Electronic Supplementary Information

Composition-Dependent Fluorescence Emission of Ternary Cd-In-S Alloyed Quantum Dots

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Experimental Section

Materials. Technical grade (90%) octadecene (ODE), indium acetate ($In(Ac)_3$, 99.99%), cadmium acetate ($Cd(Ac)_2$), Znic stearate ($Zn(Ste)_2$, 99.99%), oleic acid (OA, 90%), oleylamine (OLA), n-dodecylthiol (DDT, 99.9%), Rhodamine 6G (99%), were purchased from Aldrich. Sulfur powder (S, 99.99%), chloroform (AR), methanol (AR), were purchased from Beijing Chemical Reagent Ltd, China. All chemicals were used without further purification.

Synthesis of CdIS NCs. For a typical synthetic reaction, 0.1 mmol indium acetate, 0.01 mmol cadmium acetate, 0.4 mmol oleic acid (OA), 1 mmol dodecylthiol (DDT) and 4 g of ODE were loaded into a three-neck reaction flask. Then the mixture was heated to 180 °C until the solution became clear. 0.3 mmol sulfur dissolved in ODE was quickly injected into the reaction solution at 220 °C and reacted a fixed time. Finally, the solution was cooled to room temperature and precipitated with excess methanol. The flocculent precipitate was centrifuged at 13000 rpm for 10 min and the supernatant was decanted. Then the precipitation was redispersed in 5 mL of chloroform. The above centrifugation and isolation procedure was repeated three times for purification of the prepared CdIS NCs. The isolated NCs could be redispersed in various nonpolar organic solvents including hexane, toluene, decane, and chloroform. Varying the fraction of Cd in the precursor mixture, series of CdIS NCs with different compositions were prepared.

Synthesis of CdIS/ZnS Core/Shell NCs. The growth solution of CdIS NCs was set at 80 °C. Next, 0.1 mM zinc stearate in ODE/oleylamine (the ratio of ODE/oleylamine is 4/1, in all 0.5 mL) was injected into a reaction flask including CdIS NCs. After that, the temperature was increased to 210 °C for 30 min to allow the growth of the ZnS shell.

Transmission Electron Microscopy (TEM) and High-Resolution TEM (HR-TEM). TEM and HRTEM images were taken on a FEI Tecnai G^2 F20 transmission electron microscope with an acceleration voltage of 200 kV. Carbon-coated copper grids were dipped in the chloroform solution to deposit nanocrystals onto the film. The EDX analyses were performed using carbon-coated nickel grids.

X-ray Powder Diffraction (XRD). XRD patterns were obtained using a Rigaku D/max-2500 X-ray diffractometer with graphite monochromated Cu Kα radiation (λ=1.5418 Å).

Optical Measurements. For optical analyses, these purified CdIS NCs were redispersed in chloroform to an optical density between 0.1-0.5. Then UV-vis spectra were recorded on a Cary 50 (Varian) spectrophotometer. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra were taken using a Perkin Elmer-LS55 luminescence spectrometer. The PL quantum yields of CdIS NCs were determined by comparing the integrated emission of the samples to that of Rhodamine 6G (Rhodamine 6G in ethanol, QY=95%) solutions with the same optical density at the excitation wavelength and similar fluorescence wavelength.

ICP-MS analysis. The purified CdIS NCs were digested with HNO_3. The obtained clear solutions were diluted with distilled water and the content of In^{3+} and Cd^{2+} ions was determined by inductively coupled plasma mass spectroscopy (ICP-OES-MS, Thermo Jarrell-Ash Corporation, Franklin, MA, USA).

Stability of CdIS NCs. The purified NCs were redispersed in chloroform. UV-vis spectra, photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded with the presence of the acids (HCl or H_2SO_4), carboxyls, amines, mercapto-carboxyl, or phosphine oxide ligands, respectively. The acid treatment was performed by adding the acids (HCl or H_2SO_4) or carboxyls directly into the reaction solution or the chloroform solution containing the CdIS NCs at room temperature.

