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Supporting Information:

Phosphine-free synthesis of heavy Co^{2+}- and Fe^{2+}-doped Cu_2SnSe_3 nanocrystals by virtue of alkylthiol-assistant Se powder dissolution

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Experimental

Materials. Copper(II) chloride dihydrate ($CuCl_2·2H_2O$, 99%), tin(II) chloride dihydrate ($SnCl_2·2H_2O$, 98%), toluene (99.5%), chloroform (99%), ethanol (99.5%) were purchased from Beijing Chemical Reagent Ltd., China. Cobalt(II) acetylacetonate ($Co(acac)_2$, 98%), Nickel(II) acetylacetonate ($Ni(acac)_2$, 95%) was purchased from Alfa Aesar. Iron(II) acetylacetonate ($Fe(acac)_2$, 98%) was purchased from Aladdin Chemistry Co., Ltd. Selenium powder (100 mesh, 99.5%) and oleylamine (OLA, technical grade, 70%) 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 Co^{2+}-, Fe^{2+}- and Ni^{2+}-doped Cu_2SnSe_3 NCs. A typical synthetic procedure of heavy Co^{2+}-doped Cu_2SnSe_3 NCs was briefly described below. First, 0.5 mmol $CuCl_2·2H_2O$, 0.25 mmol $Co(acac)_2$, 0.25 mmol $SnCl_2·H_2O$ and 10 ml OLA were mixed at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 60 ^oC under vacuum for 30 min, and then heated to 180 ^oC. 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 ^oC, 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. The synthesis of Fe^{2+}- and Ni^{2+}-doped Cu_2SnSe_3 NCs followed a similar method, except using 0.25 mmol $Fe(acac)_2$ or $Ni(acac)_2$ instead of 0.25 mmol $Co(acac)_2$.

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 toluene and centrifuged at 5000 rpm for 3 min to remove poorly capped NCs and large aggregates, which settled during centrifugation. To remove excess capping ligands and remaining impurities, the product was again precipitated using ethanol and centrifuged at 6000 rpm for 5 min, then redispersed in toluene or chloroform to form a stable ink solution.

Device fabrication. A photoresponse device was fabricated from the as-synthesized Co^{2+}-doped Cu_2SnSe_3 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 Co^{2+}-doped Cu_2SnSe_3 NCs onto the quartz substrate, then immersed in 1.0 M solution of butylamine in acetonitrile for 30 min and dried at 70 ºC for 30 min. After that, the Au film (around 100 nm) was deposited by thermal evaporation and the gap width was 20 μm. The I-V characteristics were recorded using Keithley 2400 Source Meter in the dark and under simulated AM 1.5 illumination (100 mW/cm^2). The scan voltage tuned from 0 to 0.5 V. All the tests of the devices were processed in the glove box.

Characterization. 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 on a Rigaku X-ray diffractometer using Cu Kα radiation (λ=1.5418 Å). 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. The 514 nm excitation Raman scattering were from a T64000 (Horiba-JobinYvon) Raman system equipped with a charge coupled device (CCD) detector. Raman spectra were collected at room temperature with the argon ion laser exciting source. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg Kα excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV.

Figure S1. (Up) The feed ratio and actual ratio of various elements in the as-synthesized Co^{2+}-doped Cu_2SnSe_3 NCs. (Down) The corresponding XRD patterns of the as-synthesized Co^{2+}-doped Cu_2SnSe_3 NCs.

	feed ratio (molar ratio Cu/Co/Sn/Se)	actual ratio (molar ratio Cu/Co/Sn/Se)
(a)	**0.50 : 0.10 : 0.25 : 1.00**	**0.29 : 0.06 : 0.11 : 0.54**
(b)	**0.50 : 0.25 : 0.25 : 1.00**	**0.30 : 0.06 : 0.10 : 0.53**
(c)	**0.50 : 0.50 : 0.25 : 1.00**	**0.25 : 0.14 : 0.08 : 0.54**
(d)	**0.50 : 0.50 : 0.50 : 1.00**	**0.30 : 0.05 : 0.11 : 0.54**

