Colloidal Atomic Layer Deposition Growth of PbS/CdS Core/Shell Quantum Dots

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Supplementary Information

Experimental methods

Chemicals:

Sulfur (Aldrich, 99.998%), oleylamine (OLA, Aldrich, technical grade 70%), lead chloride ($PbCl_2$, Alfa-Aesar, 99.999%), hexanes (Omnisolv, 98.5%), formamide (FA, Sigma-Aldrich, >99%), ammonium sulfide ($(NH_4)_2S$, Strem, 40-44% aqueous solution), cadmium acetate dihydrate ($Cd(Ac)_2$, Sigma-Aldrich 98%), cadmium oxide (CdO, Alfa-Aesar, 99.998%), oleic acid (OA, Alfa-Aesar, technical grade 90%) and tetracholorethylene (Alfa-Aesar, 99%) were used without further purification.

$Cd(OA)_2$:

1.28 g of cadmium oxide in 20 mL of oleic acid was heated at 160°C for 1 hour under nitrogen until colorless. The solution was then degassed under vacuum at 70°C for 30 min.

Synthesis of PbS QDs:

The synthesis of PbS QDs was adapted from a previously reported procedure.[1,2]

0.080g of sulfur in 7.5 mL OLA was heated at 120°C for 20 min under nitrogen bubbling and stirring. 0.83g of $PbCl_2$ in 15 mL OLA was degassed for 30 minutes at room temperature, then under nitrogen, the temperature was increased to 120°C (with a vacuum pull at 110°C for ~5min). Once the temperature was stable at 120°C, 2.5mL of the sulfur solution was swiftly injected into the lead solution. 4mL aliquots were taken every minute and cooled down in 8mL hexane. The aliquots were then left overnight in the fridge to let the unreacted lead salt precipitate. They were then centrifuged at 3900RPM for 5 min, the supernatant was collected and precipitated with a mixture of 2:1 butanol:methanol. After centrifugation, the supernatant was discarded, and the precipitate redispersed in 5mL hexane and 5mL OA. After centrifugation, the supernatant was discarded and the precipitate redispersed in 5mL hexane and precipitated again with a 2:1 mixture of butanol:methanol. After a last centrifugation, the precipitate was collected in 1mL hexane. Before the shell growth procedure, the solution of PbS QDs was centrifuged to get rid of the excess unreacted lead salt.

Synthesis of PbS/CdS:

The growth of the CdS shell follows a previously reported procedure.[3]

In centrifuge tubes, under ambient atmosphere, 800µL of hexane, 800µL of FA and 15µL of OLA were mixed. 100µL of PbS QDs solution at 8µM was then added, and 100µL of 40-44% aqueous $(NH_4)_2S$ solution

was added. The mixture was stirred for 3 minutes, then centrifuged to separate the phases. The QDs remain in the non-polar phase (hexane) where they are stabilized by OLA, while the excess unreacted sulfur precursor remains in the polar phase (FA). The FA was discarded, and the hexane was washed twice with FA. 800µL of FA was then added followed by 15µL of a 0.1M $Cd(Ac)_2$ solution in FA. After stirring for 3 minutes, the FA was discarded, the hexane was washed twice with FA, and the procedure was repeated as many times as desired to grow CdS layers.

Addition of $Cd(OA)_2$:

After the c-ALD growth of CdS, 5µL of a solution of 0.5M $Cd(OA)_2$ in OA was added, stirred for 3 minutes, and the QDs were precipitated using isopropyl alcohol to get rid of the excess OA. The precipitate was redispersed in hexane.

Characterization:

The absorbance spectra were taken on a Cary 5000 UV-Vis-NIR spectrometer in tetrachloroethylene as the solvent in a 400µL quartz cuvette, with a dilution of about 200 compared to the reaction mixture, yielding a concentration of ~4 nM. The emission spectra were recorded on a home-build NIR fluorescence setup with a 532 nm excitation wavelength. The quantum yields were measured with an integrative sphere with a 785 nm excitation. The transmission electron microscopy images were taken on a JEOL 2010F TEM at 200kV. The HAADF STEM images were taken on a Jeol ARM200F at 200kV.

