

Supporting Information to

Shape-Dependent Multi-Exciton Emission and Whispering Gallery Modes in Supraparticles of CdSe/Multi-Shell Quantum Dots

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Synthesis of core/multi-shell quantum dots

All QD syntheses were performed in a nitrogen atmosphere and stored in a glovebox and with pre-dried chemicals.

Chemicals. Cd(Ac)₂ (Sigma-Aldrich, 99%), diethylzinc (Et₂Zn, Sigma-Aldrich, 1.0 M solution in hexane), Oleic acid (OA, Sigma-Aldrich, 90%), octadecene (ODE, Sigma-Aldrich, 90%), octadecene amine (ODA, Sigma-Aldrich, 90%) selenium (Strem Chemicals, 99.99%), sulphur (Alfa Aesar, 99%), trioctylphosphine (TOP, Sigma-Aldrich, 90%), trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%), were used for the synthesis of nanoparticles (NPs).

Solvents. Acetone (Merck), cyclohexane (Sigma-Aldrich, anhydrous, 99%), hexane (Sigma-Aldrich, anhydrous, 99.8%), methanol (Sigma-Aldrich, anhydrous, 99.8%), toluene (Sigma-Aldrich, anhydrous, 99.8%)

Synthesis of CdSe nanocrystal seeds. Following Ref. 1. Prior to the synthesis of the CdSe quantum dots 2 precursors were synthesized. OA (3.68 g), ODE (25.92 g), and Cd(Ac)₂ (0.64 g) were mixed, heated to 150°C, and kept under vacuum for 2 h to form Cd(OA)₂. Selenium (4.25 g) was dissolved in TOP (22.5 g) at 50°C, followed by the addition of ODE (35.7 g).

CdSe nanocrystal seeds were synthesized in 50 ml three-neck flask using a Schlenk-line. TOPO (1.11 g), ODA (3.20 g), and Cd(OA)₂-precursor (4.9 g) were mixed, heated to 300°C. When this temperature was reached the Se-precursor (5.2 g) was added rapidly. The size of the quantum dots can be tuned via changing the reaction time. The particles were diluted by adding 1 equivalent of hexane. The quantum dots were washed by adding 2 equivalents of methanol and collecting the upper hexane layer (coloured) and add 1 equivalent of acetone to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in toluene and stored inside a glove box under nitrogen atmosphere.

Typical synthesis of CdSe/CdS/CdZnS/ZnS nanocrystals. Prior to the synthesis of the CdSe quantum dots three precursors were prepared. The zinc precursor solution (0.1 M) was

prepared by dissolving Zn(Et)₂ (0.494 g) in oleic acid (5.05 mL) and ODE (19.8 mL) at 310 °C. The cadmium precursor solution (0.1 M) was prepared by dissolving Cd(Ac)₂ (1.10 g) in oleic acid (10.83 g) and ODE (43.20 mL) at 120°C under vacuum for 2 hours. The sulphur precursor solution (0.1 M) was prepared by dissolving sulphur (0.032 g) in ODE (10 mL) at 180 °C. The Cd-, Zn-, and Cd/Zn-precursor solutions were kept at about 80 °C, while the sulphur injection solution was allowed to cool to room temperature. For each shell growth, a calculated amount of a given precursor solution was injected with a syringe using standard air-free procedures. CdSe QDs (1·10⁻⁷M of 2.91 nm QDs), ODE (5.0 g) and ODA (1.5 g) were combined and heated up to 150 °C for 1 h to remove all toluene. The reaction temperature was increased to 240 °C and in steps with reaction periods of 30 minutes the precursors were added slowly to grow the cell half-monolayer by half-layer.

Step	Total # monolayers	Added Precursors	Amount (μ L)
1	0.5	Cd+S	130
2	1	Cd+S	165
3	1.5	Cd+S	205
4	2	Cd+S	250
5	2.5	Cd+S	295
6	3	Cd+S	350
7	3.5	Cd+S	410
8	4	Cd+S	470
9	4.5	Cd+S	540
10	5	Cd+S	610
11	5.5	CdZn+S	690
12	6	CdZn+S	770
13	6.5	Zn+S	855
14	7	Zn+S	940

Afterwards the reaction mixture was cooled to room temperature and diluted by adding 1 equivalent of hexane. The quantum dots were washed by adding 2 equivalents of methanol and collecting the upper hexane layer (coloured) and add 1 equivalent of acetone to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in cyclohexane and stored inside a glove box under nitrogen atmosphere.