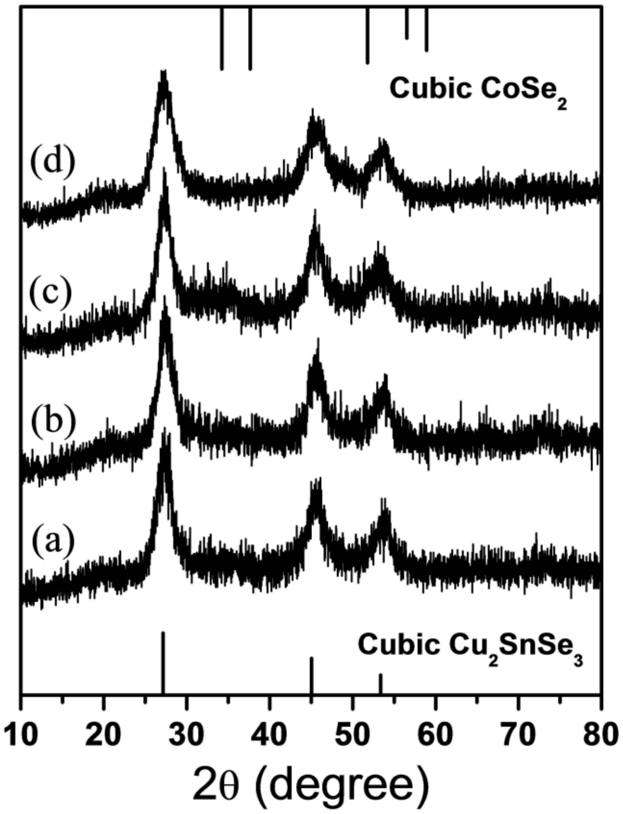

Figure S2. The Raman spectrum of the Co^{2+}-doped Cu_2SnSe_3 NCs shown in Figure 1.

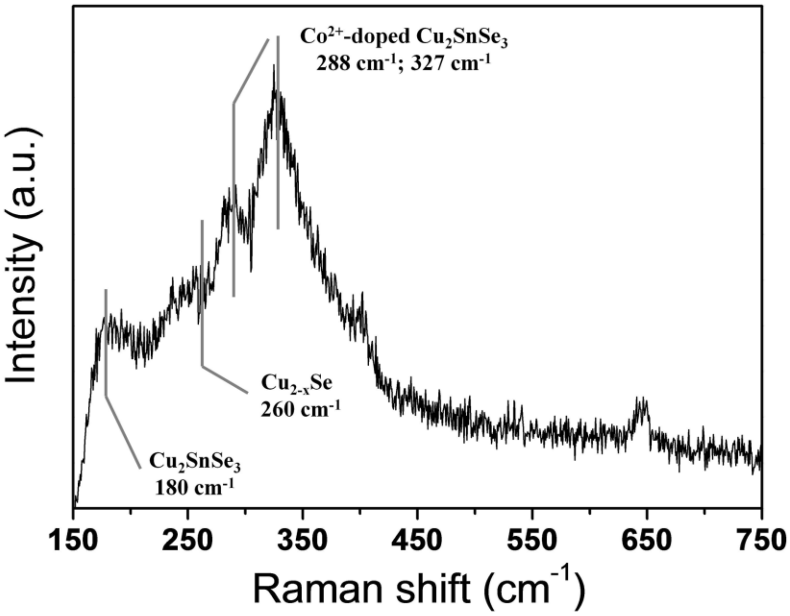

Figure S3. The survey XPS spectrum and S spectrum of the Co^{2+}-doped Cu_2SnSe_3 NCs synthesized with 0.25 mmol Co and 0.25 mmol Sn.

