

Supporting Information:

**Alkylthiol-Enabled Se Powder Dissolution in
Oleylamine at Room Temperature for the Phosphine-Free
Synthesis of Copper-Based Quaternary Selenide
Nanocrystals**

Yi Liu^a, Dong Yao^a, Liang Shen^b, Hao Zhang^{*a}, Xindong Zhang^b, Bai Yang^a

^a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin

University, Changchun 130012, P. R. China. and ^b State Key Laboratory on Integrated

Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun

130012, P. R. China.

Experimental

Materials. Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), zinc chloride (ZnCl_2 , 98%), tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%), cadmium acetate dehydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 99.5%), toluene (99.5%), chloroform (99%), ethanol (99.5%) were purchased from Beijing Chemical Reagent Ltd., China. Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 98%), indium(III) acetylacetonate ($\text{In}(\text{acac})_3$, 98%), gallium(III) acetylacetonate ($\text{Ga}(\text{acac})_3$, 99.99%) was purchased from Alfa Aesar. Selenium powder (100 mesh, 99.5%), hexadecanethiol (HT, 90%), oleylamine (OLA, technical grade, 70%), oleic acid (OA, technical grade, 90%) and 1-octadecene (ODE, technical grade, 90%) were purchased from Aldrich. Dodecanethiol (DT, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used as received.

Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ NCs. A typical synthetic procedure of $\text{Cu}_2\text{ZnSnSe}_4$ NCs was briefly described below. First, 0.5 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.25 mmol ZnCl_2 , 0.25 mmol $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, 1 ml DT and 10 ml OLA were mixed at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 60 °C under vacuum for 30 min, and then heated to 180 °C. This solution was marked as solution A. 0.5 ml OLA, 0.5 ml DT and 1 mmol Se powder were deposited in a separate flask, cycled between vacuum and nitrogen three times, and then stirred under a nitrogen atmosphere for dissolving Se powder. This solution was labeled as solution B. Once the Se powder was completely dissolved, 1 ml solution B was injected into solution A under vigorous stirring. The solution turned immediately to

dark brown. After injection, the temperature of the reaction mixture dropped to ~170 °C, and it was allowed to recover to the pre-injection temperature. The overall reaction time after injection was 30 min, after which the flask was rapidly cooled to room temperature to achieve NCs products.

Synthesis of Cu(InGa)Se₂ NCs. Following a similar method, except using 0.5 mmol Cu(acac)₂, 0.25 mmol In(acac)₃, 0.25 mmol Ga(acac)₃, and 10 ml ODE rather than 0.5 mmol CuCl₂·2H₂O, 0.25 mmol ZnCl₂, 0.25 mmol SnCl₂·H₂O and 10 ml OLA, Cu(InGa)Se₂ NCs was synthesized.

Synthesis of CdSe NCs. A typical synthetic procedure of CdSe NCs was briefly described below. First, 0.2 mmol Cd(Ac)₂·2H₂O, 0.14 ml OA and 5 ml ODE were mixed at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 120 °C under vacuum for 30 min, and then heated to 250 °C. This solution was marked as solution A. 1 ml OLA, 0.025 ml DT and 0.1 mmol Se powder were deposited in a separate flask, cycled between vacuum and nitrogen three times, and then stirred under a nitrogen atmosphere for dissolving Se powder. This solution was labeled as solution B. Once the Se powder was completely dissolved, 1 ml solution B was injected into solution A under vigorous stirring. The solution turned immediately to dark brown. After injection, the temperature of the reaction mixture dropped to ~240 °C, and it was allowed to recover to the pre-injection temperature. The overall reaction time after injection was 10 min, after which the flask was rapidly cooled to room temperature to achieve NCs products.

Purification. The NCs products were purified by precipitation with ethanol, and

followed by centrifugation at 6000 rpm for 5 min. After such a washing step, the supernatant, containing unreacted precursor and byproducts, was discarded. The NCs were in the precipitate. The precipitate was then redispersed in 10 ml chloroform. This process was repeated for a total of three times. The final precipitate was redispersed in chloroform or toluene to form a stable ink solution.

