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Supporting information for

Towards Understanding Unusual Photoluminescence Intensity Variation of Ultrasmall Colloidal PbS Quantum Dots with the Formation of Thin CdS Shell

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Materials and Methods

I. Materials

Lead chloride (98%), Nitric acid (70%), lead acetate trihydrate ($Pb(OAc)_2.3H_2O$; ≥99.9%), bis(trimethylsilyl) sulfide ($(TMS)_2S$; synthesis grade), Trioctylphosphine (TOP; technical grade, 90%), sulfur (100%), oleylamine (OLA; technical grade, 70%), cadmium oxide (99%), cardiogreen (IR-125), 1-Benzothiopyrylium (IR-26), methanol (anhydrous, 99.8%) and octadecene (ODE) were obtained from Sigma-Aldrich Inc. Hexane, oleic acid (OA), toluene and ethanol were purchased from Fisher Scientific Company. All chemicals were used as purchased.

II. Synthesis of smaller PbS quantum dots (QDs; 2.7 and 2.9 nm in diameter)

PbS QDs were synthesized following a previously reported method.[1, 2] In a typical procedure, a mixture of $Pb(OAc)_2.3H_2O$ (760 mg), OA (2.4 ml) and ODE (15 ml) was stirred and heated to 150 ^{O}C for 1 h under N_2 flow. It was then cooled to 130 ^{O}C under vacuum and the N_2 flow was recovered. After that, a mixture (2 ml) of $(TMS)_2S$ and TOP (1:10 ratio by volume) was quickly injected into the flask, resulting in a quick drop in temperature. The reaction was then quenched with cold water after about 5 minutes. The QDs were precipitated by centrifugation and then re-dispersed in cold hexane. After keeping the QD dispersion at 4 ^{O}C for two days, the QD dispersion was centrifuged at 8000 rpm for 30 minutes and the sediment was discarded. Following methanol addition, the QD dispersion was centrifuged at 3000 rpm for 5 minutes. After removing the supernatant, the QDs were dispersed in toluene. This purification step was repeated one more time.

Ш. Synthesis of larger PbS QDs (3.4 to 6 nm in diameter)

Larger PbS QDs were synthesized by using OLA as capping ligands.[3] In a typical reaction, $PbCl_2$ (10 g) and OLA (24 mL) were heated by oil bath to 160 °C and kept at this temperature for 1 h under the protection of N_2. The solution was then cooled to 120 °C and pumped for 30 min. The flask was then reopened and the N_2 flux was restored. Sulfur (115 mg) in OLA (4 mL) at room temperature was quickly injected into the $PbCl_2$-OLA suspension under vigorous stirring. The reaction cell was quenched with cold water after the reaction was conducted at 100 °C for 1-30 min to obtain PbS QDs of different sizes. The purification procedure was carried out in air using anhydrous solvents. Hexane and ethanol were added to the reaction solution followed by centrifugation to separate QDs. Obtained PbS QDs were purified one more time by redispersion and centrifugation processes. Ligand exchange with oleic acid was then performed following routine procedure.[4] Finally, the QDs were dispersed in toluene for characterizations or for the synthesis of PbS/CdS QDs.

IV. Synthesis of colloidal PbS/CdS QDs.

Core/shell QDs were synthesized following our previously reported microwave-assisted cation exchange approach.[5] CdO (3 g), OA (15 mL) and ODE (20 mL) were mixed and heated to 200-250 °C by oil bath until the solution turned colorless. The mixture was cooled to 100 °C and degassed under vacuum for 30 min. The temperature was further decreased to 20 °C and 12 mL of PbS QD dispersion was added *via* syringe. Then, 20 mL of this mixture was introduced into a 35 mL microwave reaction tube and heated *via* microwave (Discover; CEM

Corporation). The reaction was conducted at 100 °C for different time. To purify the PbS/CdS QDs, ethanol was added to precipitate the QDs. The precipitate was subsequently redispersed in toluene and again precipitated with ethanol. The redispersion/precipitation procedure was repeated additionally once or twice.