Determination of quantum yield of multi-shell quantum dots and supraparticles

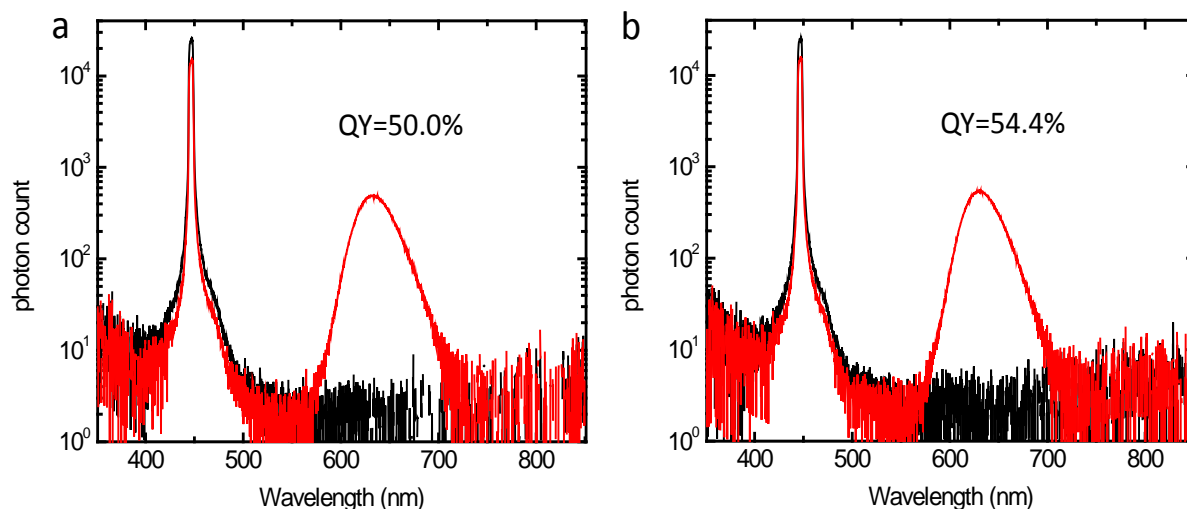


Figure S1. Integrating sphere photon emission spectra of multi-shell quantum dot and supraball dispersions. (a) Emission spectra of the quantum dot solution in cyclohexane (red line) in a capillary, and pure cyclohexane (black line) as a reference. (b) Emission spectra of the dispersion of supraballs in water (red line) in a capillary, and pure water (black line) as a reference. From these measurements we determined the quantum yields as:

$$QY = \frac{\int_{480}^{800} \text{Phot. count}_{\text{sample}} d\lambda - \int_{480}^{800} \text{Phot. count}_{\text{ref}} d\lambda}{\int_{430}^{550} \text{Phot. count}_{\text{ref}} d\lambda - \int_{430}^{550} \text{Phot. count}_{\text{sample}} d\lambda} * 100$$

Evolution of the optical resonances from core-only to core multishell nanocrystals

