Electronic Supplementary Information

A Controllable Growth-Doping Approach to Synthesize Bright White-Light-Emitting Cd:In_2S_3 Nanocrystals

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Experimental Section

Materials. Technical grade (90%) octadecene (ODE), indium acetate ($In(Ac)_3$, 99.99%), cadmium acetate ($Cd(Ac)_2$), oleic acid (OA, 90%), 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 alloyed Cd-In-S QDs and Cd:In_2S_3 NCs. Alloyed Cd-In-S QDs were prepared by a reported method. Cd:In_2S_3 NCs were synthesized by an adaptation of this method. For a typical synthetic reaction, 0.1 mmol indium acetate, 0.04 mmol cadmium acetate, 0.4 mmol oleic acid (OA) 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 240 °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 Cd:In_2S_3 NCs. The isolated NCs could be redispersed in various nonpolar organic solvents including hexane, toluene, decane, and chloroform.

Transmission Electron Microscopy (TEM). TEM 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 alloyed Cd-In-S QDs and Cd:In_2S_3 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 Cd:In_2S_3 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 alloyed Cd-In-S QDs and Cd:In_2S_3 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).

White-light-emitting LEDs. The purified Cd:In_2S_3 NCs were coated onto the commercial UV-LED (365 nm, 350 mW).

Table S1. The compositions of alloyed Cd-In-S QDs and Cd:In_2S_3 NCs determined by ICP-MS analysis (normalized to In^{3+} content)

sample	capping agent	Cd content in precursor	Cd content in purified nanoparticle
Cd:In_2S_3 NCs	OA	40%	2.09%
alloyed Cd-In-S QDs	OA+DDT+TOP	40%	38.6%

Table S2. The compositions of Cd:In_2S_3 NCs with different Cd content in precursor determined by ICP-MS analysis (normalized to In^{3+} content)

sample	Cd content in precursor	Cd content in purified nanoparticle
1	20%	1.66%
2	40%	2.09%
3	60%	2.55%

Table S3. Values of CIE coordinates and CCT for doped Cd:In_2S_3 NCs samples with different amounts of Cd precursor

sample	Cd content in precursor	X	Y	Correlated Color temperature (K)
1	20%	0.197	0.181	-
2	40%	0.298	0.264	8214
3	60%	0.416	0.254	2410

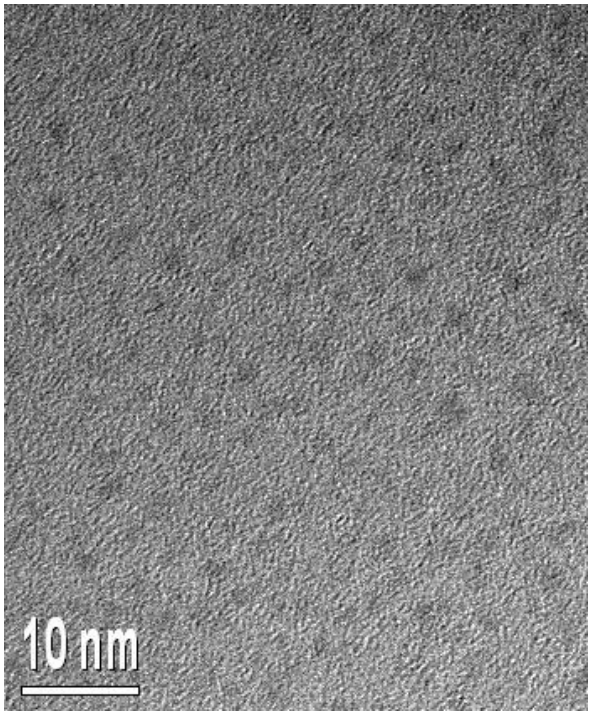

Figure S1. TEM micrograph of white-light emitting Cd:In_2S_3 NCs.

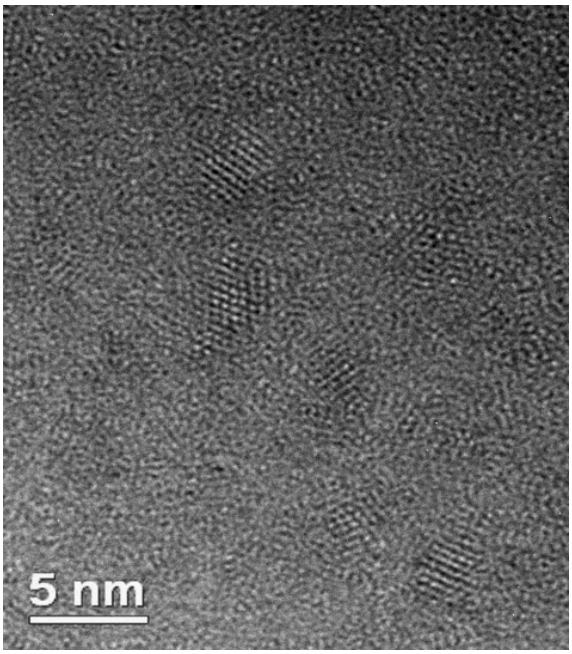

Figure S2. HRTEM micrograph of white-light emitting Cd:In_2S_3 NCs.