Structural and optical characterization of QDs

The morphology of PbS and PbS/CdS QDs was characterized by a transmission electron microscope (TEM; JEOL 2100F). The size of the QDs was measured by Nano Measure 1.2 based on their TEM images and the data were then fitted by the Gaussian function, which yielded the size distribution information. X-ray photoelectron spectrometry (XPS) was performed on a VG Escalab 220i-XL equipped with an Al KR source. Absorption spectra were acquired with a Cary 5000 UV-Vis-NIR spectrophotometer (Varian) with a scan speed of 600 nm/min. Fluorescence spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon) using charge coupled device or photomultiplier tube detectors, depending on emission wavelengths. The quantum yield (QY) of smaller sized QDs (≤ 2.9 nm) was measured by using dye IR-125 as a reference, with the same excitation wavelength at 715 nm) and the QY of larger sized QDs (≥ 3.4 nm) was measured by using dye IR-26 as a reference using excitation at 980 nm.[6] The size of PbS QDs and the PbS cores in core/shell QDs was calculated based on bandgap energy estimated from the first exciton absorption peak.[7-9] The only exception was 2.7 nm PbS/CdS core/shell QDs, for which the relationship between photoluminescence (PL) peak energy and bandgap energy was used to estimate the bandgap energy, and thereby the average size of PbS cores, due to the lack of a clear exciton absorption peak.[10] Since the overall size of PbS/CdS core/shell QDs remained the same as that of initial PbS QDs, the CdS shell thickness was estimated by subtracting the radius of PbS cores in PbS/CdS core/shell QDs from the radius of initial PbS QDs.[11] For all the studies presented herein as a function of initial PbS size, where the highest PL intensity of PbS/CdS core/shell QDs was used for the calculation. The core/shell QDs, with an optimal shell thickness and showing the highest PL intensity from differently sized parent PbS QDs, were used throughout this study.

The PL lifetimes of PbS and PbS/CdS nanocrystals (except for 2.9 nm PbS QDs) in toluene were measured using a pulsed laser diode of 2.79 eV, photomultiplier tube detectors, and a fast multichannel scaler mode. The lifetime of 2.9 nm PbS QDs cannot be measured because their emission falls into the gap (the insensitive wavelength range of detection) in between two detectors available in our lab, which can do lifetime measurements. Their steady-state emission can be measured without any problem though, since it can be detected by a CCD detector, which however is not appropriate for lifetime measurements.

PL decay curves were fit with a typical biexponential function.[12] Average lifetime (τ) was calculated from two lifetime components, τ_1 and τ_2, by using the following equation:

$$\tau = (B_1\tau_1^2 + B_2\tau_2^2) / (B_1\tau_1 + B_2\tau_2),$$

where B_1 *and* B_2 represent the relative amplitude of τ_1 and τ_2, respectively, and were also obtained from the fitting of the biexponential function. The error on τ was obtained through differentiation of the above definition and expressed as a function of the uncertainty on the fitting parameters B_1, B_2, τ_1, and τ_2. These uncertainties were calculated automatically from the software (DAS6 Fluorescence Decay Analysis).

The contents of Pb and S elements were characterized by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Agilent Technologie, 5100). Basically, PbS QDs were precipitated with ethanol, centrifuged, and then dried in vacuum. Then, the PbS QD powder was completely dissolved by nitric acid to make aqueous solution for measuring ICP-OES.