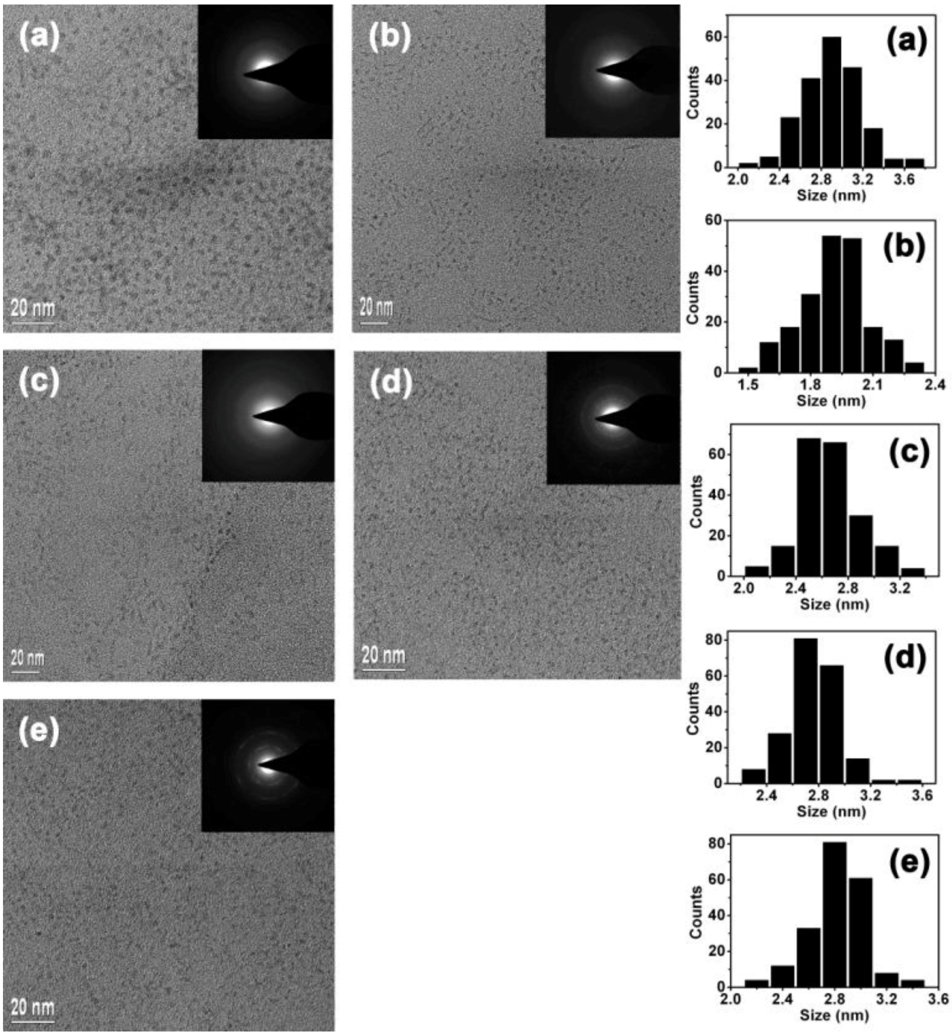

Figure S1. The size distributions of the CdIS NCs with different Cd content: (a) 40%; (b) 20%; (c) 10%; (d) 5%; (e) 1.9%

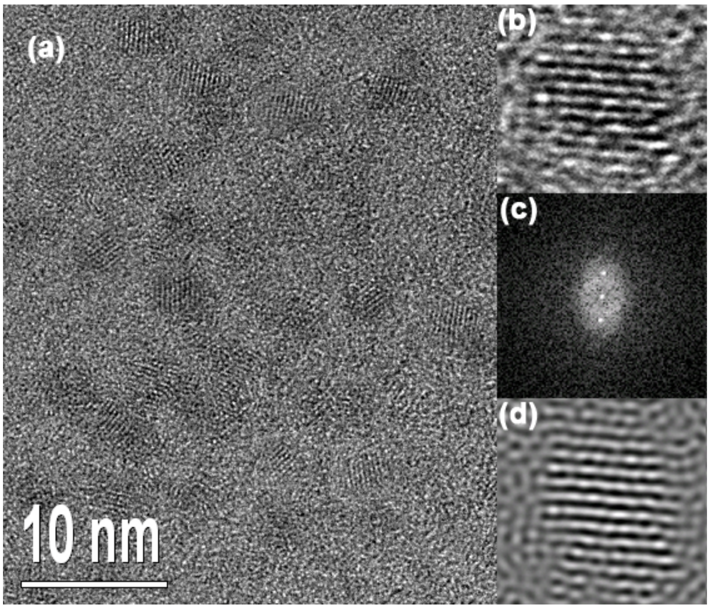

Figure S2. HRTEM micrograph of CdIS NCs (a) with the fast Fourier transform pattern (c) of the selected area of the same particle (b) and the corresponding inverse FFT pattern (d)