Device fabrication. A photoresponse device was fabricated from the as-prepared $\text{Cu}_2\text{ZnSnSe}_4$ NCs following the device configuration shown in Figure 3. The film was fabricated by spin-casting (2000 rpm for 30 s) the concentrated toluene solution of $\text{Cu}_2\text{ZnSnSe}_4$ NCs onto the quartz substrate and annealed at 150 °C for 30 min. Then the Au film with the thickness of 100 nm was deposited by radio frequency magnetron after a standard photolithography process, and the sputtering power and time were 80 W and 5 min, respectively. The gap width and electrode length were 10 and 500 μm , respectively. The I-V characteristics were recorded using Keithley 2601 Source Meter in the dark and under simulated AM 1.5 illumination (100 mW/cm^2). The scan voltage tuned from 0 to 2 V. All the tests of the devices were processed in the air.

Characterization. ^1H NMR was recorded on a Bruker Ultra Shield 500 MHz spectrometer in CDCl_3 with tetramethylsilane as an internal standard. The gas chromatography-mass spectrometry (GC-MS) analysis of the reaction mixture was carried out using an Agilent 5975 instrument. UV-visible absorption spectra were obtained using a Shimadzu 3600 UV-VIS-NIR spectrophotometer. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. High-resolution

TEM (HRTEM) imaging was implemented by a JEM-2100F electron microscope at 200 kV. X-ray powder diffraction (XRD) investigation was carried out using a Siemens D5005 diffractometer. An energy-dispersive X-ray spectroscopy (EDX) detector coupled with SEM (XL 30 ESEM FEG Scanning Electron Microscope, FEI Company) was used for elemental analysis. Raman spectra were recorded on a LabRam Aramis Raman Microscope system (Horiba-Jobin Yvon) equipped with a multichannel air cooled charge-coupled device detector. Spectra were excited using the 633 nm line of a He Ne narrow Bandwidth laser (Melles Griot). The incident laser beam was focused, and the signal was collected using a 100× objective with NA 0.9. The laser power was approximately 17 mW if no filter was used. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg K α excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV.

