Supporting Information

for

The Different Nature of Band Edge Absorption and Emission in PbSe/CdSe Core/shell Colloidal Quantum Dots

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EDX measurements on PbSe/CdSe QDs

Typical PbSe QDs have a Pb-terminated surface¹. The number of Pb atoms can be calculated from the diameter¹:

$$[Pb] = 4\frac{4\pi}{3}(\frac{d}{2a})^3 - Ad^2$$

with A = 6.8, *a* the lattice constant of PbSe and d the diameter. The last term accounts for the nonstoichiometry of PbSe QDs. Using EDX we measure the Pb/Se ratio of the original PbSe QD and of the PbSe/CdSe QD. Since the amount of Se stays constant, we can calculate the amount of Pb in the PbSe/CdSe QD. Because the stoichiometry of this core is not known, we set the stoichiometry of the PbSe core in a PbSe/CdSe core/shell QD equal to the stoichiometry of a PbSe core QD containing the same amount of Pb. This means that we work with Pb terminated cores in the core/shell QDs as well. An argument in support of this definition is that the PbSe/CdSe interfaces are mainly (111) planes, which are either anion or cation planes. Hence, using a Pb terminated core would correspond to PbSe/CdSe interfaces where the Pb planes are part of the PbSe core while the Se planes are attributed to the CdSe shell.

Determination of the oscillator strength from the absorption spec-

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In accordance to reports on the PbSe, PbS and CdSe oscillator strength ^{1–4} of the bandgap transition, we calculated the oscillator strength by integrating the low energy half of the absorption onset. Other reports on experimentally determined oscillator strengths of QDs use a fit of a series of gaussian functions with a polynomial background function, similar to the one used to determine

the Stokes shift in this work, to integrate the first excitonic absorption feature⁵. Here we include a comparison between both techniques, showing that both yield similar values and trends (see Figure 2). For the fitting procedure, we include a figure with a typical fitting result (see Figure 1) and a table (see Table 1) with the mean energy and full-with-at-half-maximum (FWHM) and their absolute error from these fits.



Figure 1: Deconvolution of the experimental absorption spectrum (red curve) into two gaussian functions and a polynomial background function (black). The resulting fitting curve is plotted in blue.

Table 1: Mean energy and FWHM with abso	lute errors of a	gaussian fit at the	first exciton p	peak on
different aliquots of two PbSe/CdSe growth	procedures.			

PbSeC	dSeY018	10min	20min	30min	40min	60min	80min	120mi	n 200min	300min
En	lergy	0.803	0.838	0.859	0.874	0.902	0.940	0.950	0.976	1.019
Error	energy	0.000	0.013	0.001	0.009	0.006	0.007	0.004	0.001	0.002
FW	VHM	106	126	125	138	121	174	173	171	219
Error	FWHM	1	0	7	0	0	0	0	0	0
	PbSeCdS	eY039	10min	20min	30min	40min	60min	80min	120min	
ĺ	Energy		1.000	1.090	1.143	1.155	1.196	1.220	1.253	
Error energy		0.005	0.003	0.006	0.002	0.006	0.001	0.001		
	FWH	Μ	165	137	250	231	243	282	333	
	Error FWHM		10	0	21	0	21	0	0	



Figure 2: Absorption oscillator strength $f_{if,abs}$ for PbSe QDs (blue markers) and PbSe/CdSe QDs (full red markers using direct integration of the lower energy half of the absorption onset and full green markers using integration of a gaussian fitting function) as a function of the core diameter.

Determination of the relative quantum yield

Quantum yield is defined as the ratio of the emitted photon flux to the absorbed photon flux:

$$QY = \frac{\Phi_{em}}{\Phi_{abs}}$$
$$= \frac{\int \frac{P(E)}{E} dE}{\frac{P_{ex}}{E_{ex}} (1 - T(E_{ex}))}$$
$$= \frac{\int \frac{P(E)}{E} dE}{\frac{P_{ex}}{E_{ex}} (1 - 10^{-\alpha(E_{ex})l})}$$

with P_{ex} the excitation power, E_{ex} the excitation energy, $\alpha(E_{ex})$ the absorbance at the excitation energy and I the path length through the cuvette. Care is taken to avoid exposure to air of the PbSe QD samples. The PL spectrum is corrected for the grating and detector efficiency and converted to an energy scale, using the formula:

$$P(E) = P(\lambda) \frac{\lambda^2}{hc}$$

with $P(\lambda)$ the intensity spectrum on a wavelength scale as measured on the PL setup. A gaussian is fitted to the P(E) spectrum and the area under the gaussian is determined.

Since P_{ex} is not known in absolute value, but is kept constant for all measurements, we can

make a relative comparison between the QY of different samples. In Figure 3 we see the relative QY for PbSe and PbSe/CdSe QDs, by assigning a value of 100 to the most luminescent sample.



Figure 3: (a) Relative QY for PbSe/CdSe (red dots) and PbSe (blue squares) as a function of the core diameter. The red line is a guide to the eye.

Effective mass model

The wavefunctions were calculated using COMSOL Multiphysics by solving the Schrödinger equation numerically in spherical coordinates for a free particle in a spherical potential well. At the interface between PbSe and CdSe, the wavefunctions satisfy the following conditions:

$$\begin{aligned} \Psi_c(r_c) &= \Psi_{sh}(r_c) \\ \frac{1}{m_c} \frac{d\Psi_c}{dx} \mid_{r_c} &= \frac{1}{m_{sh}} \frac{d\Psi_{sh}}{dx} \mid_{r} \end{aligned}$$

The overlap is calculated as $\int_0^\infty r^2 \Psi_e \Psi_h^* dr$.

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