Supplemental figures

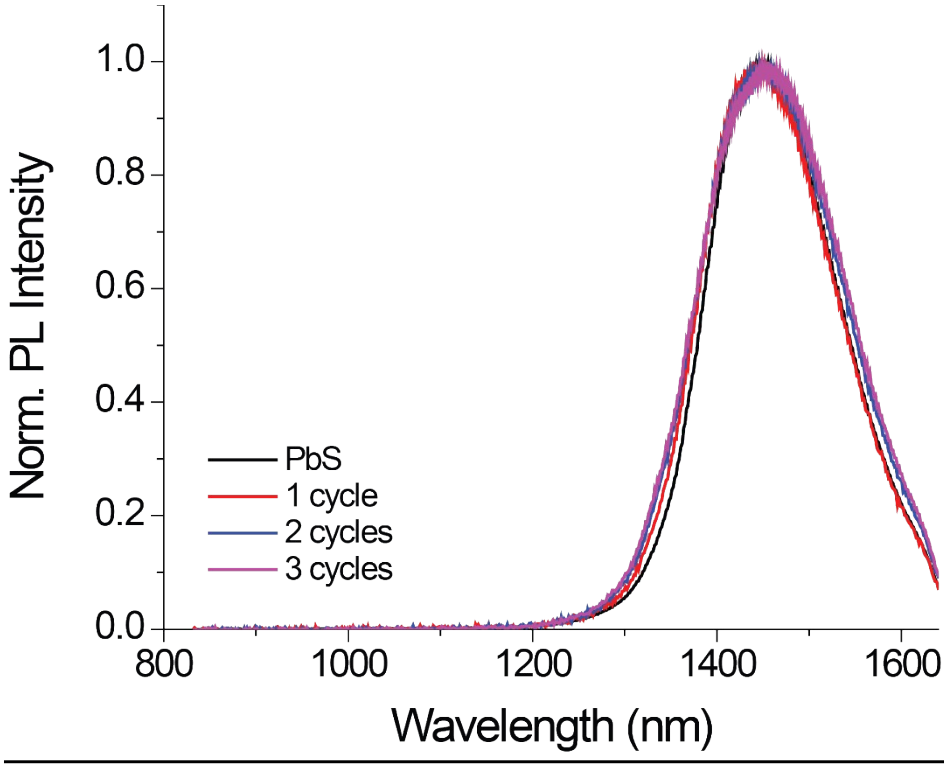


Figure S1: Photoluminescence spectra of PbS QDs after 0, 1, 2 and 3 c-ALD cycles with no Cd or S precursor added.

After performing the c-ALD cycles without adding Cd or S precursors, the PL spectrum of the PbS QDs shows no shift, confirming that the PbS QDs do not undergo dissolution or ripening during the c-ALD process, and that the red shift observed when growing a CdS shell is actually due to the CdS growth.

