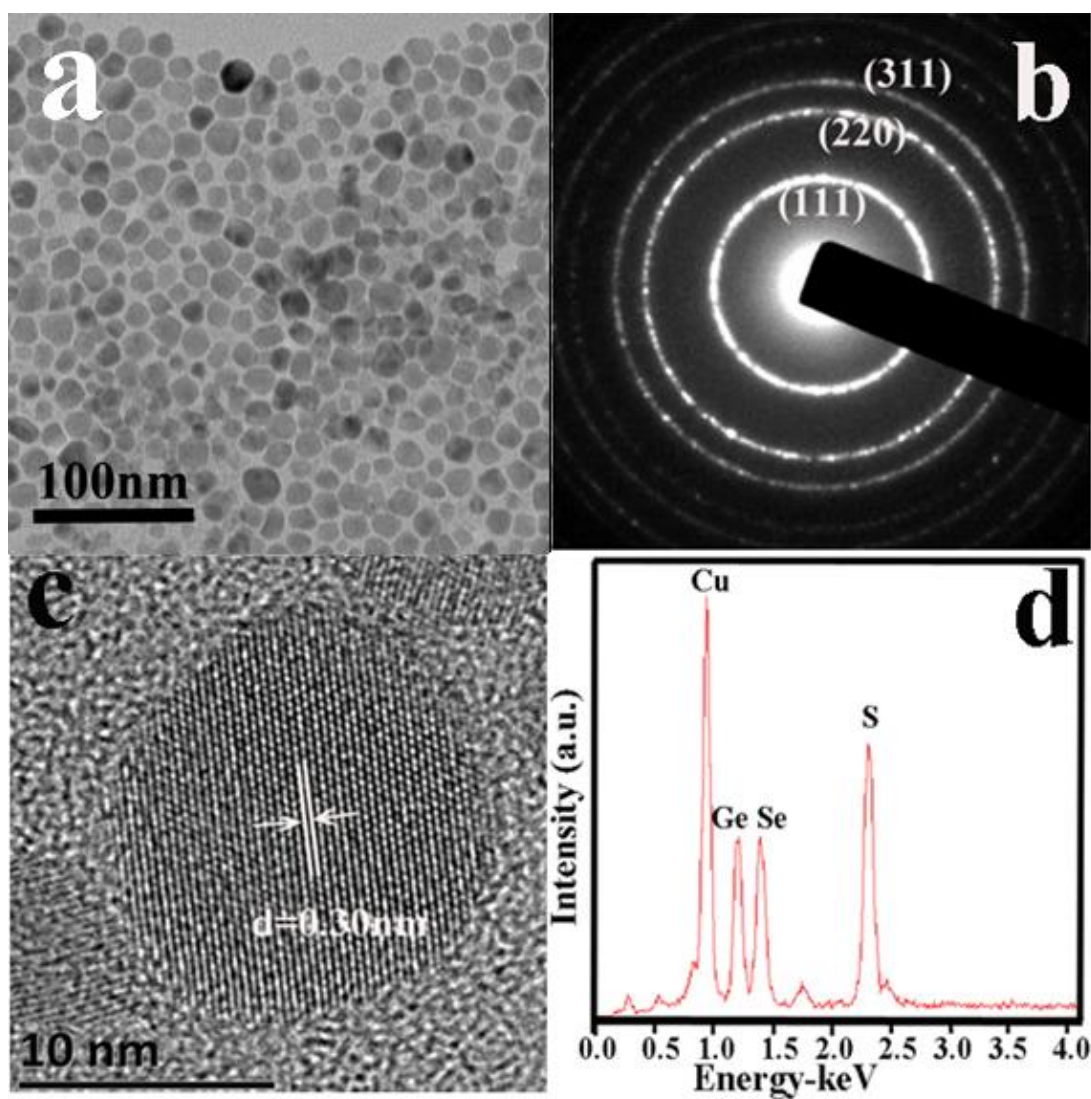
**Structural characterization.** X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max- 2500 powder diffraction system using Cu K $\alpha$  radiation source (  $\lambda$  = 1.54 Å) operating at 40 kV and 200 mA. For Cu<sub>2</sub>GeS<sub>3</sub> and Cu<sub>2</sub>GeSe<sub>3</sub> samples, the TEM images showing the morphology of the NCs were obtained on a Hitachi HT 7700, operating at an accelerating voltage of 120 kV. Selective area electron diffraction (SAED) patterns and HRTEM images were obtained with a FEI TECNAI F30 microscope. For Cu<sub>2</sub>Ge(S<sub>2</sub>Se) and Cu<sub>2</sub>Ge(SSe<sub>2</sub>) samples, all the TEM images and SAED patterns were obtained on a JEOL JEM-2010F microscope. Element analysis as an ensemble measurement was conducted on FEI Quanta 200F scanning electron microscope equipped with energy dispersive spectroscopy (EDX) detector.