Transient absorption (TA) spectroscopy was performed with a Quantronix-designed femtosecond transient absorption laser system comprising an Er-doped fiber oscillator, regenerative amplifier, and a diode-pumped, Q-switched, second-harmonic Nd:YLF pump laser (527 nm, 10 W capacity). After amplification, the as-generated fundamental beam (~800 nm, 760 Hz repetition rate) was split in a 1/9 ratio to generate a white light continuum probe pulse and a pump pulse, respectively. The pump pulse was subsequently routed through an optical parametric amplifier to generate the desired 350 nm pump beam with a pulse duration of ~180 fs. Pump power was modulated by the use of absorptive neutral density filters before illuminating the sample. The pump and probe beams were overlapped spatially and temporally at the sample and the spectra were recorded after excitation with the pump and interrogation with the probe over a delay interval of 0–1000 ps between the pump and probe pulses. Variation in time delay was achieved by a motor-controlled translation stage with 1 µm resolution (6 fs time resolution). The difference absorption of each sample was measured over the aforementioned interval two times and the data averaged to achieve lower overall noise.

Theoretical calculation of wave functions

To calculate the electron and hole wave functions, we solved analytically the stationary Schrödinger equation in spherical geometry within the effective mass model, which is based on the bulk band energies and effective masses[13]. The values used for the bulk effective masses of electrons (m_e*) and holes (m_h*), are $m_e^* = 0.085\ m_e$ and $m_h^* = 0.085\ m_e$ for Pbs, and $m_e^* = 0.2\ m_e$ and $m_h^* = 0.7\ m_e$ for CdS, where m_e is the electron mass at rest in vacuum.[14] The potentials for electrons and holes as a function of position used in the Schrödinger equation were approximated as the lowest unoccupied molecular orbital and highest occupied molecular orbital levels, respectively, for the bulk materials. For PbS, we used the values -4.7 and -5.0 eV, respectively[15,16], while for CdS we used -3.5 and -5.9 eV, respectively[14]. Outside the QD, the potentials were set as 0 and -10.6 eV for electrons and holes, respectively.

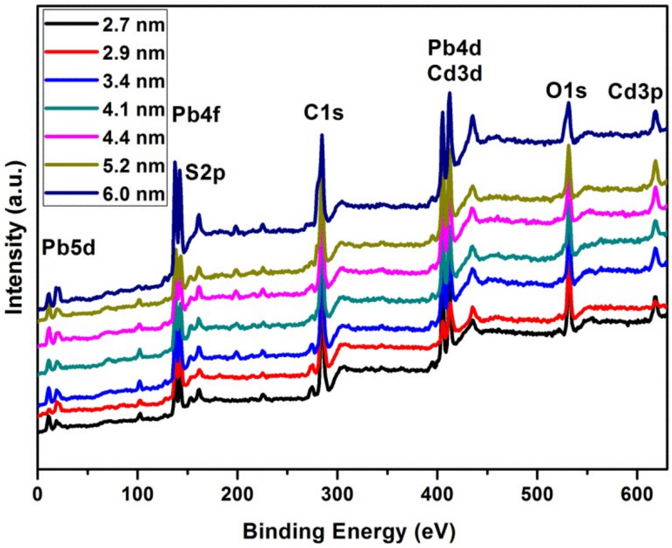

Figure S1. XPS survey spectrum of PbS/CdS core/shell QDs.

