Dual emission in Asymmetric "Giant" PbS/CdS/CdS Core/Shell/Shell Quantum Dots

SUPPORTING INFORMATION

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1. Structural and optical characterization

TEM

For the core@shell QDs, the solution was directly drop casted on the Cu grid. For the observation of the QDs grafted on TiO_2 surface, the TiO_2 film was sonicated for 10 min into a toluene solution. Then the detached film formed a concentrated mixture that was drop casted on the Cu grid for TEM observation. TEM characterization of the PbS and PbS/CdS QDs was carried out with a Jeol 2100 F TEM and with a FEI Tecnai F20 ST TEM/STEM equipped with a HAADF-STEM detector and an EDS spectrometer. Both microscopes were operated at 200 keV.

Transient transmission ΔT/T measurements

The system drives an optical parametric amplifier (OPA) which generates the pump pulses. The OPA can be tuned in the 440-650 nm wavelength region. The pulse energy is of the order of 1 μJ and its bandwidth is 10 nm, corresponding to pulse durations ranging from 70 to 100 fs. The probe beam was the supercontinuum light generated by self-phase modulation in a thin sapphire plate. The supercontinuum spectrum extends almost regularly from 420 nm to 1.6 microns, with a gap only around the fundamental wavelength at 800 nm. Pump and probe beams are then focused onto the sample (pump spot size (radius): 100 μm. The pump-probe delay is adjusted by a computer-controlled optical delay line. After the sample, the probe beam enters in a spectrometer equipped with electronics designed for fast read-out times and low noise allowing single-shot recording of the probe spectrum at the full 1 kHz repetition rate. The temporal resolution of pump-probe experiments is given by the duration of the cross-correlation between the pump and the (transform-limit) probe pulses; our system has a temporal resolution of the order of about 100 fs.

2. **Supporting Tables and Figures**

Table S1

	QD size (nm, TEM)	Cd/Pb (ICP-OEM)	Core size (nm)		Shell thickness (nm)	
			ICP-OES	Abs/PL	ICP-OES	Abs/PL
Cyc 8	12.10 ± 0.5	670	1.15 ± 0.05	1.2	5.48 ± 0.04	5.4

The mass ratio of Cd/Pb was directly measured by ICP-OES. The core size and shell thickness were calculated based on the following equation:

$$\frac{\rho_{CdS}R^3 - r^3}{\rho_{PbS} \quad r^3} = K\frac{M_{Cd}}{M_{Pb}}$$

Where R is QD radius, calculated from TEM, r is the core radius, ρ_{CdS} and ρ_{PbS} are the nominal densities of CdS and PbS, respectively, and K is 1.84. M_{cd}/M_{pb} is the mass ratio of Cd/Pb which can be directly measured by ICP-OES.

Table S2 QY, PL position (nm) and lifetime (ns) of pure PbS QDs and core/shell/shell QDs before and after SILAR reaction. The average lifetimes are obtained by using Equation S1.

Sample	QY (%)	PL position (nm)	Lifetime (ns)			
			τ_1	τ_2	τ_3	$\tau_{average}$
PbS	30	1350	1693	576	----	1450 ± 80
Cyc 0	4.5	690	1398	517	95	1130 ± 30
Cyc 2	4.2	690	1357	382	62	1180 ± 30
Cyc 4	2.3	690	1309	326	52	1190 ± 30
		480	16	3	----	13 ± 1
Cyc 6	2.3	690	1331	300	46	1150 ± 30
		480	17	3	----	16 ± 1
Cyc 8	2.1	690	1380	303	52	1140 ± 30
		480	18	3	----	17 ± 1