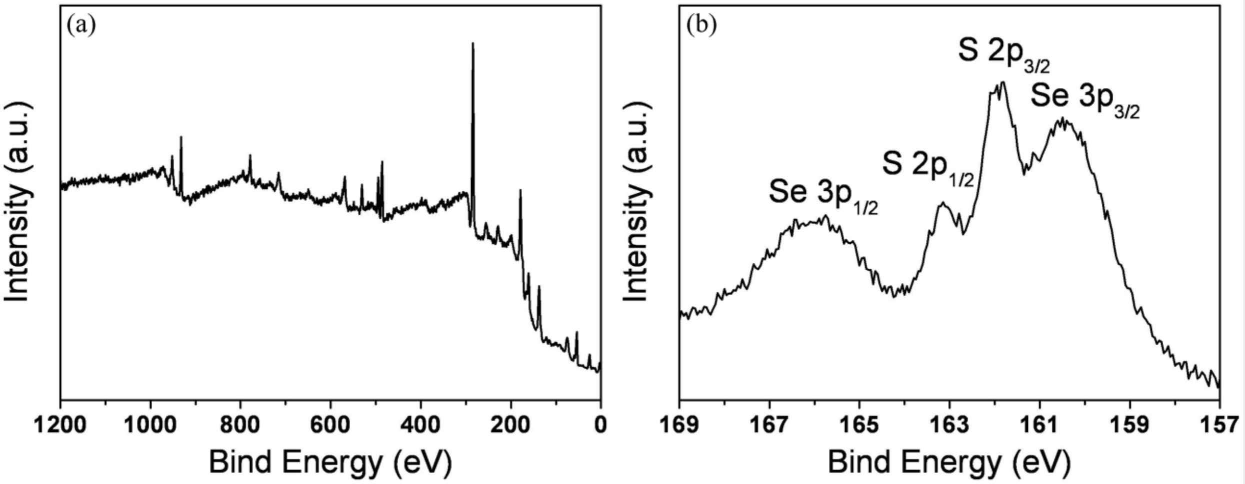

Figure S4. EDX spectrum of the Co^{2+}-doped Cu_2SnSe_3 NCs shown in Figure 1. The relative elemental ratio for Cu/Co/Sn/Se/S is 0.30/0.06/0.10/0.53/0.09.

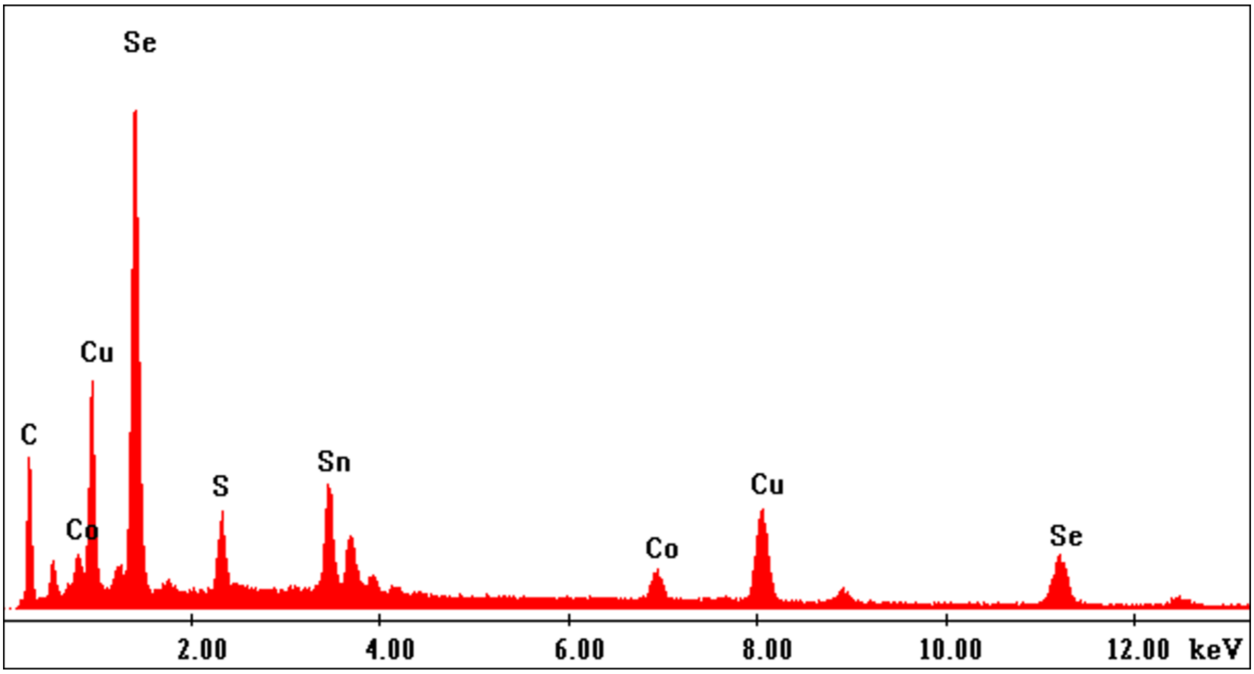

Figure S5. TEM (a), HRTEM (b) images, and size distribution of Co^{2+}-doped Cu_2SnSe_3 NCs synthesized with 0.5 mmol Co and 0.5 mmol Sn. The average diameter of the NCs is 3.4 nm.