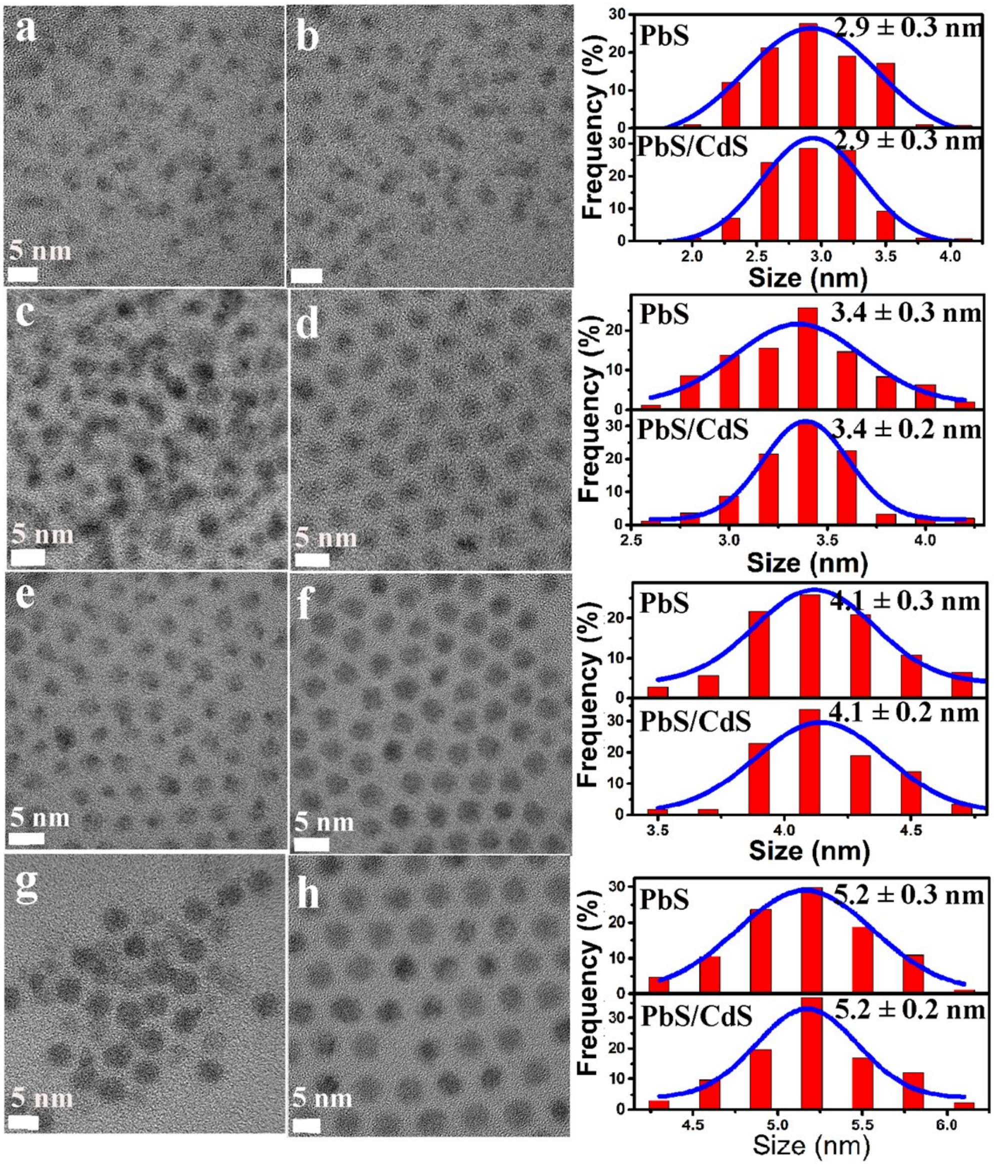

Figure S2. TEM images of differently sized PbS (a: 2.9 ± 0.3 nm, c: 3.4 ± 0.3 nm, e: 4.1 ± 0.3 nm, g: 5.2 ± 0.3 nm) and PbS/CdS (b: 2.9 ± 0.3, d: 3.4 ± 0.2 nm, f: 4.1 ± 0.2 nm, h: 5.2 ± 0.2 nm) QDs and their corresponding histograms (right).