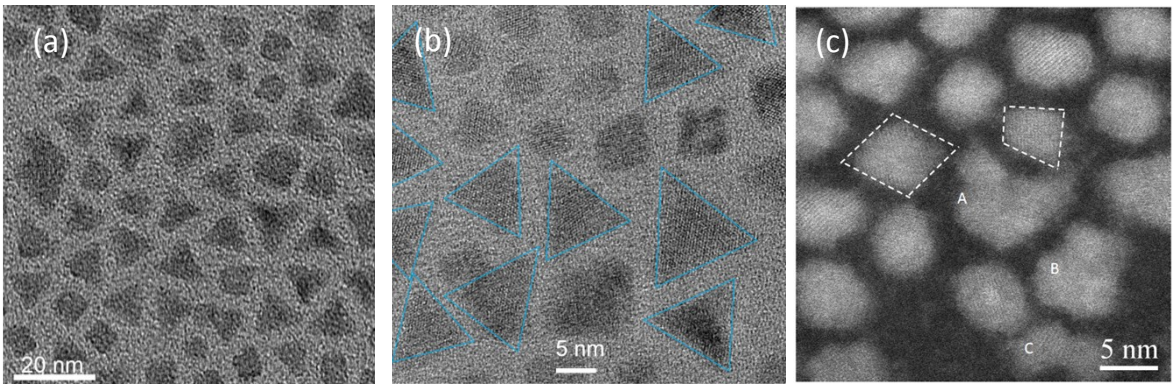

Figure S 1. (a) TEM image and (b) HRTEM image of PbS/CdS/CdS QDs after coating with 8 SILAR cycles at 200 °C (Cyc 8), which highlight the formation of nano-pyramids during low-*T* SILAR. (c) HAADF-STEM image of PbS/CdS QDs. The polygonal projected shape of the CdS nanoparticles is clearly observed, as highlighted by the dotted-line shapes. Coalescence of the smallest particles give rise to complex projected shapes (see particles labelled with A, B and C). Lattice spacing are compatible with {111}Sp.

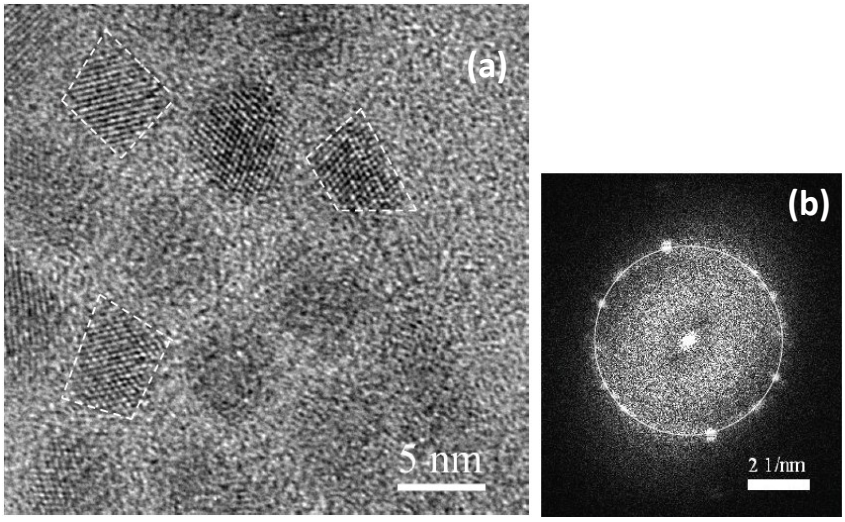

Figure S 2. (a) HREM image of PbS/CdS QDs (Cyc 0). A projected trapezoidal shape (see dotted-lie shapes) is compatible with what expected from tetrahedral nanoparticles observed in different orientations. (b) SAD pattern showing reflections at 0.331±0.07 nm that correspond to the {111}Sp spacing at 0.337 nm. Wurtzite reflections (0.359 nm) are not observed.

