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Communication

## Supporting Information

# Hierarchical CdSe-Gold Hybrid Nanocrystals: Synthesis and Optical Properties

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### 1. Experimental section

#### 1.1. Preparation of Cadmium myristate

Cadmium myristate was synthesized and purified by the reported procedure.<sup>1</sup> Cadmium nitrate tetrahydrate (1.542 g, 5 mmol) was dissolved in anhydrous methanol (50 mL). A sodium myristate solution was prepared by dissolving sodium hydroxide (0.600 g, 15 mmol) and myristic acid (3.420 g, 15 mmol) in anhydrous methanol (500 mL). Then the cadmium-nitrate solution was added dropwise into the sodium-myristate solution with vigorous stirring. After the addition of all the cadmium-nitrate solution, the reaction was continued for 30 min for complete reaction. The resulting white precipitate was washed with methanol three times to remove unreacted precursors, and then dried at 65 °C under vacuum overnight.

#### 1.2. Preparation of 8 nm ZB CdSe NCs.

CdSe NCs about 8 nm were synthesized and purified by the reported procedure.<sup>2</sup> In brief, Se powder (1mmol, 0.0784g) and 15 mL of ODE were added into a flask, and then heated to 280 °C for 30 min under N<sub>2</sub> to get a transparent solution. 5 mL oleic acid and 0.266g Cd(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O were mixed and heated to 120 °C under N<sub>2</sub> to get a clear solution. The Cd precursor was quickly injected into the Se precursor solution by a syringe. The temperature of the reactive system was kept at 260 °C for 40 min. The reaction was terminated by cooling down to room temperature. The resultant CdSe NCs were precipitated from the reaction solution with ethanol and collected by centrifugation. CdSe NCs about 8 nm were obtained and dispersed in toluene for further use.

#### 1.3. Preparation of Au<sup>(I)</sup> stock solution

Synthesis of the organometallic complex Au<sup>(I)</sup>-SR according to the previously reported procedure.<sup>3</sup> The Au<sup>(I)</sup>-SR complex was prepared by using Au<sup>(III)</sup> organometallic compound and alkanethiol. In a typical synthesis, tetraoctylammonium bromide (200 mg) was dissolved in toluene (20 mL). Then, HAuCl<sub>4</sub> aqueous solution (20 mL, 10 mM) was added under magnetic stirring. The upper organic layer turned to wine color after 20 min and was washed three times with distilled water (30 mL once) in a separation funnel. After the separation of the mixture,

dodecyl mercaptan (0.2 mL) was added to the wine colored organic solution. After ultrasonication for about 15 min, the solution became transparent and colorless, indicating the formation of Au<sup>(I)</sup>-SR organometallic complex, which was then used as the Au<sup>(I)</sup> stock solution.

#### 1.4. Preparation of Au NPs

Au nanoparticles (NPs) were synthesized based on the Brust-Schiffrin method.<sup>4-5</sup> Briefly, an aqueous solution (35mL) containing 0.31g HAuCl<sub>4</sub>·4H<sub>2</sub>O is added to vigorously stirred 80 mL toluene solution containing 1.8 g tetraoctylammonium bromide. After 15 min of stirring, the aqueous solution turns to colorless and the toluene solution becomes orange-brown. The organic phase is collected, and 0.313g dodecyl mercaptan was added to the organic phase. After 10 min stirring at room temperature, the toluene solution was cooled down by an ice-water bath. To the vigorously stirred toluene solution, an aqueous solution (25mL) containing 0.378g NaHB<sub>4</sub> was added quickly. The dark toluene solution was stirred at the ice-water bath for 30 min, and then at room temperature for 4 h. The organic phase was collected, and toluene was removed on a rotary evaporator at 45 °C. The dark product was dispersed in 30 mL ethanol and collected using glass filtration frit, then washed with 100 mL of ethanol and 150 mL of acetone, respectively. The product was dried in vacuum oven overnight, and redispersed in toluene for further characterization.

### 2. Characterization and instruments

#### 2.1. TEM measurement

For TEM measurement, CdSe NCs and CdSe-Au hybrid NCs were dispersed in toluene and dropped on carbon-coated copper grids, which were dried in ambient condition overnight. TEM and high-resolution TEM images were collected using a JEM 2100F (JEOL) instrument working at 200 kV, equipped with an EDX analyzer (Oxford TEM200).

#### 2.2. XRD measurement

XRD measurements were performed on a D8 focus Powder X-ray Diffractometer (XRD, Bruker, Cu K $\alpha$  radiation,  $\lambda=1.5406$  Å). The specimens were prepared as followings: about 15 mg of

the purified NCs were dissolved in 0.5 mL of toluene and then dropped on a low-scattering quartz sample-holder and dried in a vacuum oven overnight.