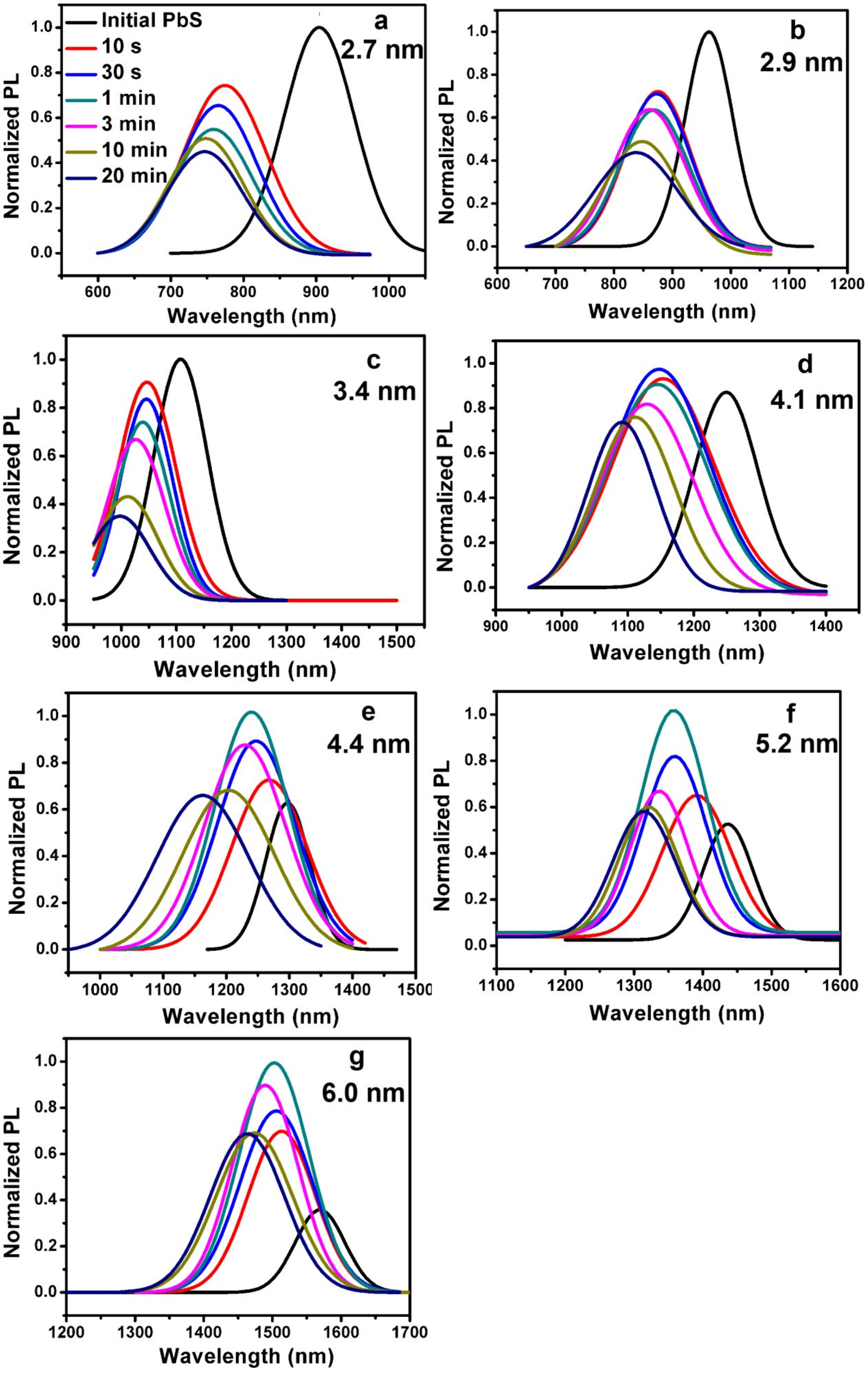
Initial PbS
10 s
30 s
1 min
3 min
10 min
20 min
a
2.7 nm
b
2.9 nm
c
3.4 nm
d
4.1 nm
e
4.4 nm
f
5.2 nm
g
6.0 nm
Normalized PL
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700

Figure S3. PL spectra of differently sized PbS QDs and PbS/CdS core/shell QDs synthesized by microwave-assisted cation exchange at different reaction time.