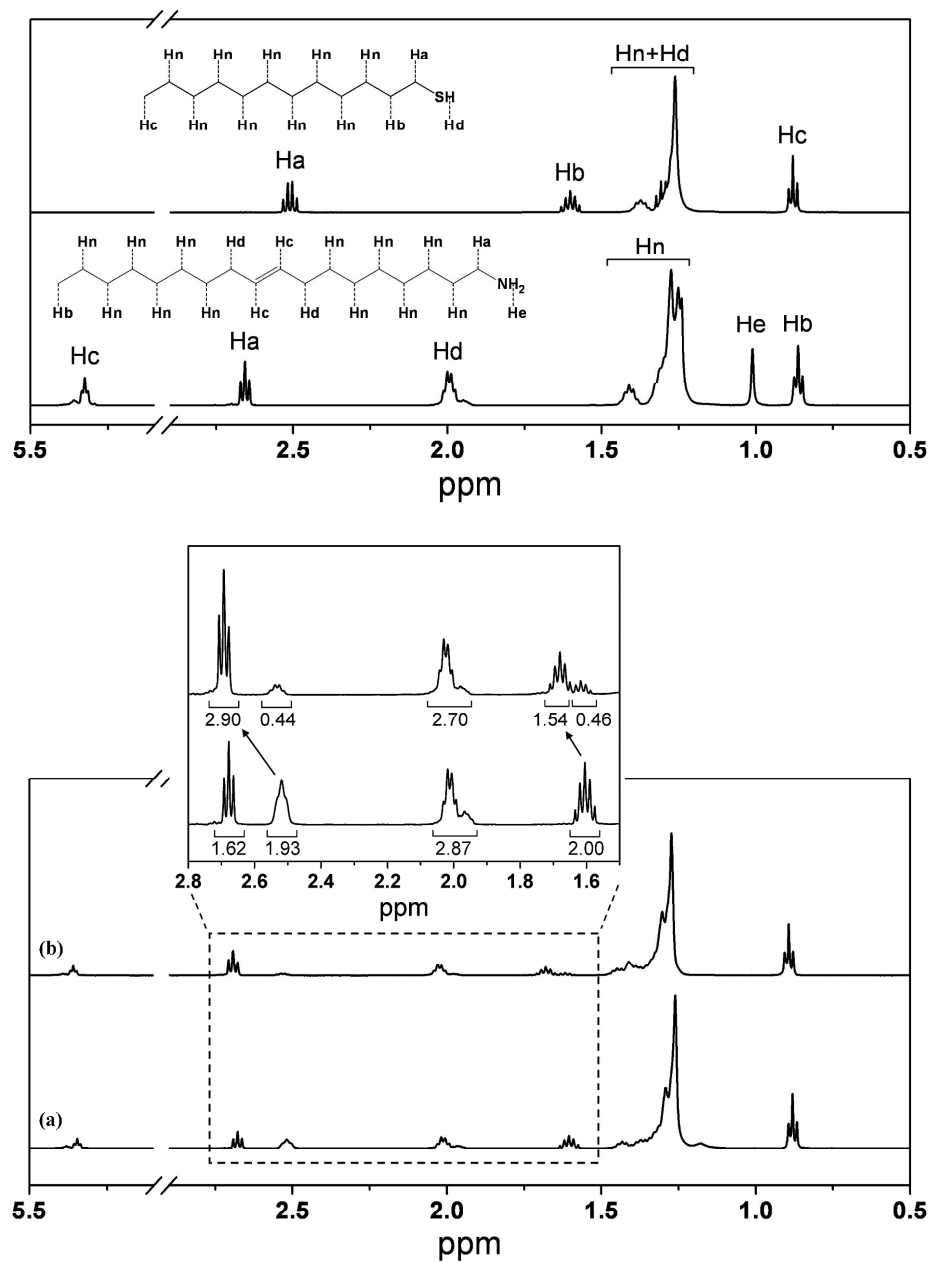


Figure S1 (Upper panel) The ^1H NMR spectra of OLA and DT (CDCl_3). (Lower panel) The ^1H NMR spectra of the mixture of OLA and DT (CDCl_3) before (a) and after (b) the addition of Se. Inset: the enlarged picture of the chemical shift and area of the corresponding peaks, which confirms the formation of didodecyl disulfide (*J. Org. Chem.* 2011, 76, 4173-4177.).