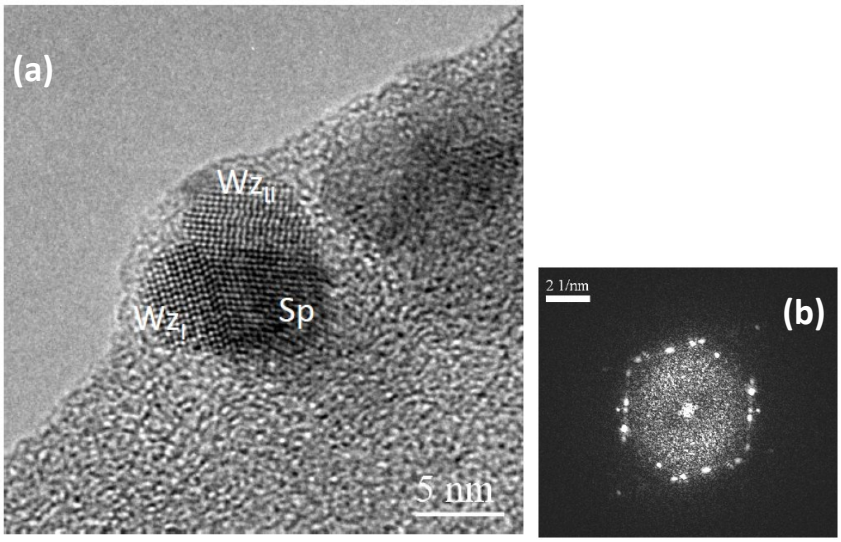

Figure S 3. (a) HREM image and corresponding SAD pattern of Cyc 8 sample (b). Another example of the relative orientation of the Wurtzite CdS grains on the Sphalerite seeds.

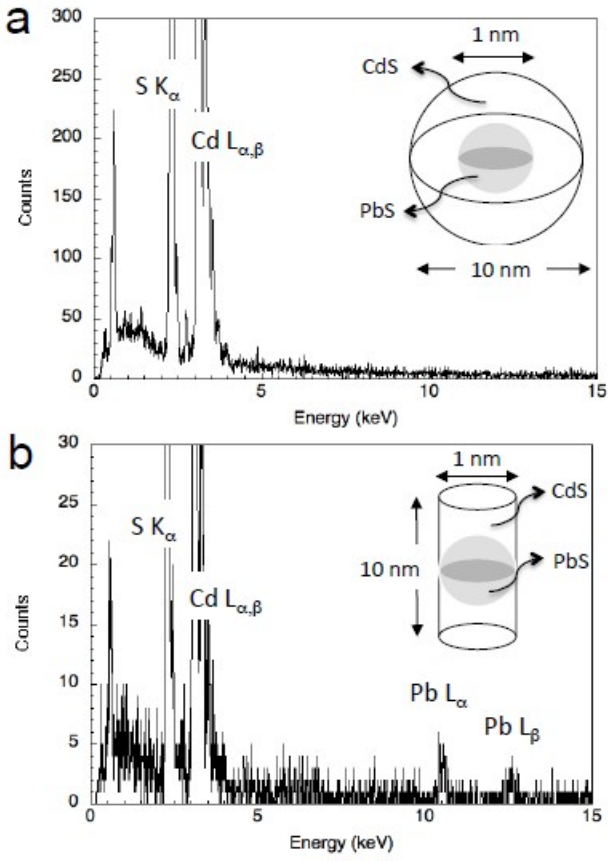

Figure S 4. EDS simulations (NIST Desktop Spectrum Analyser (DTSA) engine by Fiori et al. 1991[1]) obtained using sample compositions corresponding to TEM (a) and STEM (b) configurations schematically shown on the right hand of the figures (not in scale). The parameters of a standard Si(Li) detector with an ultrathin window were assumed and realistic

values of the incident current of 1 and 0.1 nA were considered, respectively. The dwell time was fixed at 60 s in both the case and Poisson random noise added to the calculated spectra. In (a) a rather large electron beam (>10 nm in diameter) is supposed to be transmitted through the whole particle represented by a PbS/CdS core-shell particle, whereas in (b) a focused electron beam samples the central region of the core-shell particle. The Pb weight concentrations corresponding to the two schematic models are 0.14% and 9.2%, respectively. From the simulations, in agreement with the expected sensitivity of the EDS technique, it is clear that the Pb L peaks may be detected uniquely in STEM conditions, when a focused electron beam is positioned just above the nanoparticle core.