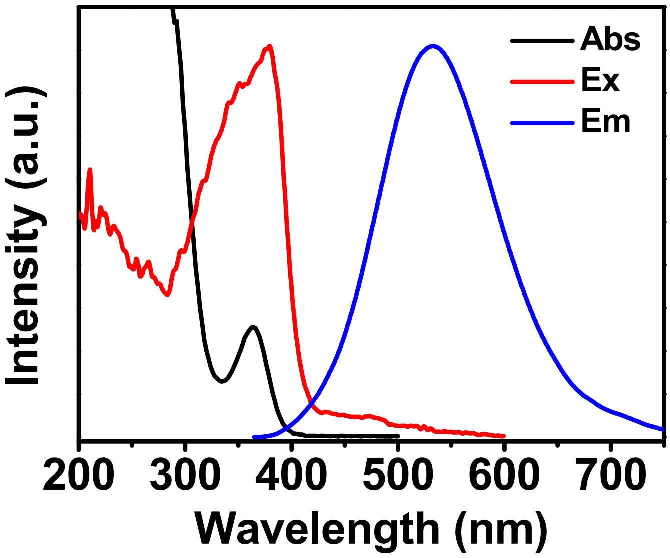

Figure S3. UV-vis, PLE and PL spectra (excited at 360 nm) of D-2

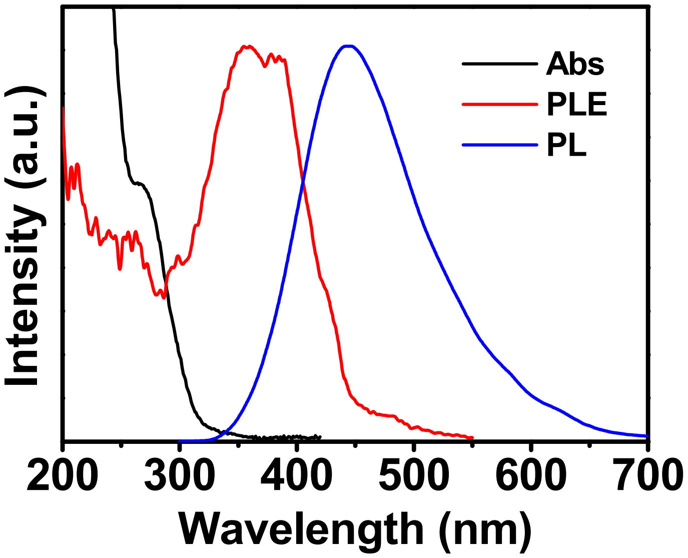

Figure S4. The absorption, PLE and PL spectra (excited at 360 nm) of pure indium sulfide nanocrystals

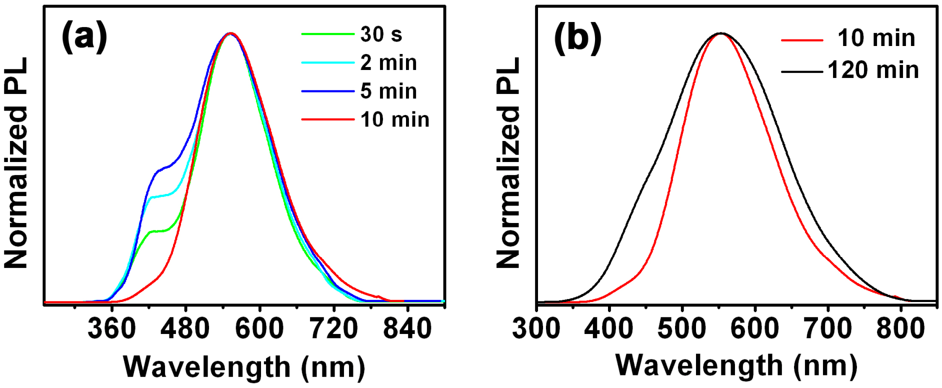

Figure S5. The evolution of PL spectra (excited at 360 nm) of D-3 with different reaction time (0.5, 2, 5, 10 and 120 min, respectively)