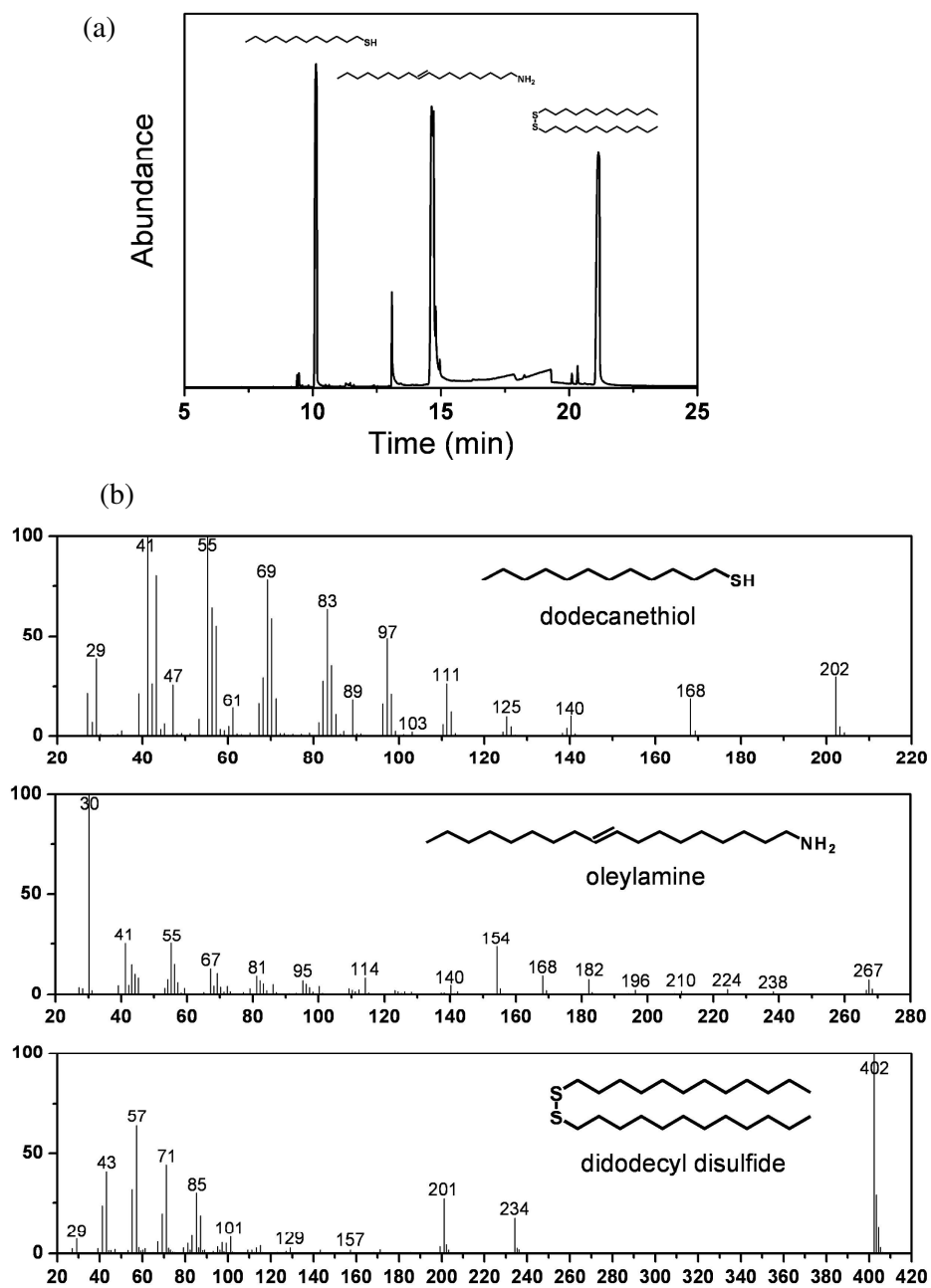


Figure S2 (a) Total ion chromatogram of the reaction mixture of OLA and DT after the addition of Se. (b) Mass spectra of OLA, DT, and didodecyl disulfide in Figure a. The three products are identified.

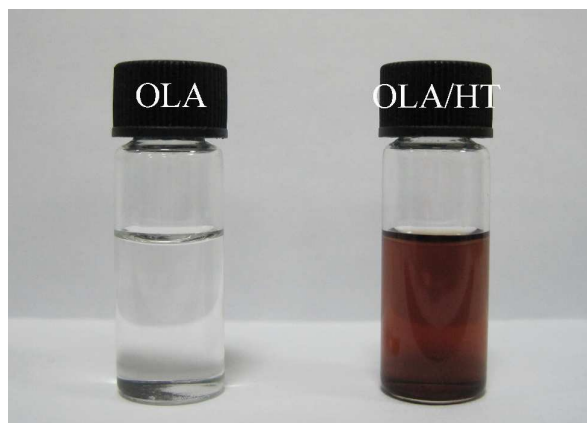


Figure S3 The photograph of 0.0125 mmol Se powder dissolved in 1.5 ml OLA (left) and 1.5 ml OLA/HT mixture with HT-to-Se molar ratio of 4/1 (right).

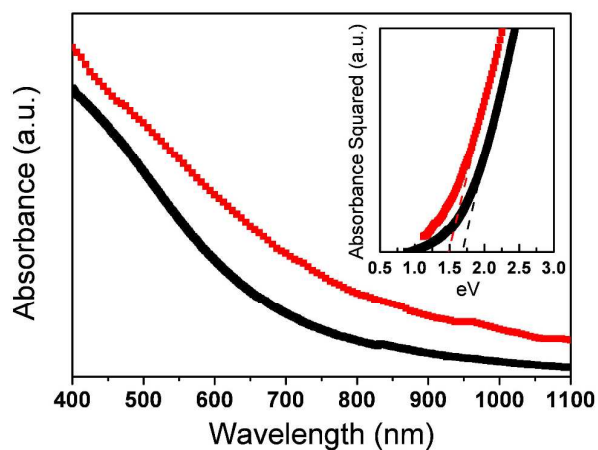


Figure S4 The UV-vis absorption spectra of $\text{Cu}_2\text{ZnSnSe}_4$ NCs synthesized by our method (black) and the $\text{Cu}_2\text{ZnSnSe}_4$ NCs with the average size of 17 nm reported in the precious publication (red, *Materials Letters* 2010, 64, 1424-1426.). It clearly reveals that the large band gap of our NCs is associated with the small size.