### 2.3. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) measurement

A solution of 1 mL of purified CdSe NCs toluene solution with known absorbance was carefully dried by gentle heating in a vacuum oven, and then the residual was digested by 1 mL of aqua regia (**Caution!** Aqua regia is highly corrosive and extremely dangerous). The digested sample was transferred into a volumetric flask to make an aqueous solution for the ICP-MS measurement. The cadmium concentration was determined using ICP-MS.

### 3. Supplementary results

Table S1 Details for the growth of CdSe-Au hybrid NCs using 3.5 nm, 5 nm and 8 nm ZB CdSe NCs.

Seeds	Sample	CdSe NCs	Au <sup>(I)</sup> complex	Au/Cd ratio
3.5 nm CdSe NCs	1#	6.8 μmol	4.0 μmol	0.59
	2#	6.8 μmol	5.0 μmol	0.73
	3#	6.8 μmol	6.0 μmol	0.88
5 nm CdSe NCs	1#	6.8 μmol	1.37 μmol	0.20
	2#	6.8 μmol	2.72 μmol	0.40
8 nm CdSe NCs	1#	3.8 μmol	0.42 μmol	0.11
	2#	3.8 μmol	1.0 μmol	0.26

### 2.4. Optical limiting performance measurement

Optical limiting properties were studied using 532 nm laser beams produced by a Q-switched frequency-doubled Nd:YAG laser (8ns, 10Hz, Spectra Physics Inc., Quanta-Ray). Samples were prepared by dispersing the nanoparticles in toluene and the solution was placed in the 10 mm cuvette. The laser pulses were focused into the center of the sample with a 30 cm focal length lens. The laser pulse intensity was tuned by neutral density filter, and the laser pulse energies in front of and behind the sample were monitored by optical power meter M1 and M2 (Newport, Model 1916-R).