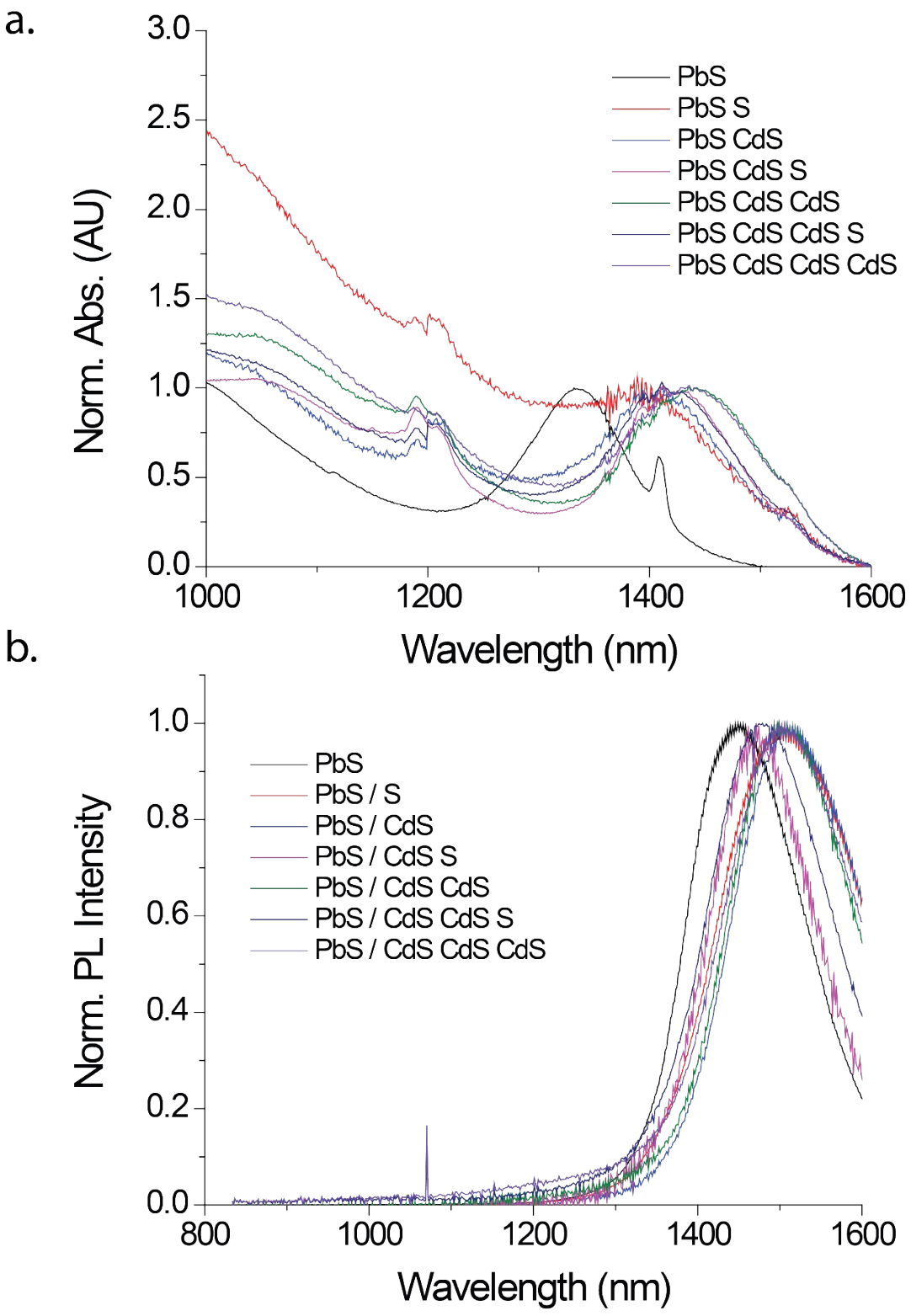


Figure S2: Absorbance (a.) and photoluminescence (b.) spectra of PbS QDs before and after each cycle of CdS shell growth.

The absorbance spectra are polluted by the presence of the overtones of the C-H vibrations of residual hexane or from the ligands. The most significant red-shift is observed after the first deposition of sulfur,

confirming the hypothesis of Sagar *et al*. that the first sulfur layer effectively increases the size of the PbS core. However, after measuring the absorbance and PL after the addition of every precursor, we observe that the spectra shift even for additions after the first S layer. Especially, the emission and absorption seem shifted more towards higher wavelengths when the QDs are Cd terminated (in the caption, those are the QDs ending with CdS), while the emission shifts slightly towards shorter wavelength when the QDs are S terminated. Without contradicting Sagar's *et al*. hypothesis, it seems that the surface still plays an important role as an excess S or Cd or the surface give different optical properties. This tends to confirm that the wavefunction can leak through the thin CdS shell and reach the surface (as confirmed by Sagar's *et al.* for PbS cores around 4 nm) where the cations and the ligands present will affect the recombination efficiencies and dynamics of the charges.