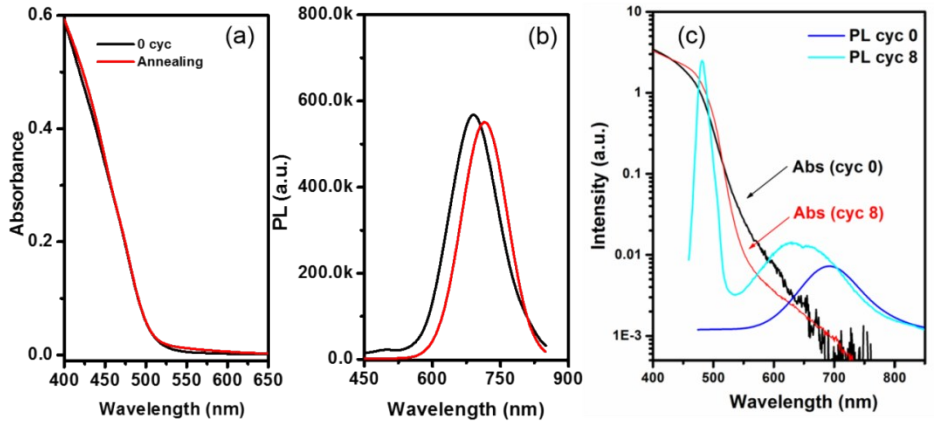

Figure S 5. The absorption (a) and PL (b) spectra of the core/shell QDs (Cyc 0) before (black) and after (red) annealing at 240 °C. The excitation position is set at 430 nm. For the annealing process, the core/shell QDs were dispersed into the solvent without the precursors of CdS. (c) The absorption and PL spectra in semi-log scale of the core/shell QDs (Cyc 0) and the giant QDs after 8-cyc SILAR growth (Cyc 8). Peak position, peak width and quantum yield (QY) remain almost constant after annealing, with a slight red shift of PL position, due to modification of the surface capping ligand during high temperature annealing. This high stability at high temperature allowed us to grow the thick shell by SILAR without any etching and/or shrinking of the core, which typically occurs during the growth of, for instance, "giant" InP/CdS and PbSe/CdSe/CdS QDs, leading to a strong blue-shift of the emission.[2]

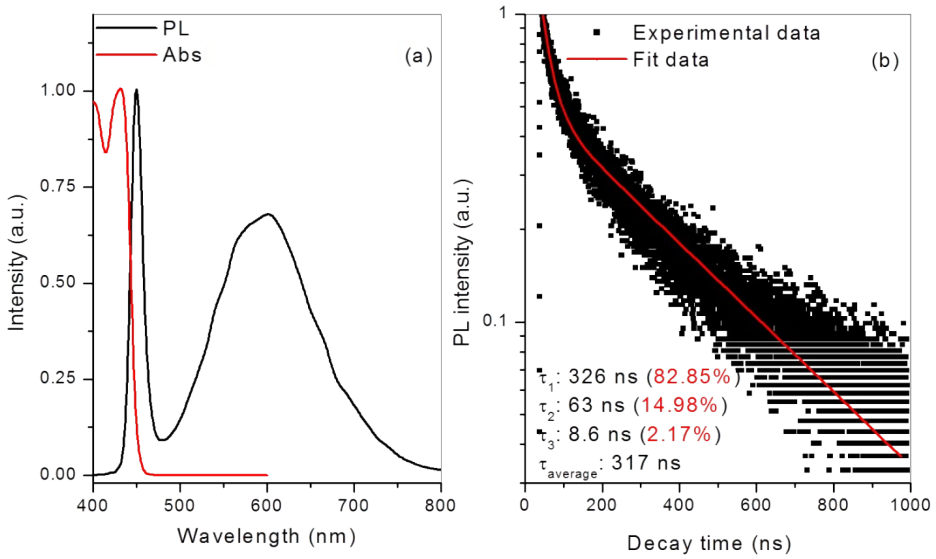

Figure S 6. (a) Absorbance and double emission PL (for a pump beam at 400 nm) of CdS QDs. The band at 594 nm is attributed to CdS trap states. (b) PL intensity decay of the broad band centered at 594 nm. The averaged lifetime for this band is reported as an inset, together with the three components of the three-exponential decay, and their relative weight.

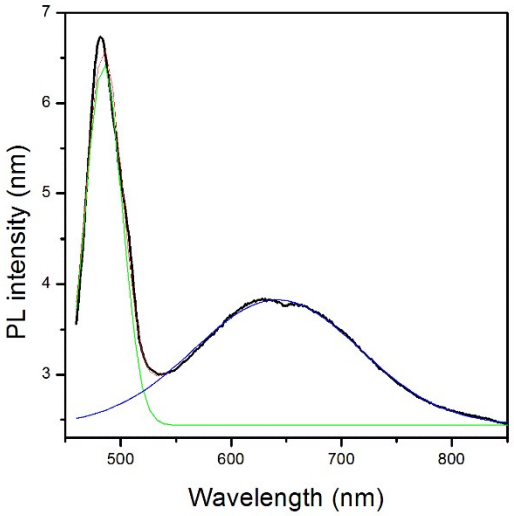

Figure S7. The PL spectrum of the the giant QDs after 8-cyc SILAR growth (Cyc 8). The spectrum can be fitted well by Gaussian with two peak located at 480 nm and 650 nm.