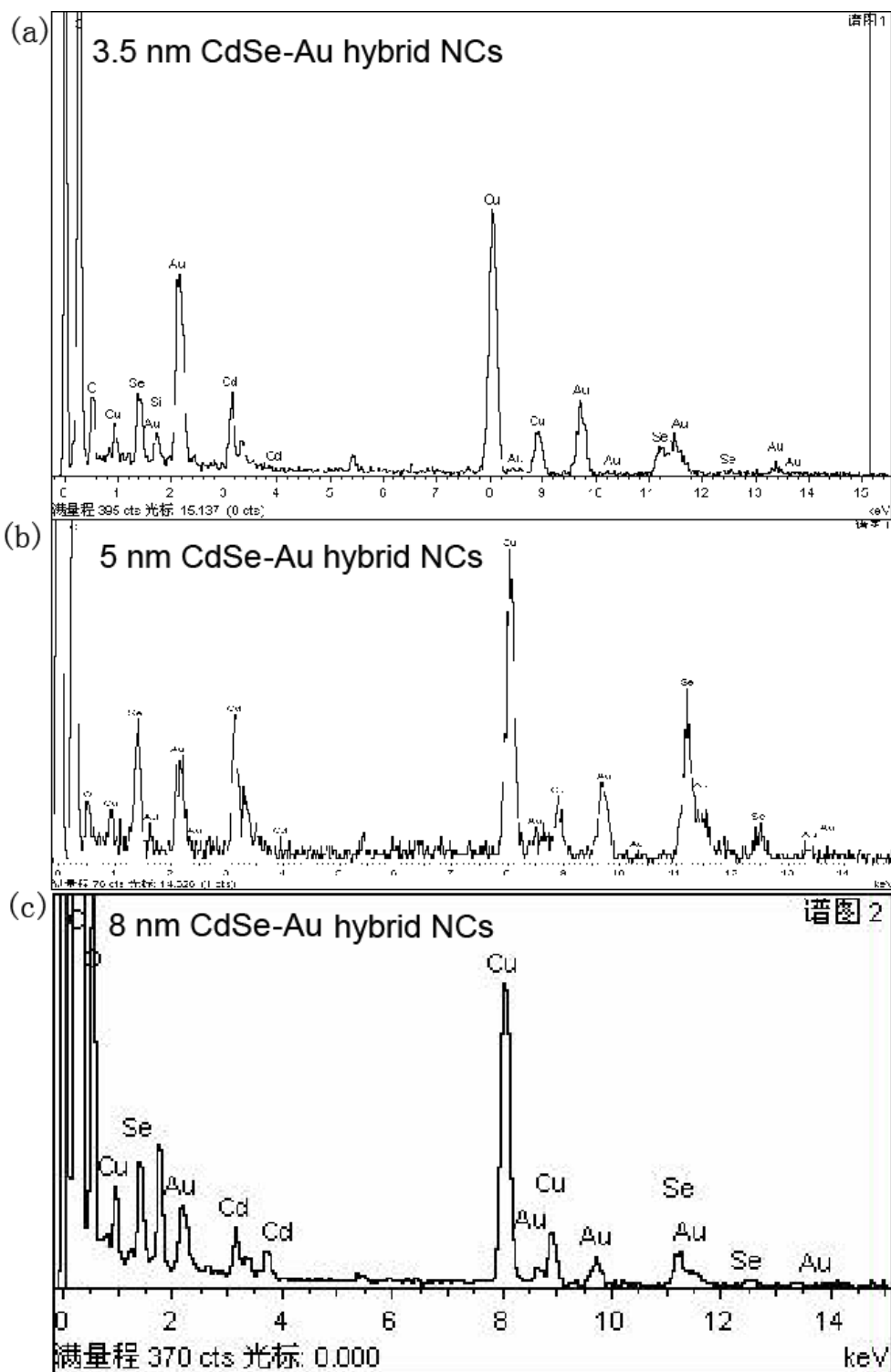


Fig. S1 Energy Dispersive X-ray (EDX) spectrum of (a) 3.5 nm CdSe-Au hybrid NCs (Au/Cd ratio=0.73), (b) 5 nm CdSe-Au hybrid NCs (Au/Cd ratio=0.4), and (c) 8 nm CdSe-Au hybrid NCs (Au/Cd ratio=0.26).

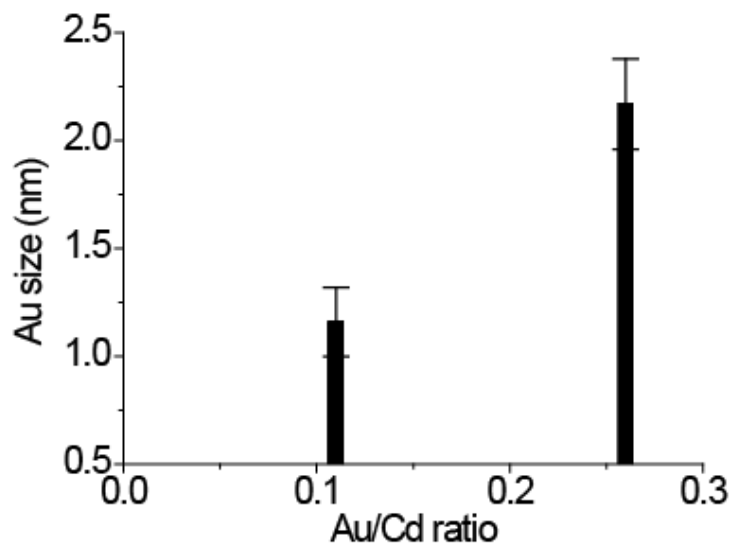


Fig. S2 Average Au size on 8 nm CdSe-Au hybrid NCs with different Au/Cd ratio, the black lines are the standard deviation.