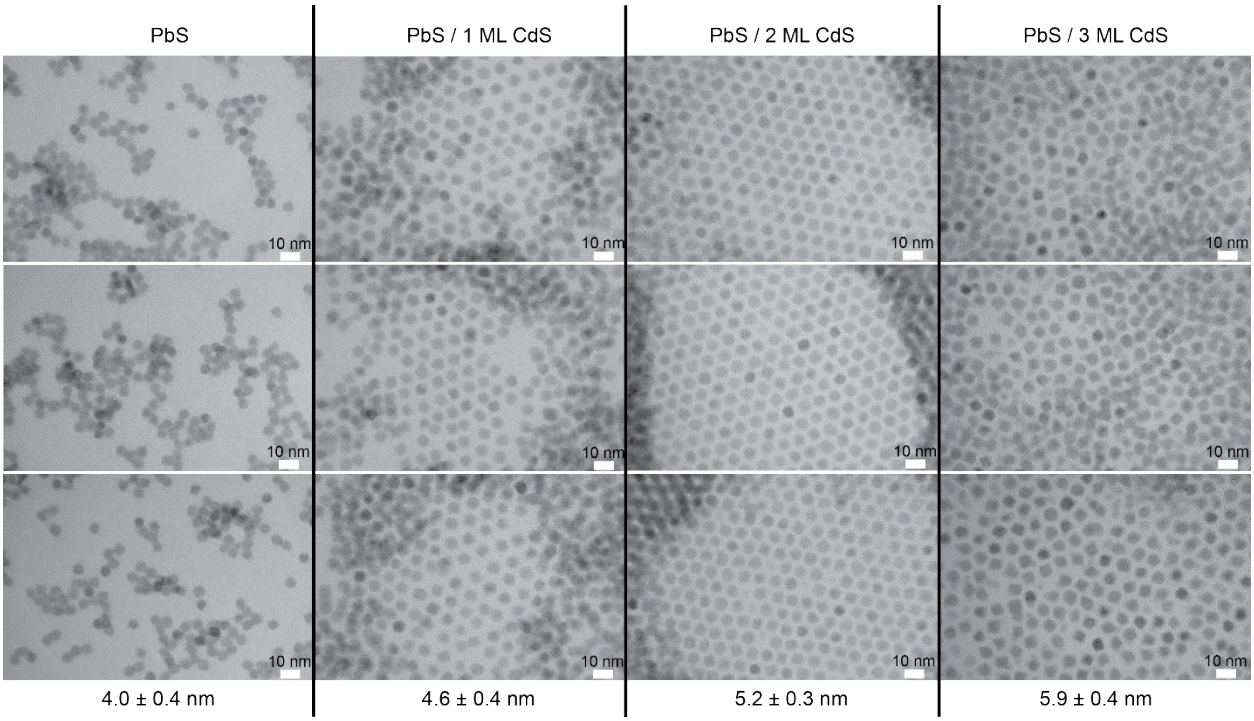


Figure S3: Transmission electron microscopy images of PbS QDs and the same QDs after capping with 1, 2 or 3 monolayers of CdS. Each column shows three images representative of the whole sample.