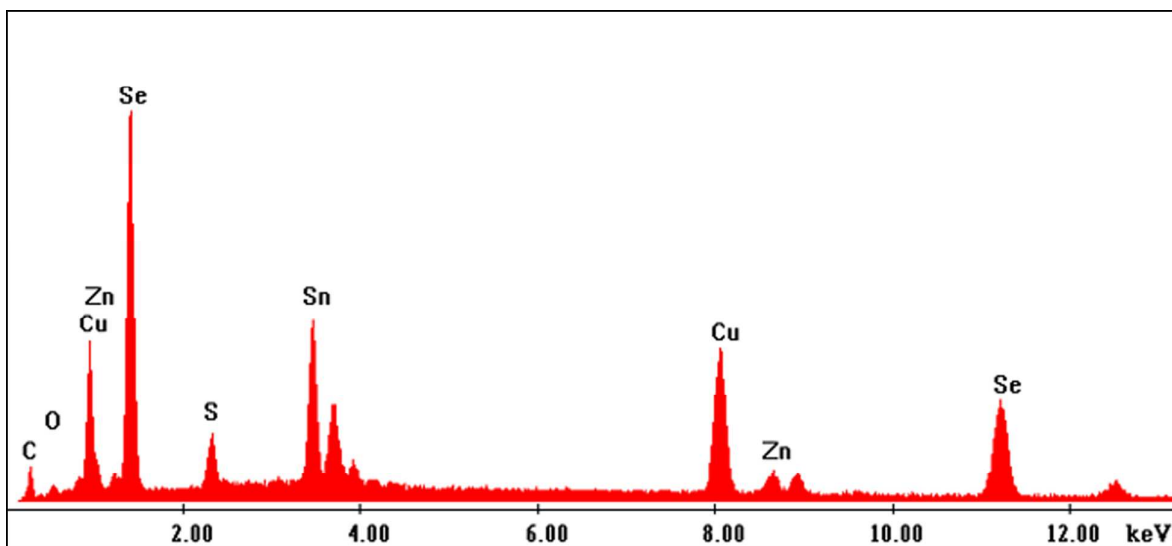


Figure S5 EDX spectrum of the $\text{Cu}_2\text{ZnSnSe}_4$ NCs shown in Figure 2. The relative elemental ratio for Cu/Zn/Sn/Se/S is 2.02/0.37/1.00/3.43/0.59.

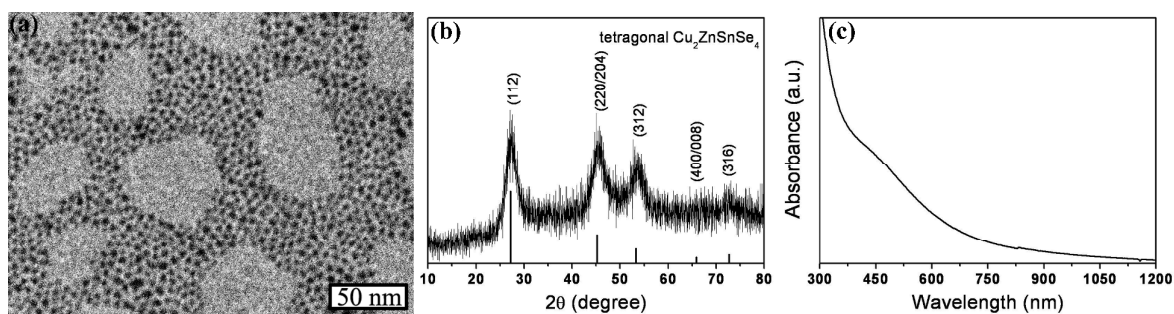


Figure S6 (a) TEM image, (b) XRD pattern and (c) UV-vis absorption spectrum of $\text{Cu}_2\text{ZnSnSe}_4$ NCs. The relative elemental ratio for Cu/Zn/Sn/Se/S is 2.15/0.49/1.00/3.78/0.55. In comparison to Figure 2, we doubled the zinc precursor in the synthesis of NCs.