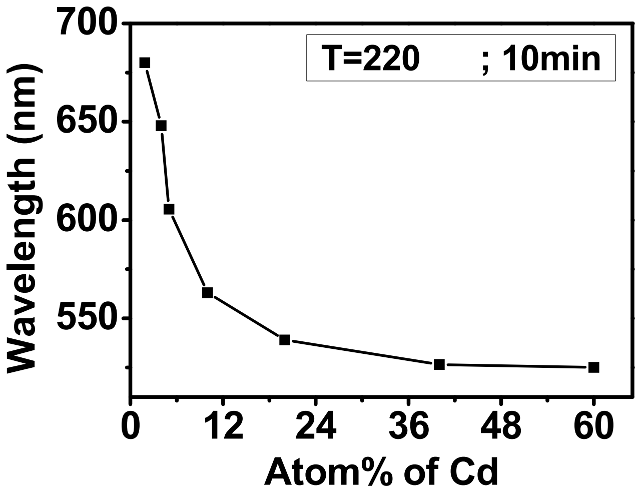

Figure S6. Temporal evolution of PL emission wavelength (excited at 360 nm) of CdIS NCs with varying Cd concentration.

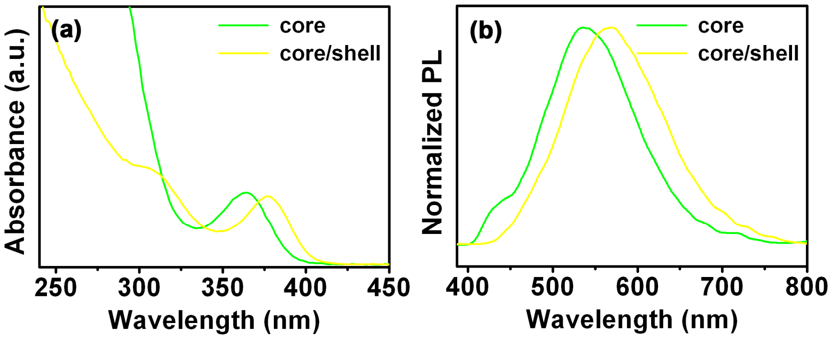

Figure S7. The evolution of the absorption and PL spectra (excited at 360 nm) of the NCs with growing of ZnS shell

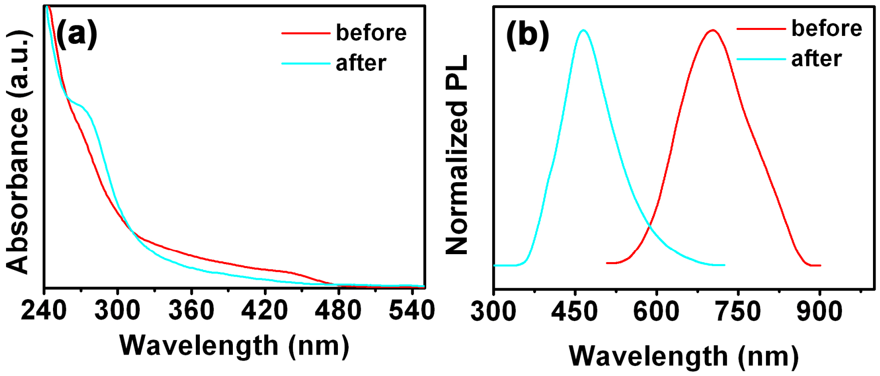

Figure S8. The absorption and PL spectra (excited at 360 nm) of the CdIS NCs before and after etched by acids

Table S1. The compositions of CdIS NCs determined by ICP-MS analysis (normalized to In^{3+} content)

sample	PL quantum yields	Cd in precursor	Cd in purified nanoparticle
D-1	18.6	40%	38.6%
D-2	19.1	20%	17.74%
D-3	16.4	10%	8.61%
D-4	12.3	5%	4.25%
D-5	6.20	1.9%	1.63%