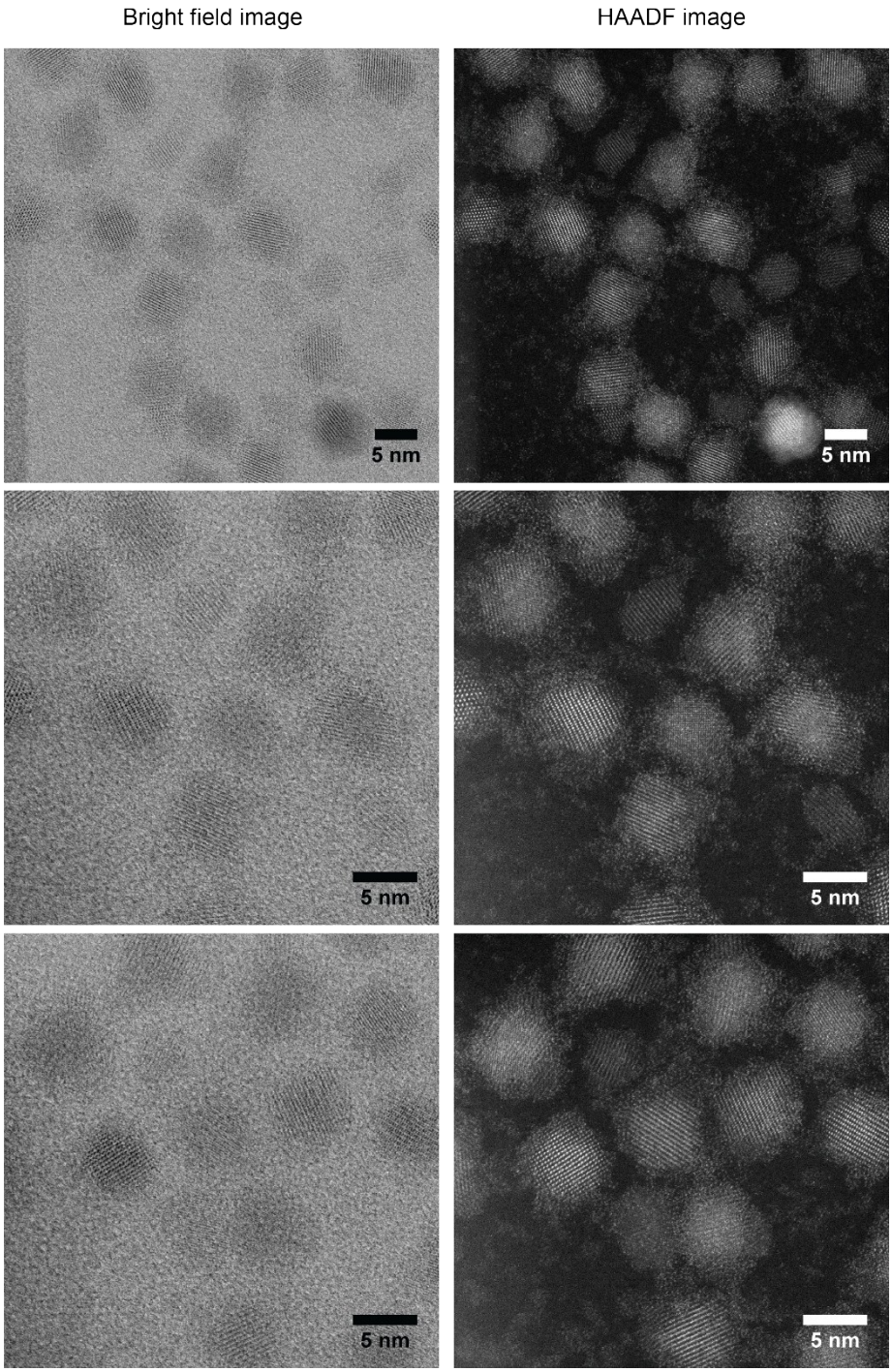


Figure S4: High-resolution high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) of PbS / 3 ML CdS.

The contrast between the PbS core and the CdS shell is visible on the images, as well as some smaller nanocrystals that have a lower contrast, which are probably CdS nanocrystals that nucleated during the addition of the Cd and S precursors for the shell growth.

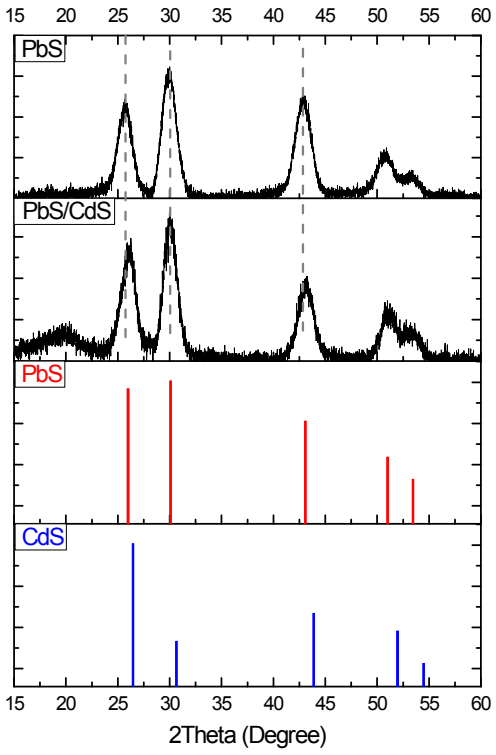


Figure S5:XRD diffractograms of PbS and PbS/CdS (upper two panels) and reference patterns for cubic PbS and CdS (lower two panels).

The XRD peaks for cubic PbS and CdS are very close to each other, but the CdS peaks are on the higher 2θ side, which explains the slight shift of the peak positions between the PbS core only and the PbS/CdS QDs, and confirms the presence of a CdS phase. This shift may also be due to a compressive strain of the PbS by the CdS shell (which has a smaller lattice parameter), which also confirms the presence of a CdS phase.