UV-Vis-NIR absorption spectra of NC suspensions in toluene were acquired in 1 cm path length quartz cuvettes using a Cary 5000 spectrophotometer.

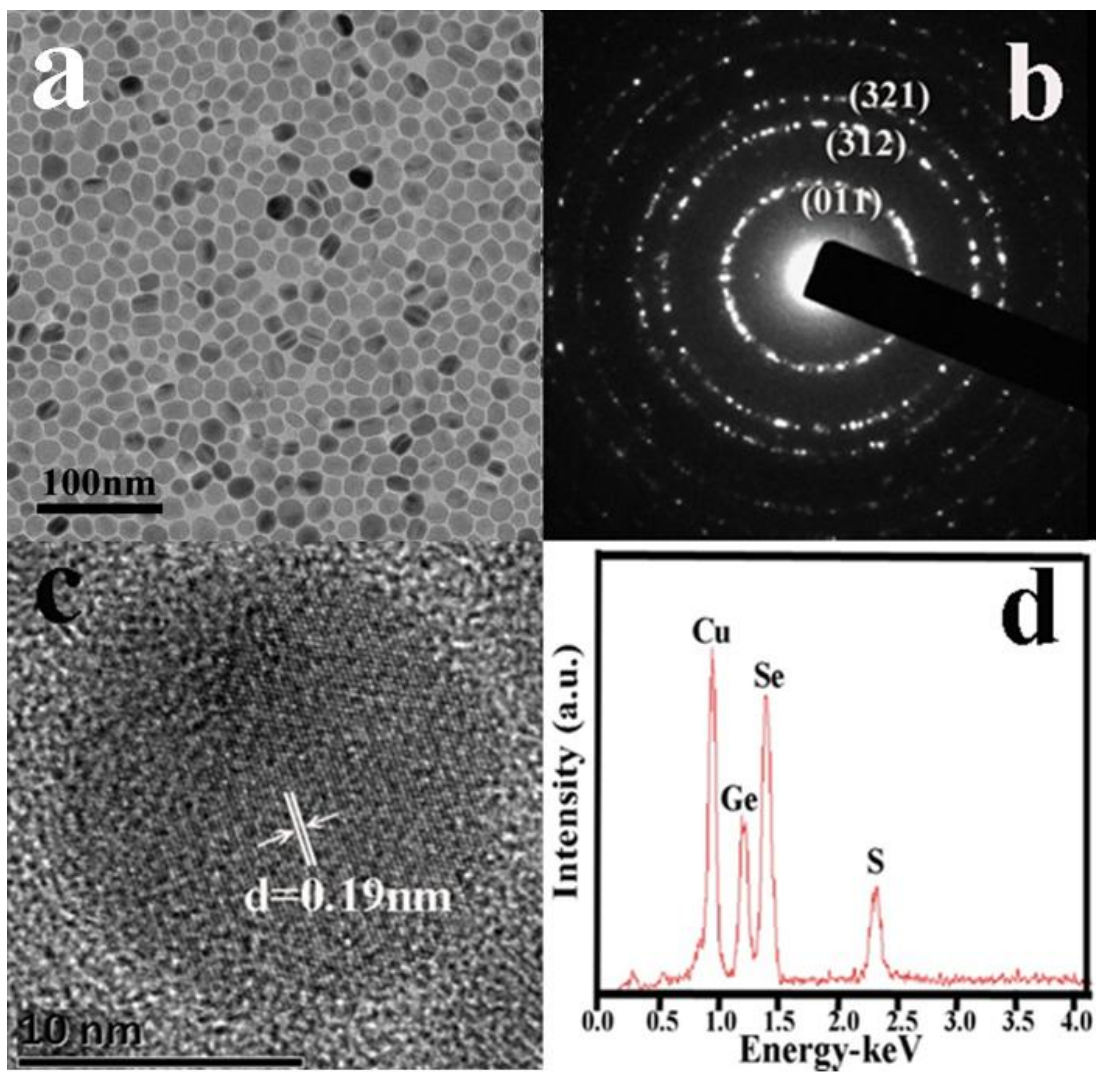
**Cyclic Voltammetry.** Cyclic voltammetry was recorded on a CHI760C electrochemical workstation (CH Instruments), using 5 mm glassy carbon as the working electrode, a Pt wire as the counter electrode, a Ag/Ag<sup>+</sup> as the reference electrode and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) dissolved in acetonitrile (0.1 M) as supporting electrolyte, respectively. The nanoparticles were purified