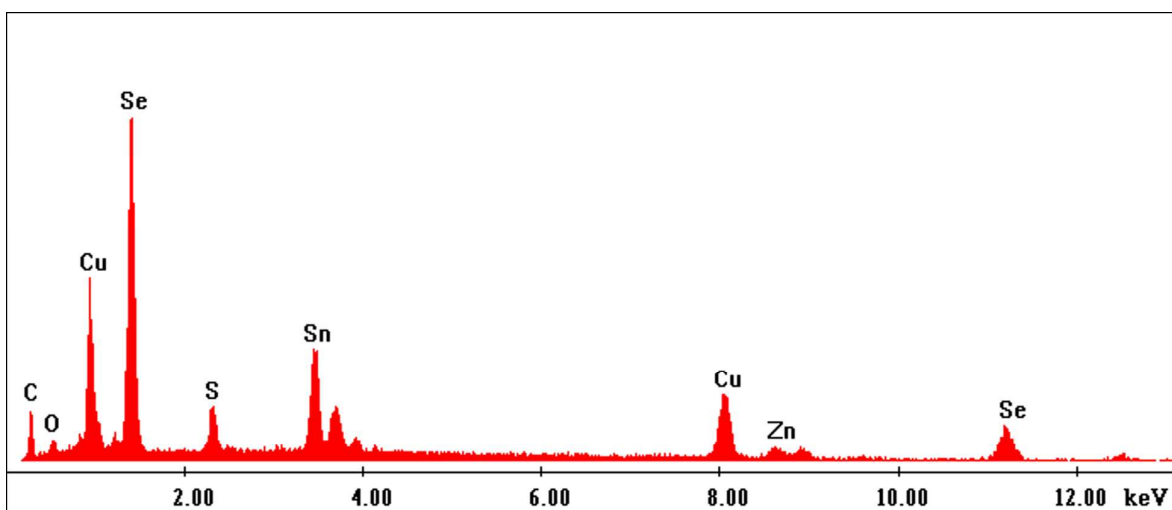


Figure S7 EDX spectrum of the $\text{Cu}_2\text{ZnSnSe}_4$ NCs shown in Figure S6. The relative elemental ratio for Cu/Zn/Sn/Se/S is 2.15/0.49/1.00/3.78/0.55.

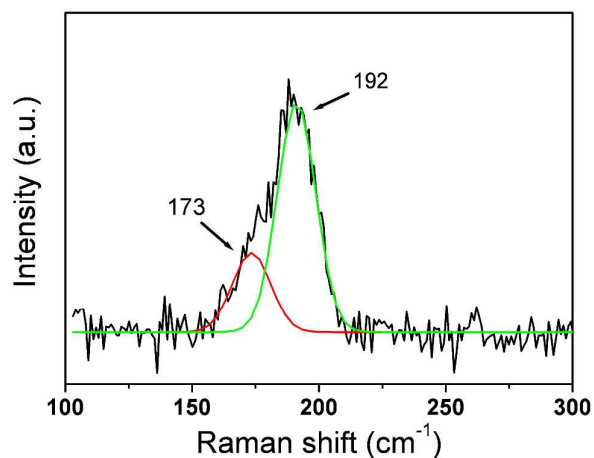


Figure S8 The Raman spectrum and the peak-fit processing of $\text{Cu}_2\text{ZnSnSe}_4$ NCs. Because of the small size of the as-synthesized NCs, the spectrum exhibits a broad peak centered at 190 cm^{-1} rather than the two sharp peaks of bulk $\text{Cu}_2\text{ZnSnSe}_4$ crystal respectively at 173 and 192 cm^{-1} (*Thin Solid Films* 2011, 519, 7386-7389; *phys. stat. sol. (a)* 2008, 205, 167-170.). Nevertheless, the peak-fit processing confirms that the NCs are mainly quaternary $\text{Cu}_2\text{ZnSnSe}_4$, though we can not arbitrarily exclude the coexistence of a small amount of Cu_2SnSe_3 (characteristic peak at 180 cm^{-1}).