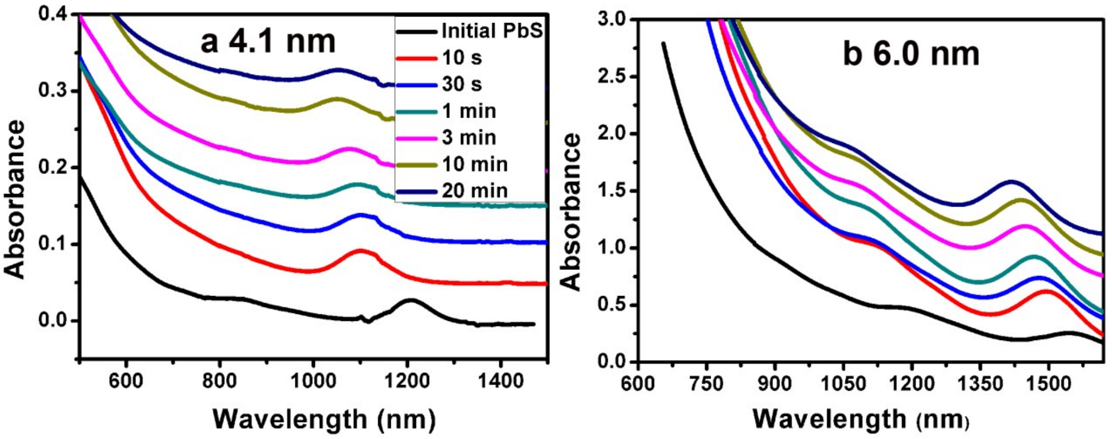

Figure S4. Typical absorption spectra evolution of QDs during microwave-assisted cation exchange (a: 4.1 nm, b: 6 nm).

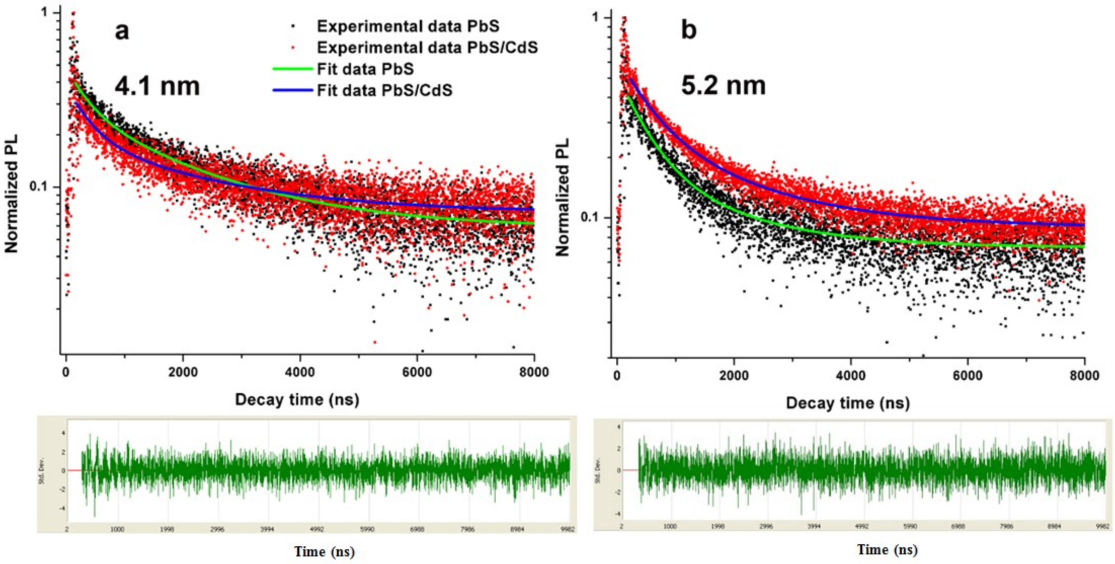

Figure S5. Typical PL decay curves of PbS and PbS/CdS QDs of different size (a: 4.1 nm, b: 5.2 nm) and corresponding residuals of the fittings for PbS/CdS QDs.