thoroughly and the capping ligands were replaced by pyridine before each measurement. The sample was prepared by drop-casting a drop of nanoparticles/hexane solution onto the working electrode. This film was dried under vacuum for 5 minutes. The scan rate was set at 30 mV/s, and the electrolyte solutions were thoroughly deoxygenated by bubbling with high purity nitrogen for 15 min before measurement and a nitrogen atmosphere was maintained over the solutions.

**Transient photocurrent measurement.** Transient photocurrent measurements were conducted in a quartz cell under nitrogen in aqueous 0.01 M  $\text{Eu}(\text{NO}_3)_3$  /0.1 M KCl using 472 nm LED illumination with a Ag wire pseudo-reference electrode and a Pt wire counter electrode. The nanocrystal film was spun-cast onto ITO and treated with hydrazine. The photoelectrochemical response of the  $\text{Cu}_2\text{Ge}(\text{S}_{3-x}\text{Se}_x)$  nanocrystal films was assessed without bias potential under 10 s on/off chopped illumination.

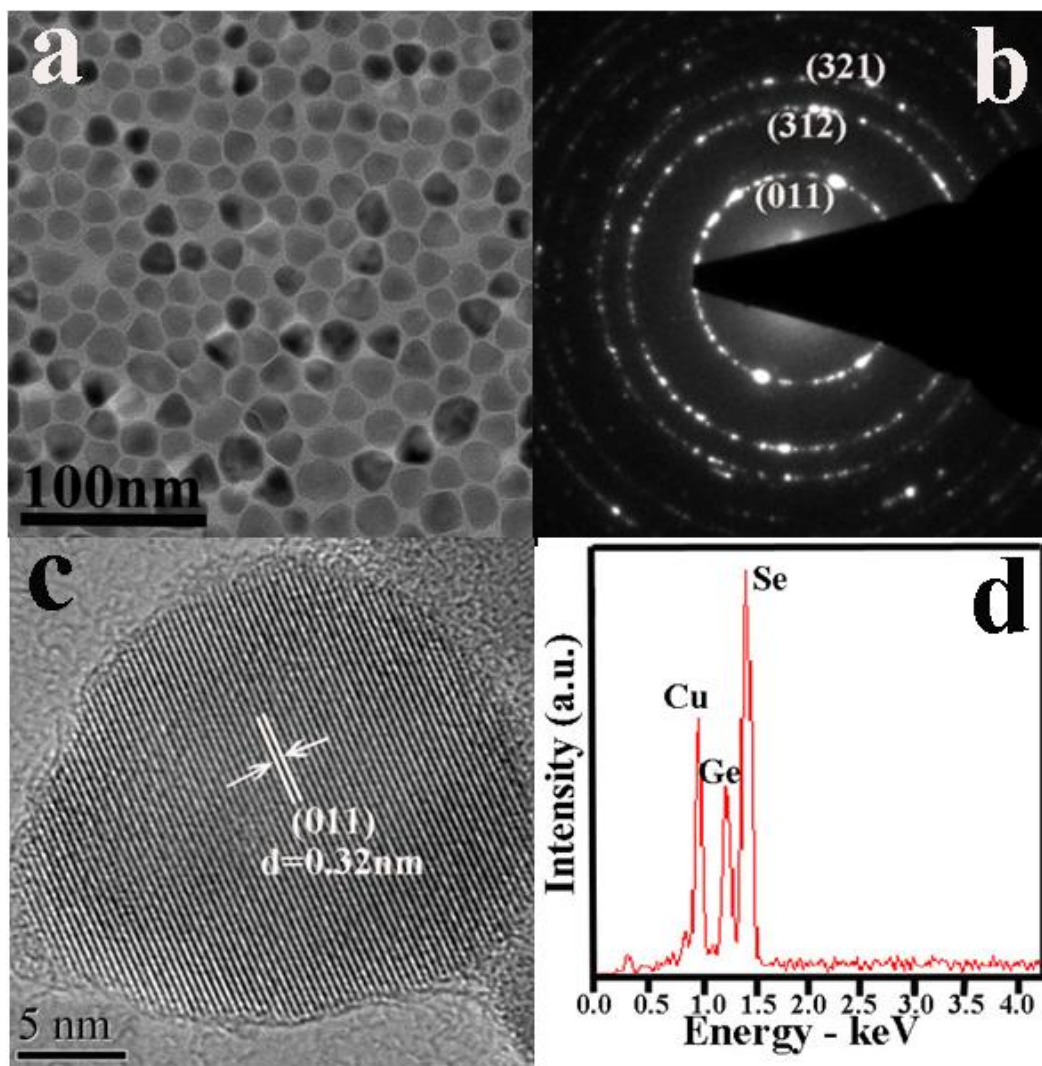


**Figure S1.** (a) Low-magnification TEM, (b) SAED, (c) HRTEM, and (d) EDX spectrum for the  $\text{Cu}_2\text{Ge}(\text{S}_2\text{Se})$  NCs.