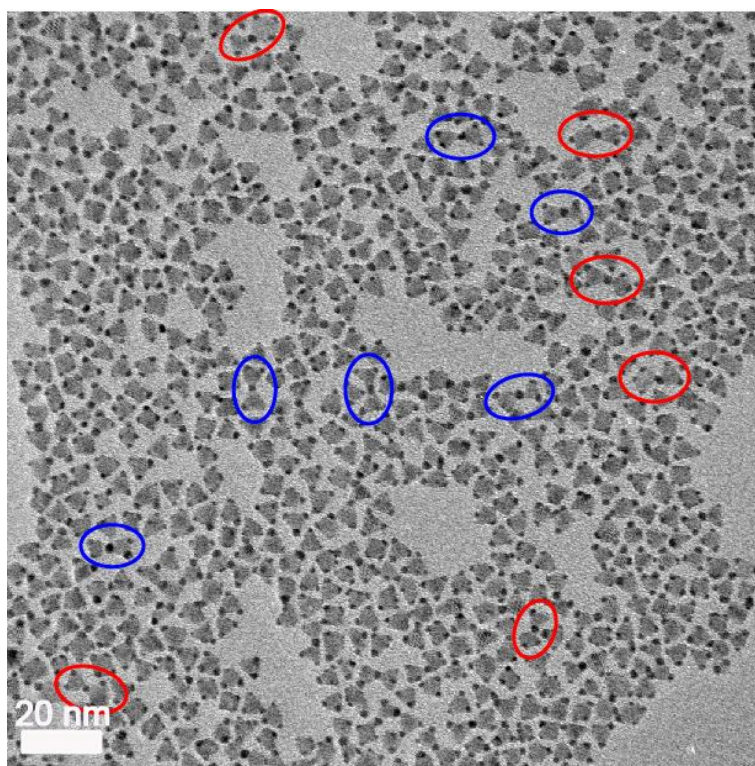
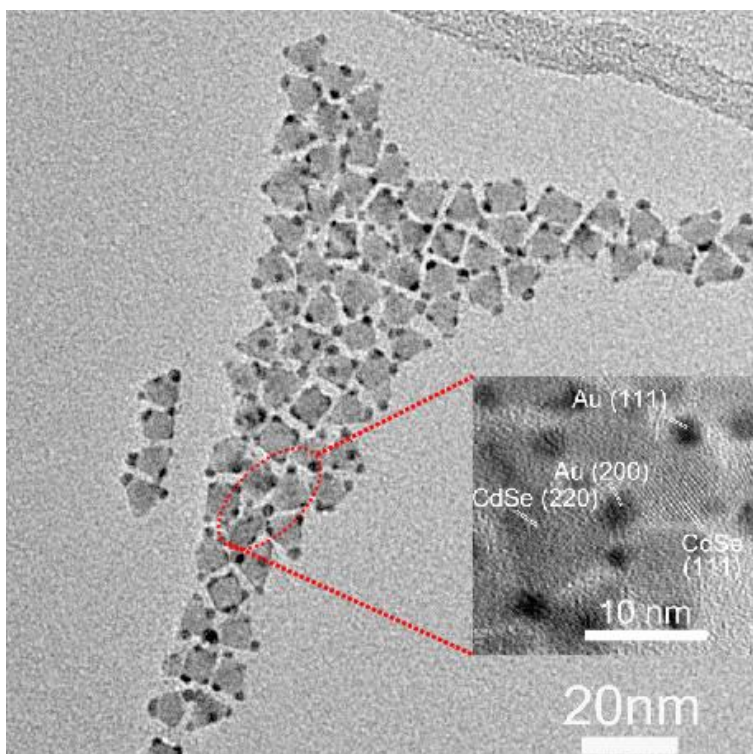
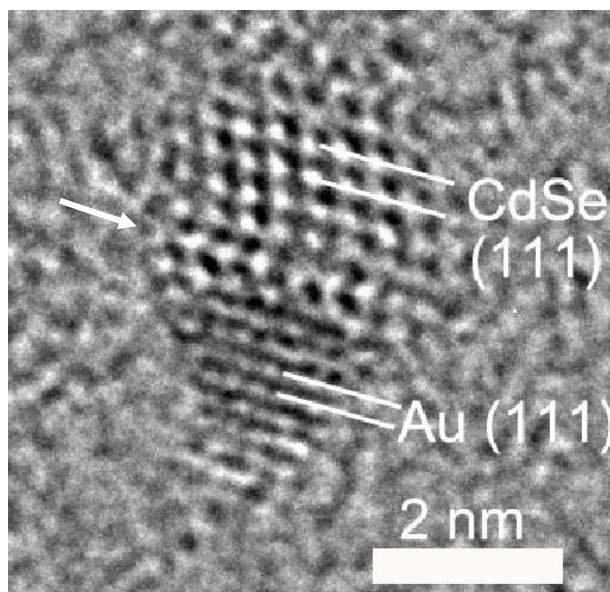


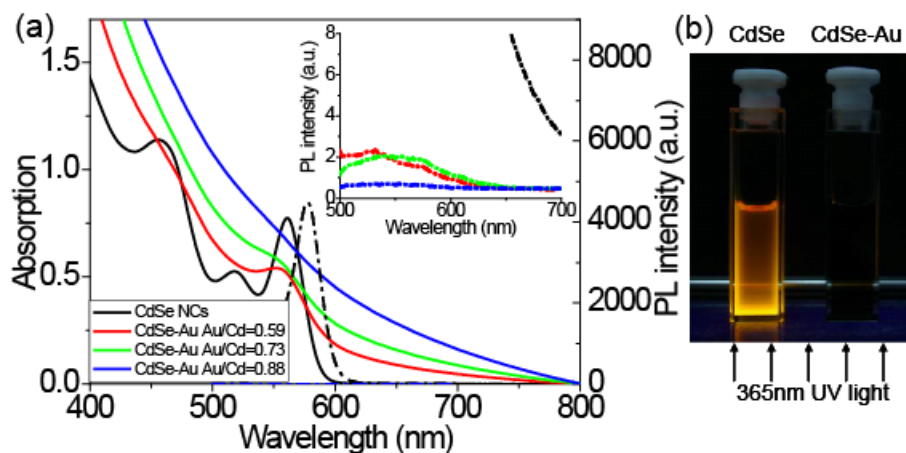
Fig. S3 TEM image of the CdSe-Au hybrid NCs using 5 nm CdSe NCs with Au/Cd ratio=0.4. Red circles point out the cubic-tetrahedral CdSe NCs joined by Au nanoparticles; blue circles point out the tetrahedral-tetrahedral CdSe NCs joined by Au nanoparticles.