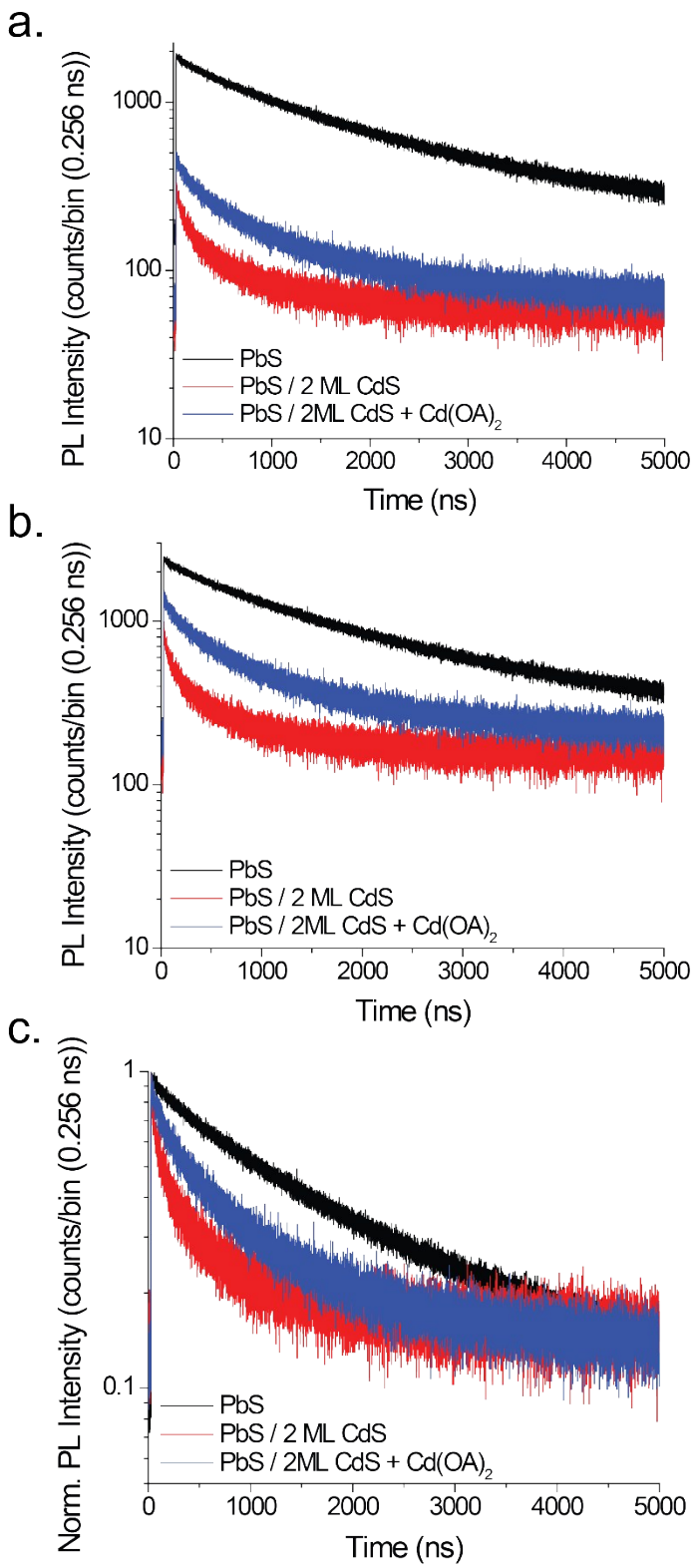
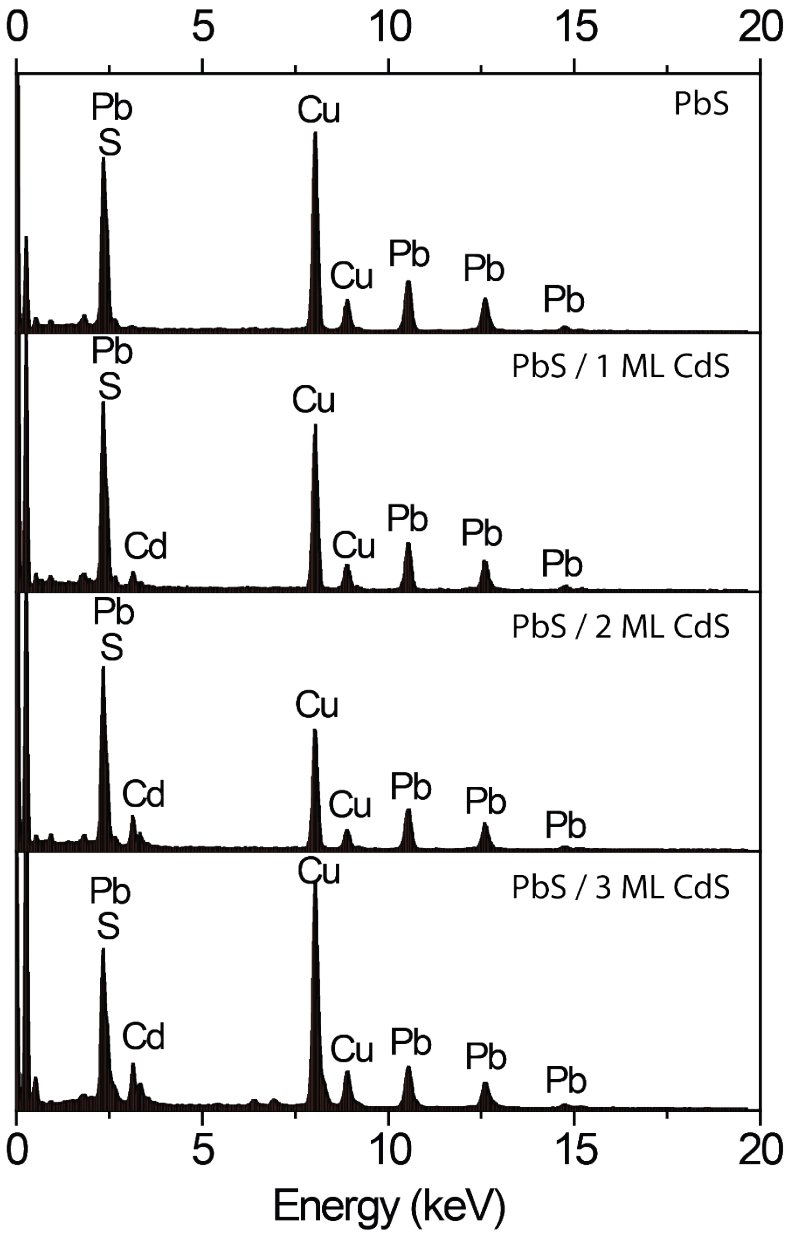