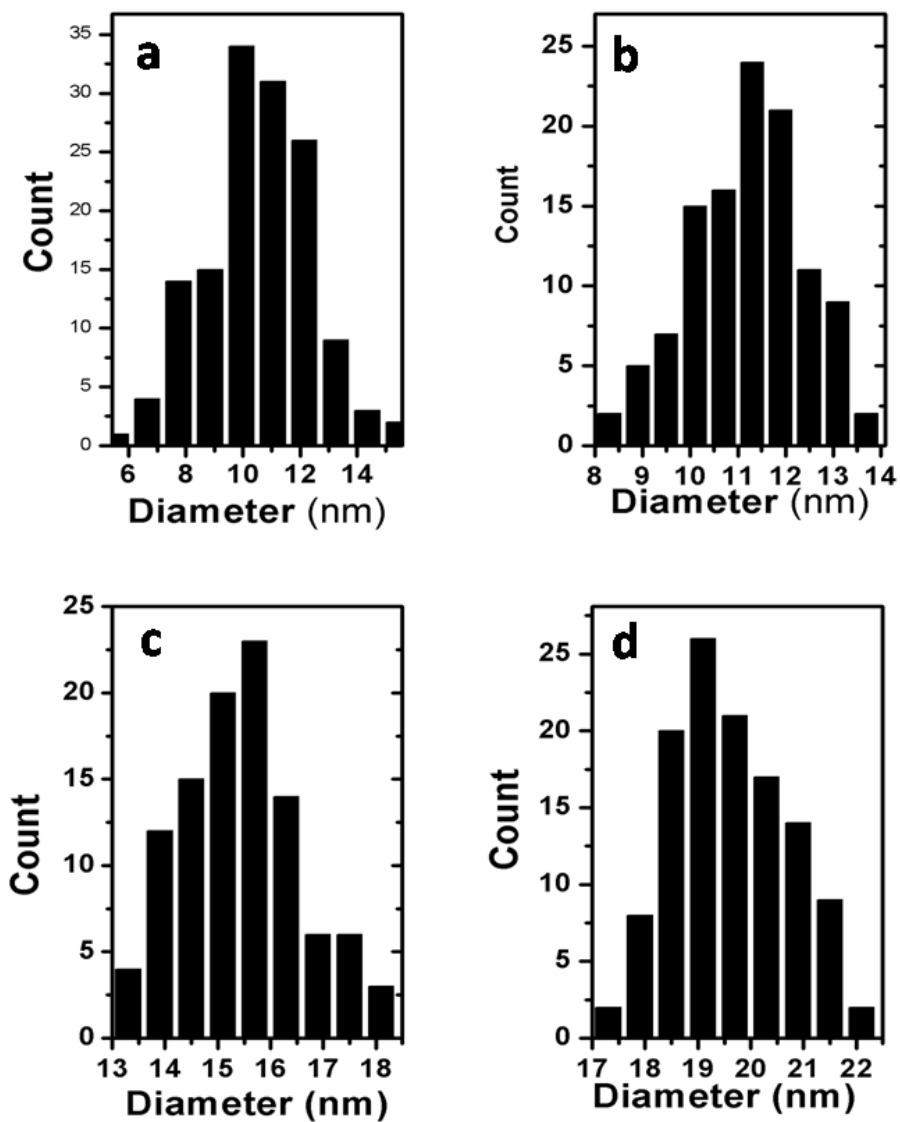


**Figure S2.** (a) Low-magnification TEM, (b) SAED, (c) HRTEM, and (d) EDX spectrum for the  $\text{Cu}_2\text{Ge}(\text{SSe}_2)$  NCs.



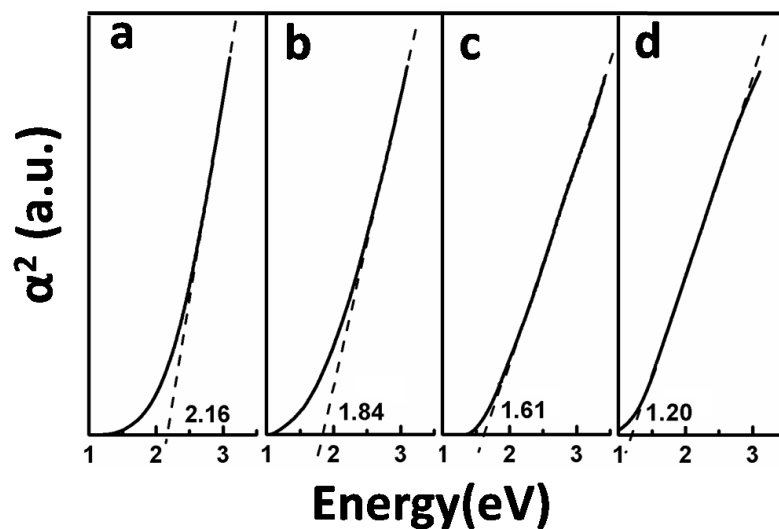


**Figure S3.** (a) Low-magnification TEM, (b) SAED, (c) HRTEM, and (d) EDX spectrum for the  $\text{Cu}_2\text{GeSe}_3$  NCs.