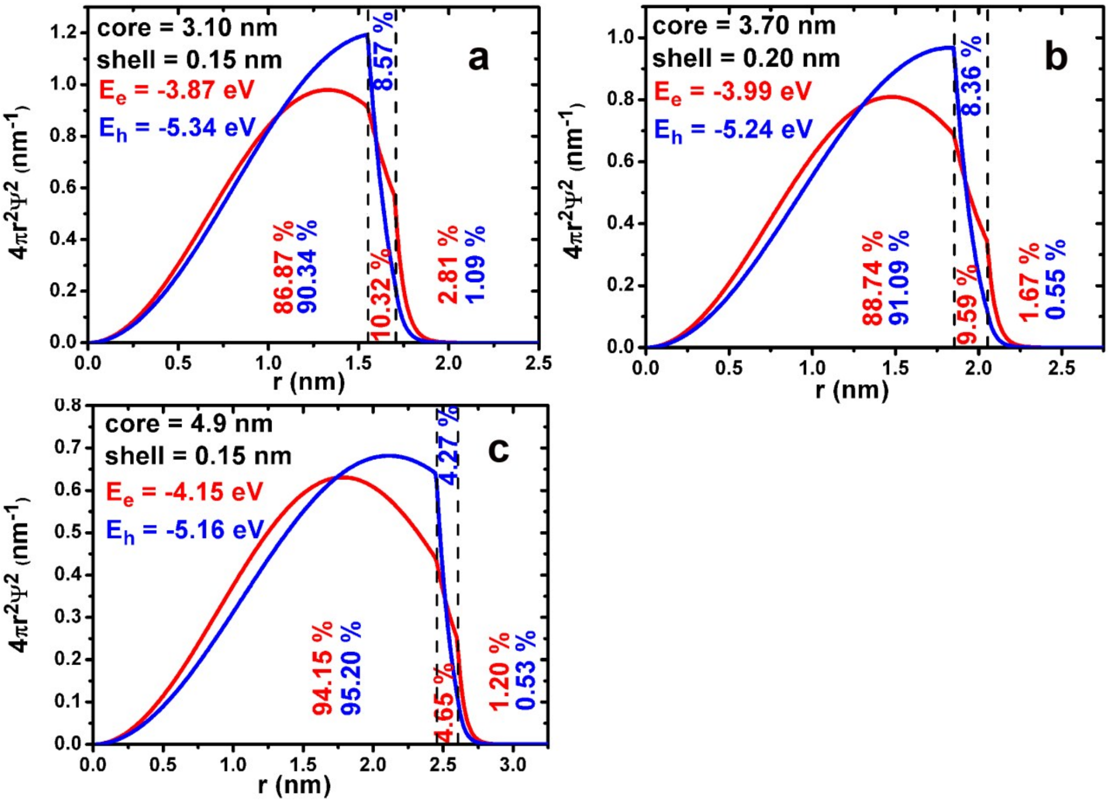

Figure S6. The energies for electrons and holes of differently sized PbS/CdS QDs (a: 3.4 nm, b: 4.1 nm, c: 5.2 nm) and the probability of finding them in each of the 3 regions (core, shell, outside).