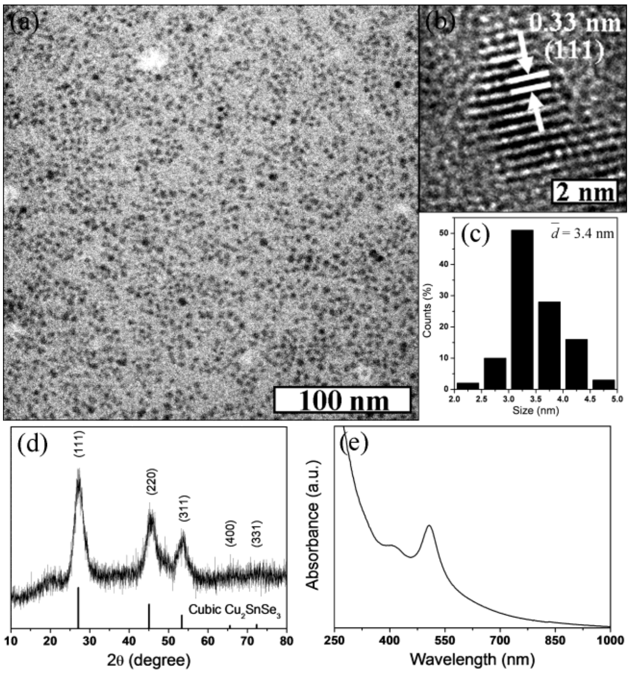

Figure S6. TEM image (a), XRD pattern (b) and UV-vis absorption spectrum of Fe^{2+}-doped Cu_2SnSe_3 NCs.

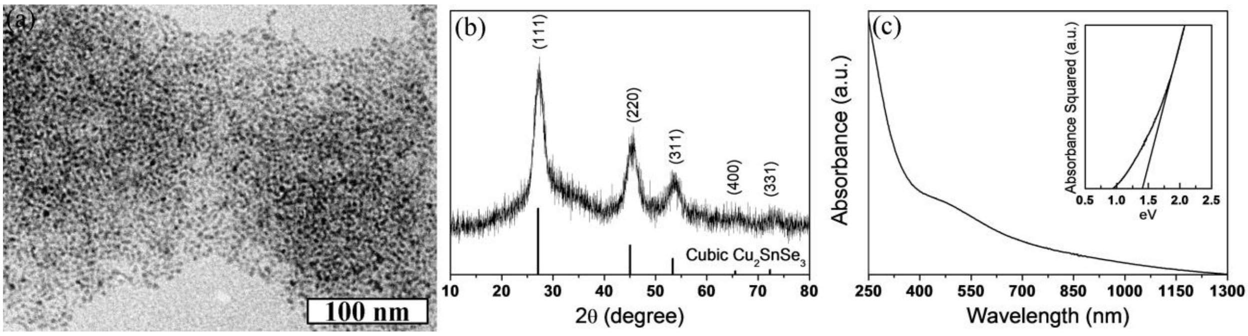

Figure S7. EDX spectrum of the Fe^{2+}-doped Cu_2SnSe_3 NCs shown in Figure S5. The relative elemental ratio for Cu/Fe/Sn/Se/S is 0.30/0.05/0.11/0.54/0.01.