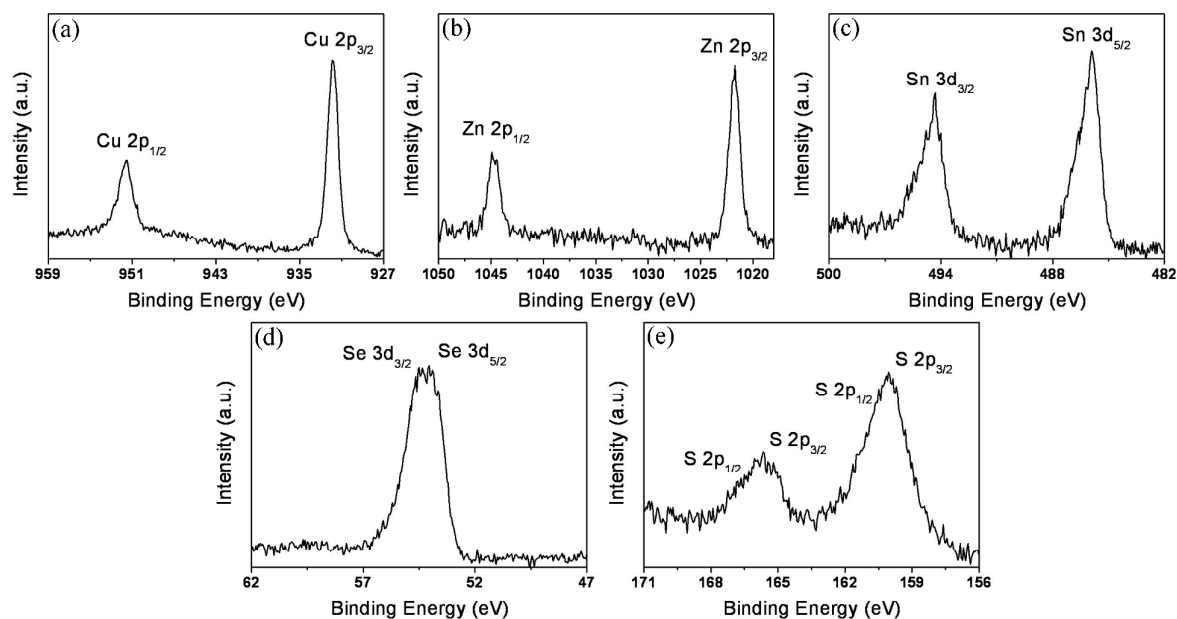


Figure S9 XPS Cu2p, Zn2p, Sn3d, Se3d and S2p spectra of the $\text{Cu}_2\text{ZnSnSe}_4$ NCs.

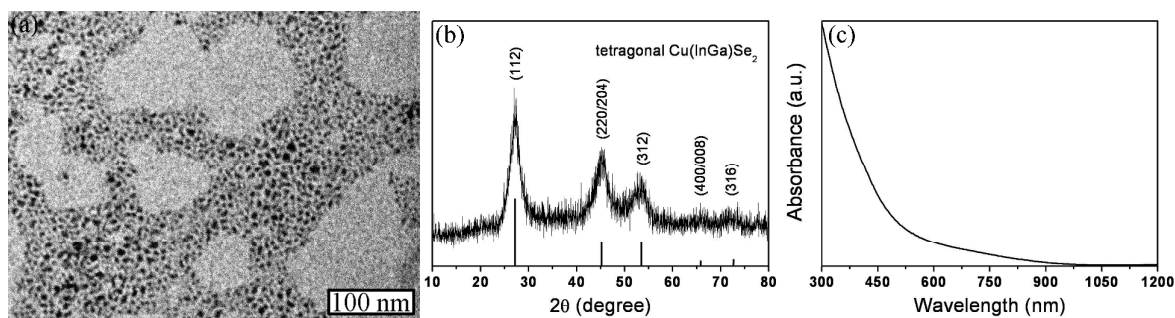


Figure S10 (a) TEM image, (b) XRD pattern and (c) UV-vis absorption spectrum of Cu(InGa)Se_2 NCs. The relative elemental ratio for Cu/In/Ga/Se/S is 2.10/1.00/0.81/3.74/0.72.