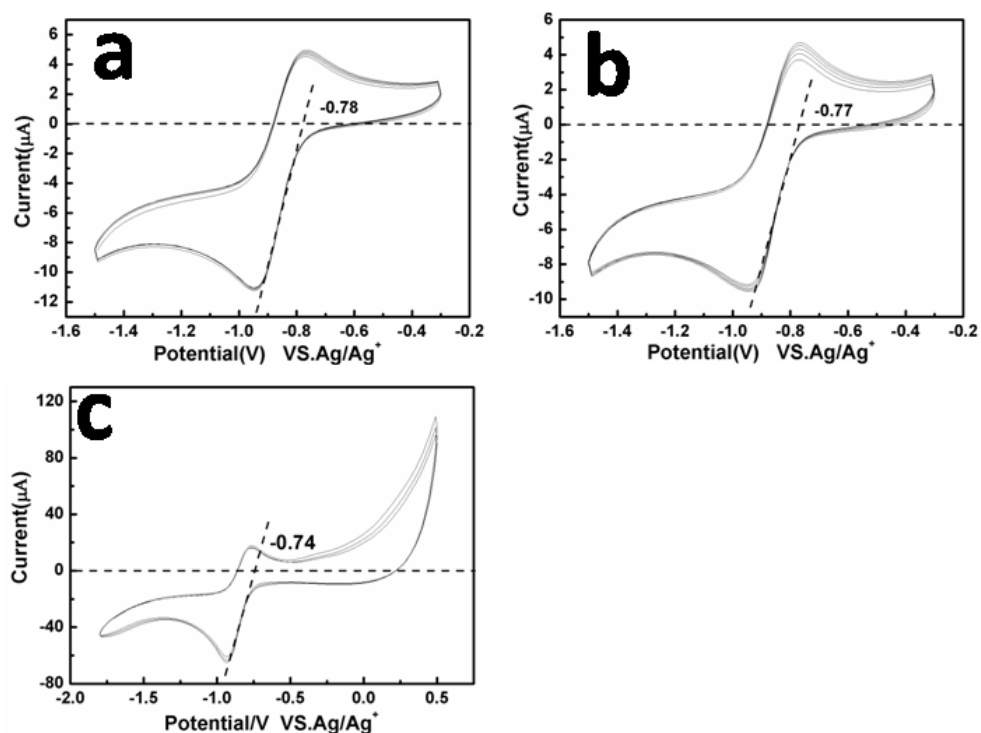


**Figure S4.** Size distributions of (a)  $\text{Cu}_2\text{GeSe}_3$ , (b)  $\text{Cu}_2\text{Ge}(\text{S}_2\text{Se})$ , (c)  $\text{Cu}_2\text{Ge}(\text{SSe}_2)$ , and (d)  $\text{Cu}_2\text{GeSe}_3$  NCs.

