## 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 surface ${ }^{1}$. The number of Pb atoms can be calculated from the diameter ${ }^{1}$ :

$$
[P b]=4 \frac{4 \pi}{3}\left(\frac{d}{2 a}\right)^{3}-A d^{2}
$$

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 $\mathrm{Pb} / \mathrm{Se}$ ratio of the original PbSe QD and of the $\mathrm{PbSe} / \mathrm{CdSe} \mathrm{QD}$. Since the amount of Se stays constant, we can calculate the amount of Pb in the $\mathrm{PbSe} / \mathrm{CdSe} \mathrm{QD}$. Because the stoichiometry of this core is not known, we set the stoichiometry of the PbSe core in a $\mathrm{PbSe} / \mathrm{CdSe}$ 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 $\mathrm{PbSe} / \mathrm{CdSe}$ interfaces are mainly (111) planes, which are either anion or cation planes. Hence, using a Pb terminated core would correspond to $\mathrm{PbSe} / \mathrm{CdSe}$ 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-

## trum

In accordance to reports on the $\mathrm{PbSe}, \mathrm{PbS}$ 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 feature ${ }^{5}$. 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 absolute errors of a gaussian fit at the first exciton peak on different aliquots of two $\mathrm{PbSe} / \mathrm{CdSe}$ growth procedures.

| PbSeCdSeY018 | 10min | 20 min | 30 min | 40 min | 60 min | 80 min | 120 min | 200 min | 300 min |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Energy | 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 |
| FWHM | 106 | 126 | 125 | 138 | 121 | 174 | 173 | 171 | 219 |
| Error FWHM | 1 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 |
| PbSeCdSeY039 10 min 20 min 30 min 40 min 60 min 80 min $\mathbf{1 2 0 \mathrm { min }}$ |  |  |  |  |  |  |  |  |  |
| Energy |  | 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 |  |  |
| FWHM | 165 | 137 | 250 | 231 | 243 | 282 | 333 |  |  |
| Error FWHM | 10 | 0 | 21 | 0 | 21 | 0 | 0 |  |  |



Figure 2: Absorption oscillator strength $f_{i f, a b s}$ for PbSe QDs (blue markers) and $\mathrm{PbSe} / \mathrm{CdSe} \mathrm{QDs}$ (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:

$$
\begin{aligned}
Q Y & =\frac{\Phi_{e m}}{\Phi_{a b s}} \\
& =\frac{\int \frac{P(E)}{E} d E}{\frac{P_{e x}}{E_{e x}}\left(1-T\left(E_{e x}\right)\right)} \\
& =\frac{\int \frac{P(E)}{E} d E}{\frac{P_{e x}}{E_{e x}}\left(1-10^{-\alpha\left(E_{e x}\right) l}\right)}
\end{aligned}
$$

with $P_{e x}$ the excitation power, $E_{e x}$ the excitation energy, $\alpha\left(E_{e x}\right)$ the absorbance at the excitation energy and 1 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:

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

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 $P_{e x}$ 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 $\mathrm{PbSe} / \mathrm{CdSe} \mathrm{QDs}$, by assigning a value of 100 to the most luminescent sample.

(a)

Figure 3: (a) Relative QY for $\mathrm{PbSe} / \mathrm{CdSe}$ (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:

$$
\begin{aligned}
\Psi_{c}\left(r_{c}\right) & =\Psi_{s h}\left(r_{c}\right) \\
\left.\frac{1}{m_{c}} \frac{d \Psi_{c}}{d x}\right|_{r_{c}} & =\left.\frac{1}{m_{s h}} \frac{d \Psi_{s h}}{d x}\right|_{r_{c}}
\end{aligned}
$$

The overlap is calculated as $\int_{0}^{\infty} r^{2} \Psi_{e} \Psi_{h}^{*} d r$.

## References

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