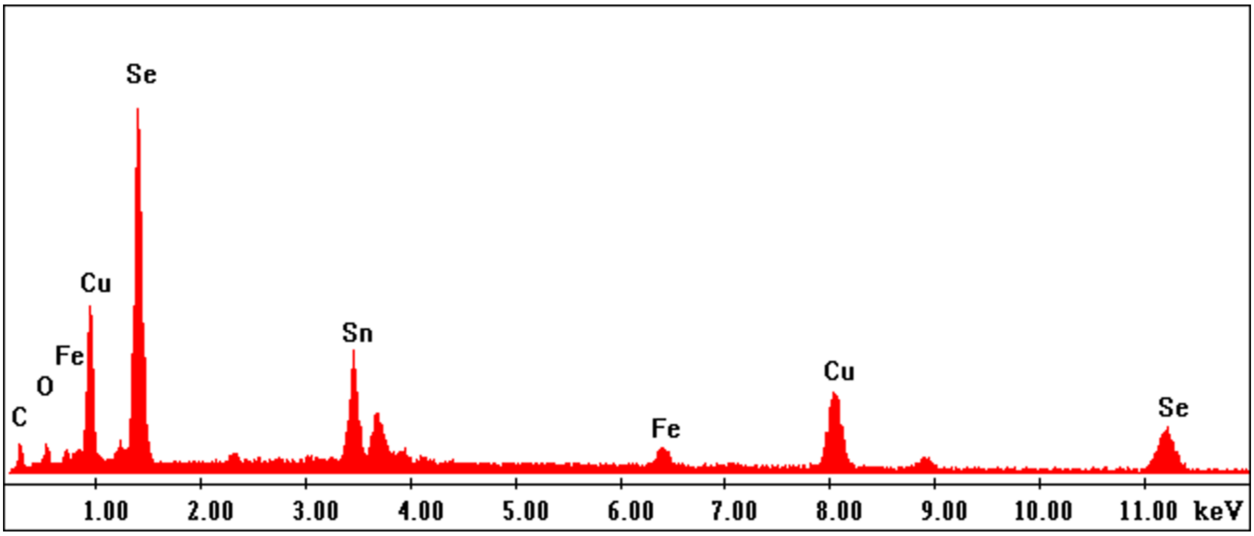

Figure S8. TEM image (a), XRD pattern (b), and UV-vis absorption spectrum of Ni^{2+}-doped Cu_2SnSe_3 NCs.

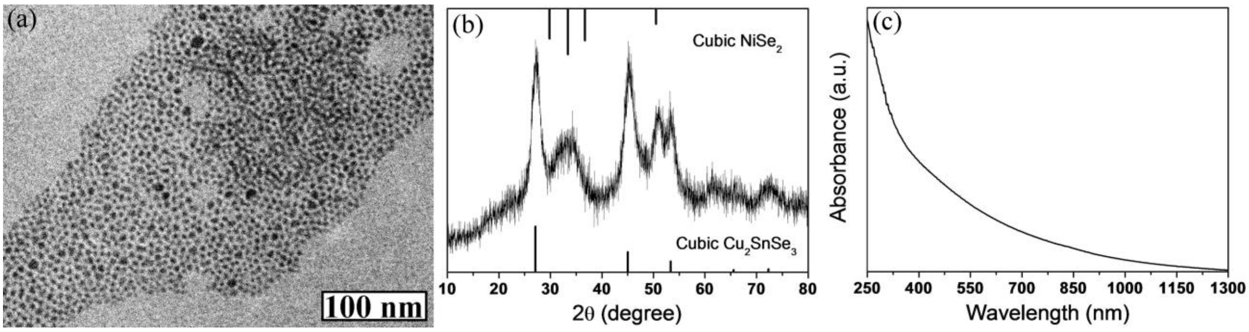

Figure S9. XRD pattern of the quartz substrate.

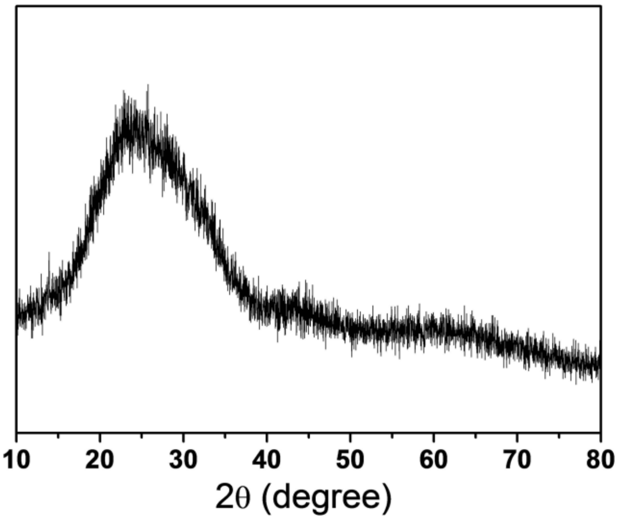

Figure S10. The abs^2 vs eV for the Co^{2+}-doped Cu_2SnSe_3 NCs.