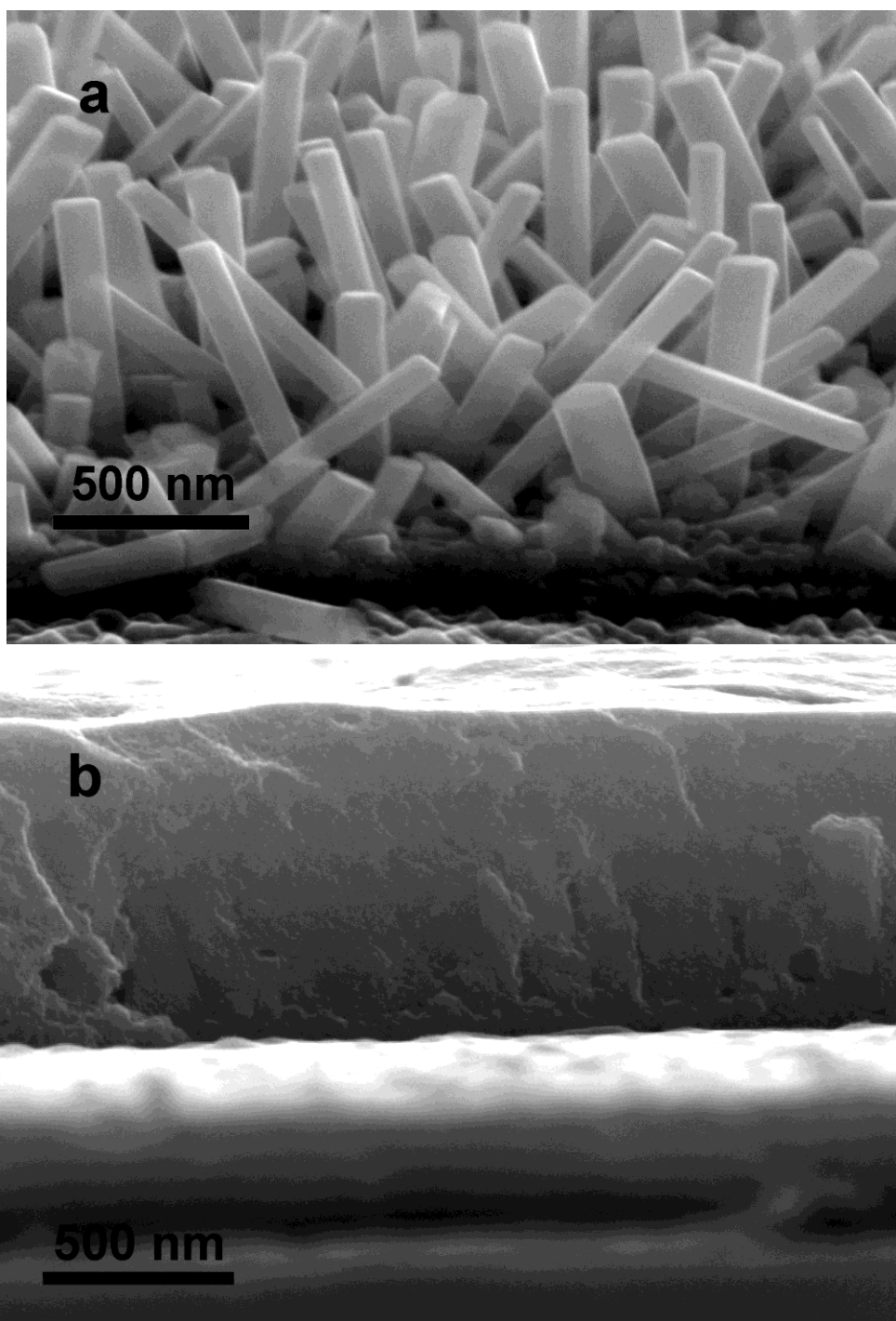




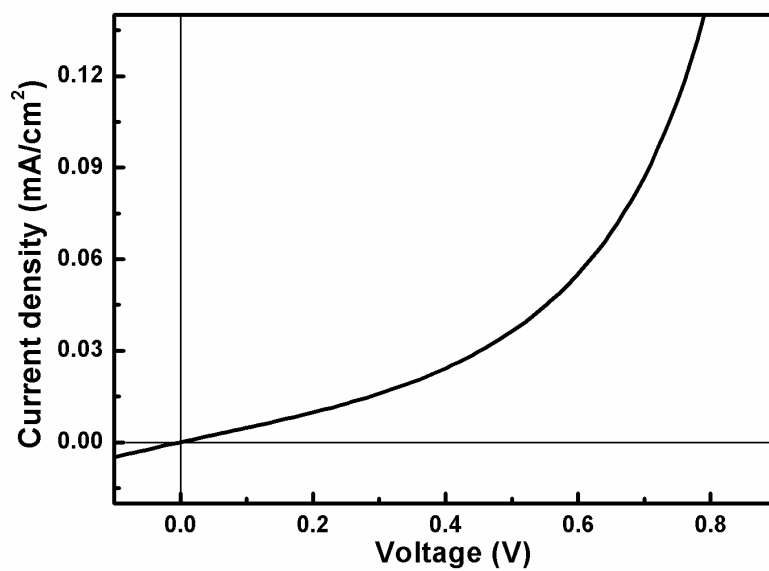
**Figure S5.** Band gaps of (a)  $\text{Cu}_2\text{GeS}_3$ , (b)  $\text{Cu}_2\text{Ge}(\text{S}_2\text{Se})$ , (c)  $\text{Cu}_2\text{Ge}(\text{SSe}_2)$ , and (d)  $\text{Cu}_2\text{GeSe}_3$  NCs derived from UV-vis absorption spectra. The band gap energies ( $E_g$ ) were calculated by plotting the square of the absorption coefficient ( $\alpha$ ) as a function of photon energy ( $h\nu$ ) and extrapolating the linear portion to intercept the x abscissa.



**Figure S6.** Cyclic voltammograms (CV) of (a)  $\text{Cu}_2\text{Ge}(\text{S}_2\text{Se})$ , (b)  $\text{Cu}_2\text{Ge}(\text{SSe}_2)$ , and (c)  $\text{Cu}_2\text{GeSe}_3$  NCs using a  $\text{Ag}/\text{Ag}^+$  reference electrode.



**Figure S7.** The cross-section SEM images of (a) CdS nanorod arrays on FTO substrate, and (b) Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs/CdS NR array solar cell



**Figure S8.** The dark I-V curve of the Cu<sub>2</sub>Ge(S<sub>2</sub>Se) NCs/ CdS NR array solar cell

#### REFERENCES.

- [1] H. Yu, S. Zhang, H. Zhao, G. Will, P. Liu, *Electrochimica Acta* **2009**, *54*, 1319.
- [2] 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.