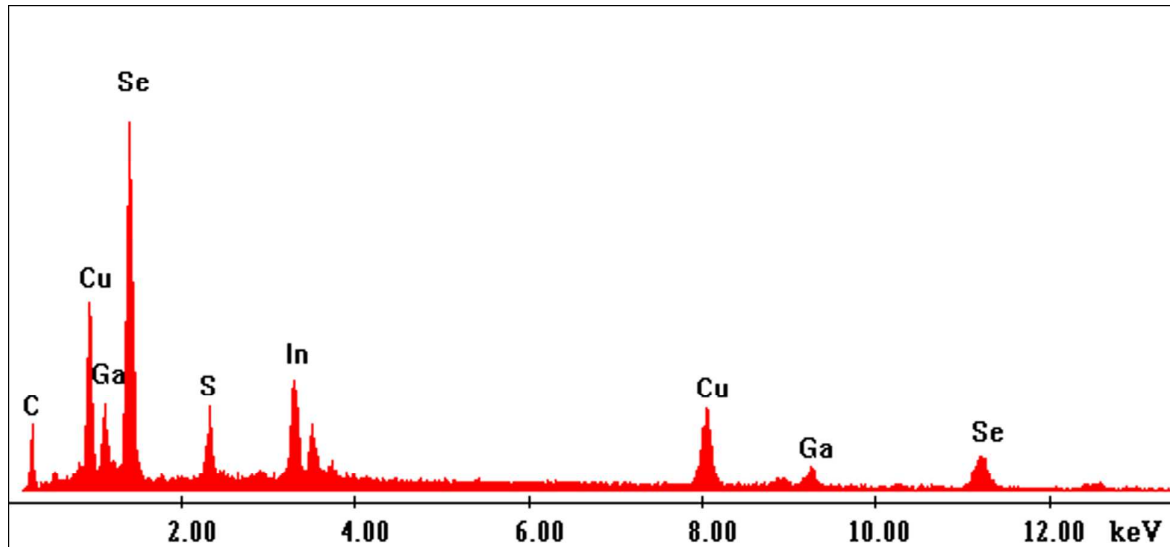


Figure S11 EDX spectrum of the Cu(InGa)Se_2 NCs shown in Figure S10. The relative elemental ratio for Cu/In/Ga/Se/S is 2.10/1.00/0.81/3.74/0.72.

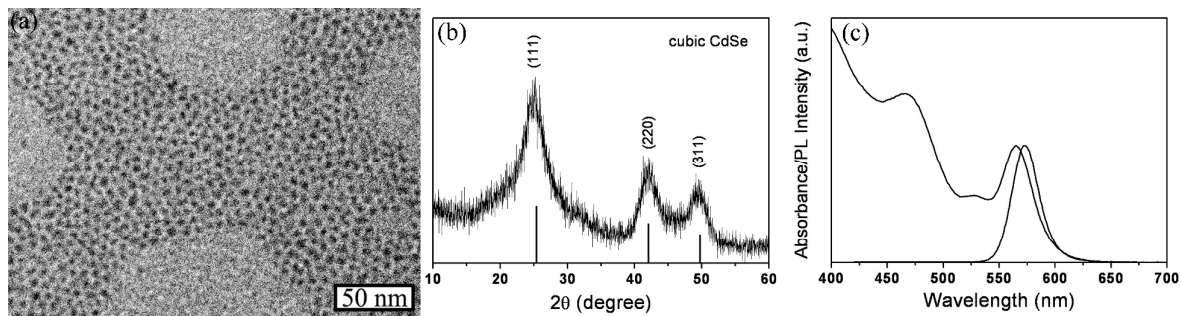


Figure S12 (a) TEM image, (b) XRD pattern and (c) UV-vis absorption and photoluminescence spectra of CdSe NCs.