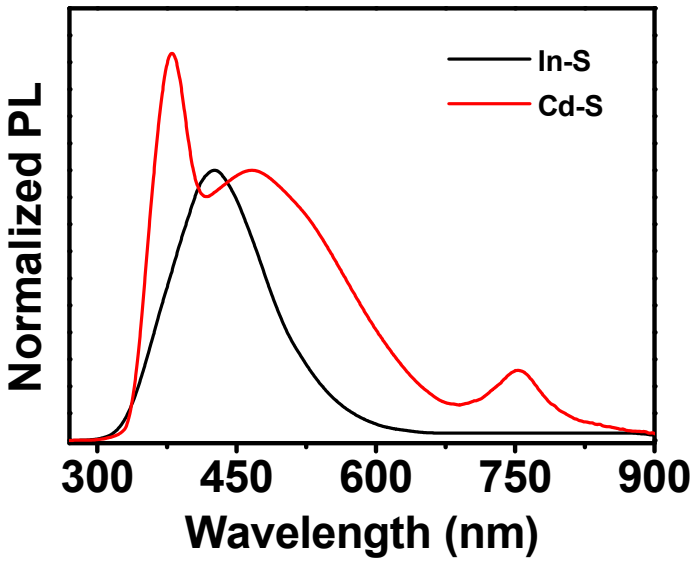

Figure S3. PL spectrum (excited at 360 nm) of In_2S_3 and CdS synthesized under the same reaction condition.

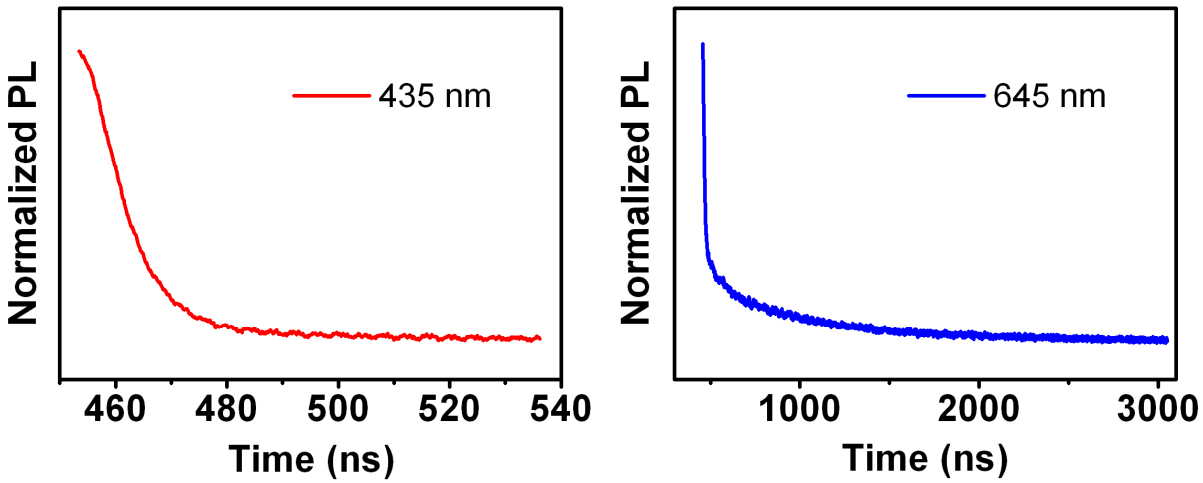

Figure S4. PL decay curves (excited at 360 nm) of white-light emitting Cd:In_2S_3 NCs (recorded at 435 and 645 nm, respectively)

Table S4. Decay Times and Amplitude Constant Ratios of In_2S_3, alloyed Cd-In-S and white-light emitting Cd:In_2S_3 NCs (excited at 360 nm).

Sample	In_2S_3	alloyed Cd-In-S	white-light emitting Cd:In_2S_3	
recording wavelength	435 nm	645 nm	435 nm	645 nm
τ_1 / ns	9.28	14.3	11.3	17.9
a	100.0	98.3	100.0	99.7
τ_2 / ns		390.3		558.0
b		1.7		0.3