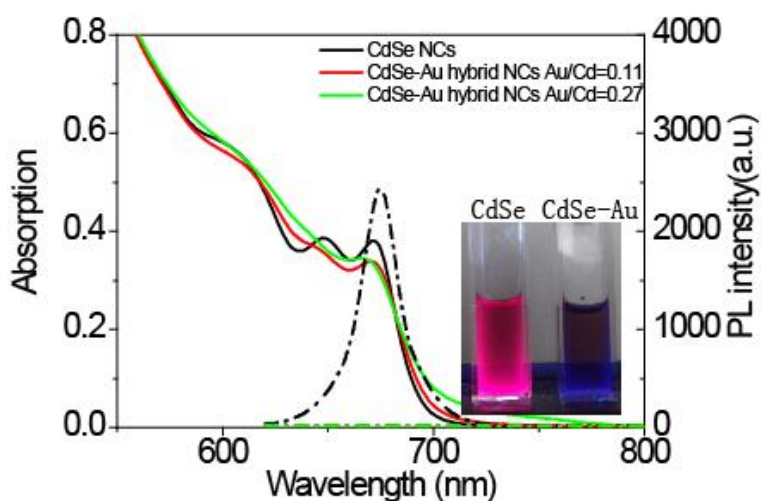
**Fig. S4** TEM image of CdSe-Au hybrid NCs using 8 nm CdSe NCs with Au/Cd ratio=0.26; Red circles point out the tetrahedral-tetrahedral CdSe NCs joined by Au clusters. Inset is the HR-TEM image of the CdSe-Au hybrid NC.



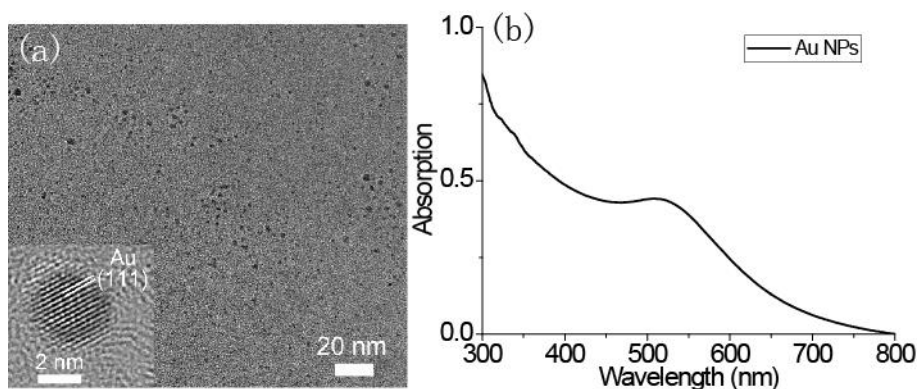
**Fig. S5** HR-TEM image of the CdSe-Au hybrid NC using 3.5nm CdSe NCs with Au/Cd ratio=0.73. The arrow points to the defect in the CdSe NC.



**Fig. S6** (a) UV-Vis absorption (solid) and PL (dash dot) spectra of 3.5 nm CdSe NCs and resultant CdSe-Au hybrid NCs with different Au/Cd ratios. Inset is the magnified PL spectra of CdSe NCs and CdSe-Au hybrid NCs. (b) Photograph of CdSe NCs and CdSe-Au hybrid NCs dispersed in toluene under 365 nm UV lamp irradiation.



**Fig. S7** UV-Vis absorption (solid) and PL (dash dot) spectra of 8 nm CdSe NCs and resultant CdSe-Au hybrid NCs with different Au/Cd ratios. Inset is the photograph of CdSe NCs (left) and CdSe-Au hybrid NCs (right) dispersed in toluene under 365 nm UV lamp irradiation.



**Fig. S8** (a) TEM image of synthesized Au NPs. The inset is the HR-TEM image of Au NP. (b) UV-Vis absorption spectrum of the Au NPs dispersed in toluene.

## Notes and references

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