Figure S6: PL decay for PbS QDs (black), PbS/ 2 ML CdS QDs (red) and PbS/ 2 ML CdS QDs with added $Cd(OA)_2$ (blue). a. Raw data. b. Raw data normalized by the concentration of the solution. c. Raw data normalized to the excitation pulse. Excitation wavelength: 785 nm, repetition rate 100 kHz.

To measure the lifetime decay dynamics by time-correlated single-photon counting (TCSPC), samples are excited by a pulsed diode laser (PicoQuant LDH-P-FA-530-B) at λ=785 nm. The excitation power (35nW) is scaled to ensure that the probability of detecting a photon during a single excitation pulse is below 5% for the PbS sample, the threshold above which pile-up artefacts can cause inaccuracies. The same excitation power is kept for the other samples, which are less concentrated and of a lower or similar QY (and thus the probability stays below 5%). The emission from the nanocrystals is collected using parabolic mirrors and detected by a InGaAs/InP single-photon avalanche photodiode (Micro Photon Devices $IR-DH-025-C), for 1h. Scattered excitation laser light is removed with a 900 nm long pass filter (Chroma Technology Corp. ET900LP). A PicoQuant PicoHarp 300 records the photon arrival times resulting in the decay histogram.

The quantum yield is related to the area under the PL decay curve. Assuming a 7% QY for the initial PbS QDs, the areas under the curves for PbS/CdS and PbS/CdS+Cd$(OA)_2$ give QY values of 2.1 and 3.5 % respectively, which corresponds, within experimental error, to the values measured with the integrative sphere.



Pb	**100%**
Cd	**0%**

Pb	**85%**
Cd	**15%**

Pb	**69%**
Cd	**31%**

Pb	**60%**
Cd	**40%**

Figure S7: Energy Dispersive X-ray Analysis (EDX) for PbS QDs and PbS coated with 1, 2 or 3 monolayers of CdS. In the tables are presented the atomic proportion of Pb and Cd. The lines used for the quantification were the L line for Cd (~3 keV) and L line for Pb (~11-14 keV). The K line for S (~~2.3 keV) has some overlap with the M line for Pb (~2.4 keV) which makes the quantification of S unreliable.

1 L. Cademartiri, J. Bertolotti, R. Sapienza, D. S. Wiersma, G. von Freymann and G. A. Ozin, *J. Phys. Chem. B*, 2006, **110**, 671–673.

2 I. Moreels, Y. Justo, B. De Geyter, K. Haustraete, J. C. Martins and Z. Hens, *ACS Nano*, 2011, **5**, 2004–2012.

3 S. Ithurria and D. V. Talapin, *J. Am. Chem. Soc.*, 2012, **134**, 18585–90.