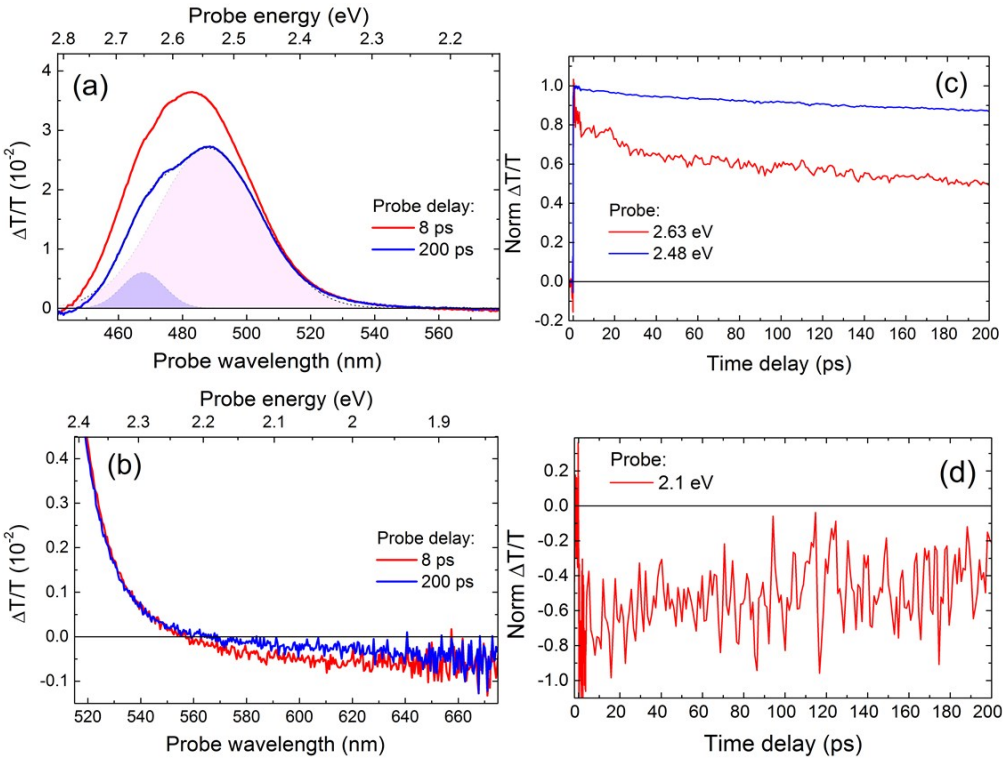

Figure S 8. ΔT/T for the Cyc 8 sample, at a pump wavelength of 470 nm (2.64 eV) and high absorbed fluence (46.1 μJ·cm^{-2}). (a-b) ΔT/T spectra at different pump-probe delays; dashed line is the fit to the blue spectrum with the two Gaussian components (dotted lines). (c-d) ΔT/T Dynamics at different probe wavelengths.

Eq. S1 for the estimate of the intensity-weighted average lifetime <τ> based on a three-component decay:

$$<\tau>=\frac{a_1\tau_1^2+a_2\tau_2^2+a_3\tau_3^2}{a_1\tau_1+a_2\tau_2+a_3\tau_3}$$

a_i (i=1,2,3) are the coefficients of the fitting of PL decay and τ_i (i=1,2,3) are the lifetimes.

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[1] Fiori C, Swyt C, Myklebust R: Desktop Spectrum Analyzer (DTSA), a Comprehensive Software Engine for Electron-Excited X-Ray Spectrometry, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD (1991).

[2] . D. C. Lee, I. Robel, J. M. Pietryga and V. I. Klimov, *J. Am. Chem. Soc.* 2010, **132** (29), 9960–9962.