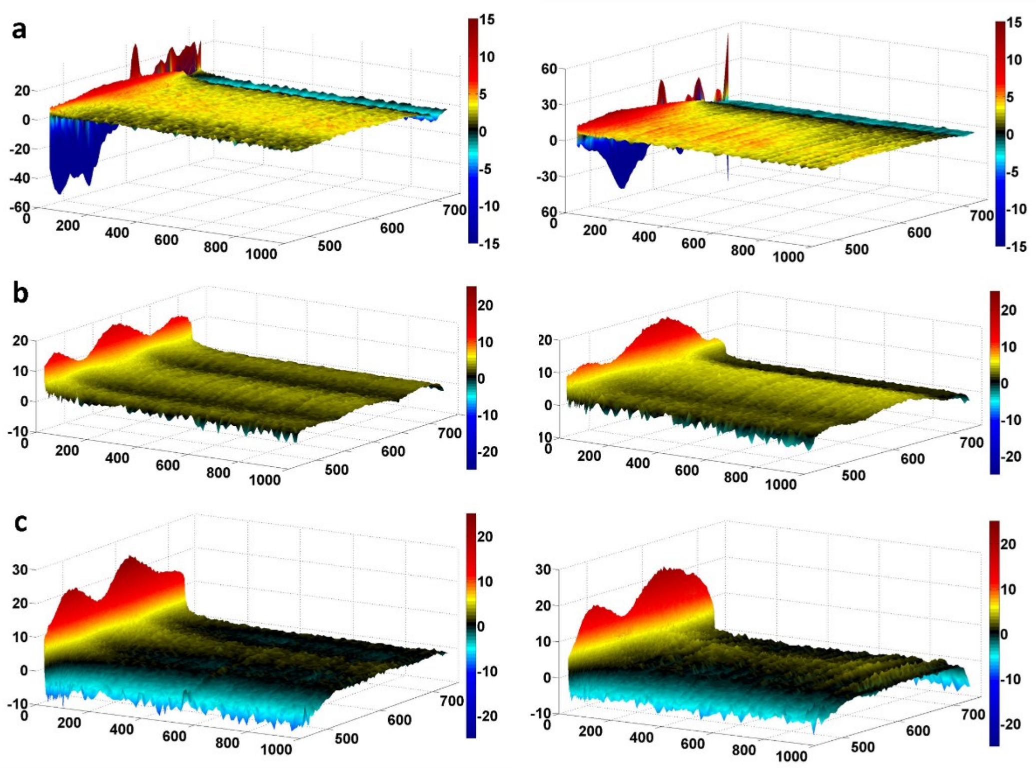

Figure S7. 3D transient absorption difference absorption spectra of PbS (left) and PbS/CdS (right) of different particle size a: 2.9 nm, b: 4.4 nm, c: 6 nm at probe wavelengths spanning 480 – 720 nm after 750 nm, 2.5 μJ/pulse excitation.

Table S1. Single wavelength fitting parameters for transient absorption difference absorption spectra of 2.9, 4.4, and 6.0 nm PbS core and PbS/CdS core/shell QDs. The samples were excited with 750 nm, 2.5 μJ/pulse and probed from 480 – 720 nm. Single probe wavelengths of interest (574 nm and 541 nm for 2.9 nm PbS and PbS/CdS QDs, respectively; 590 nm and 630 nm for 4.4 nm PbS and PbS/CdS QDs, respectively; 620 nm and 634 nm for 6.0 nm PbS and PbS/CdS QDs, respectively) were fit with a triple exponential decay. The lifetimes ($\tau_1 - \tau_3$) and associated relative amplitudes ($A_1 - A_3$) for each fit are tabulated below.

	PbS Core						**PbS/CdS Core/Shell**					
QD	**A_1**	**A_2**	**A_3**	**τ_1(ps)**	**τ_2(ps)**	**τ_3 (ps)**	**A_1**	**A_2**	**A_3**	**τ_1(ps)**	**τ_2(ps)**	**τ_3(ps)**
2.9 nm	0.29	0.31	0.40	7	30	12000 ± 5000	0.33	0.27	0.40	5	40	1680 ± 90
4.4 nm	0.43	0.34	0.23	4	40	4400 ± 800	0.41	0.30	0.29	4	40	13000 ± 6000
6.0 nm	0.61	0.32	0.07	5	50	5000 ± 2000	0.57	0.33	0.10	3	30	3000 ± 1000

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