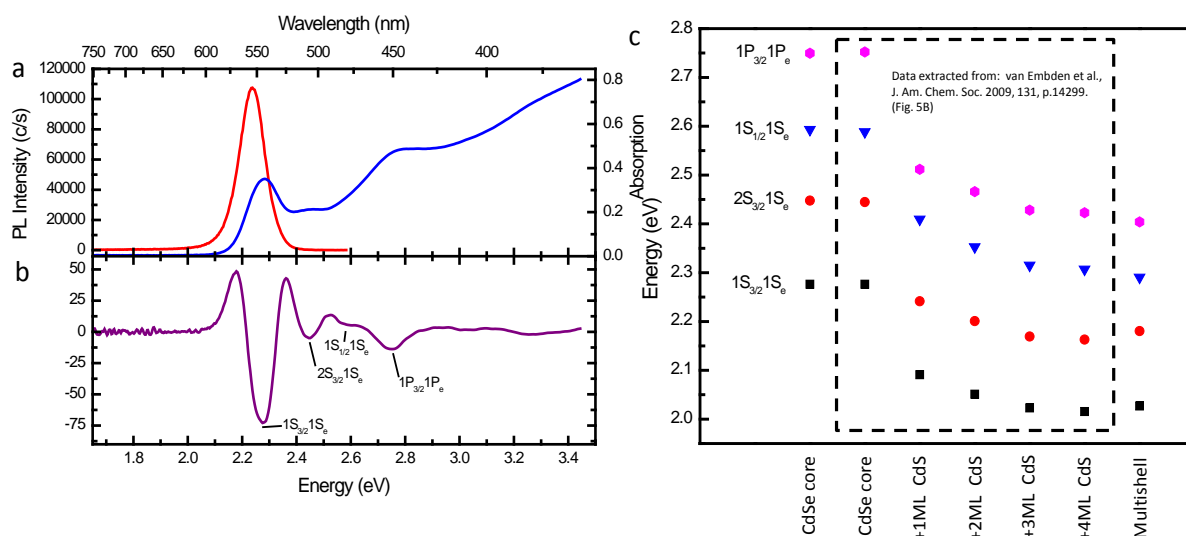


Figure S2. Determination and assignment of transition energies of core-only and core/multi-shell quantum dots. (a) Low excitation intensity PL (left axis, red line) and absorption (right axis, blue line) spectra of the CdSe core-only quantum dots. (b) Assignment of the transitions in the second derivative of the absorption spectrum shown in a. (c) Comparison of the determined transition energies of our CdSe core only (first column) and multi-shell (last column) quantum dots with those extracted from absorption spectra taken during the incremental CdS monolayer shelling of a similarly sized CdSe core published by Van Embden *et al.* [2] As can be seen, the largest transition energy (red)shift of 190 meV occurs upon the application of the first monolayer of CdS. Subsequent addition of the second CdS monolayer already yields a much smaller redshift of 40 meV and the fourth monolayer yields only a redshift of 7 meV. In any case, the energetic position of the lowest energy absorption peak of the multi-shelled nanocrystals gives a good indication of the total shift of the core levels which can thus be assigned to the $1S_{3/2}1S_e$, $2S_{3/2}1S_e$, $1S_{1/2}1S_e$ and $1P_{3/2}1P_e$ levels in the multi-shell quantum dots.

The power dependence of multi-exciton emission

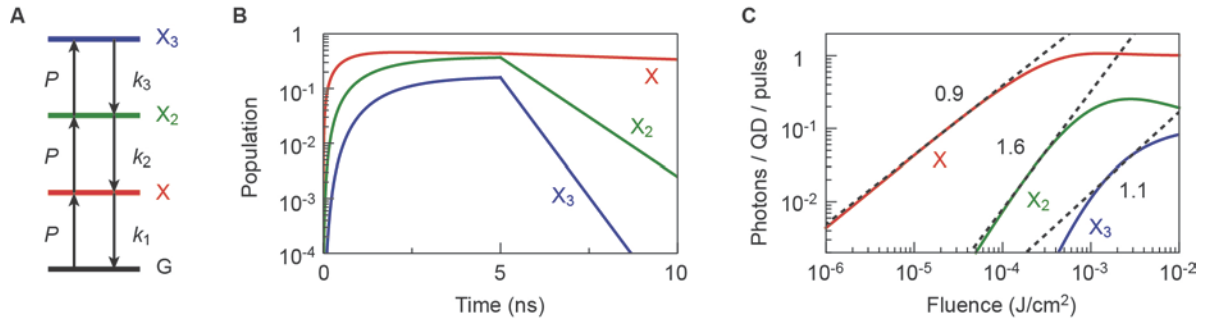


Figure S3. Rate equation modeling of multi-exciton populations. (a) We employ a four-level rate equation model to simulate the consecutive population of multi-exciton states. The system is pumped from the ground state G to higher states X (single exciton), X_2 (biexciton) and X_3 (triexciton) at a rate P (non-resonant absorption followed by carrier cooling). The excited states X , X_2 and X_3 decay at rates k_1 , k_2 and k_3 , respectively. We use values of $k_1 = 1/20$ ns, $k_2 = 1/1$ ns and $k_3 = 1/500$ ps [3,4]. We model the experiment with 10 ns pulses with a time-dependent pump rate of $P(t) = J\sigma/T\hbar\nu$ (with J the fluence, $\sigma = 5 \times 10^{-15}$ cm² the absorption cross-section of the QDs, $T = 5$ ns the pulse duration, and $\hbar\nu = 3.56$ eV the photon energy) if $t < 5$ ns, and $P(t) = 0$ if $t > 5$ ns. (b) The evolution of the population of multi-exciton states simulated for a fluence of $J = 10^{-3}$ J/cm². They reach a steady state within 5 ns. (c) The simulated emission intensity from each of the three states as a function of excitation power: $I_i = \eta_i k_i \int N_i(t) dt$, where I_i , η_i , k_i and N_i are the emission, the quantum efficiency, the decay rate, and the population of level i , respectively. We assume that for the bright fraction of QDs in the ensemble $\eta_1 = 1$, $\eta_2 = 0.1$ and $\eta_3 = 0.01$. The resulting slopes in the log-log plot are not constant, but depend on the fluence. If we nevertheless fit a single power exponent to the data points between 10^{-2} and 5×10^{-2} photons / QD / pulse, we obtain values well below the naively expected powers of 2 and 3 for biexciton and triexciton emission (namely, 1.6 and 1.1).

Chemical mapping of the multi-shell quantum dots using STEM-EDS

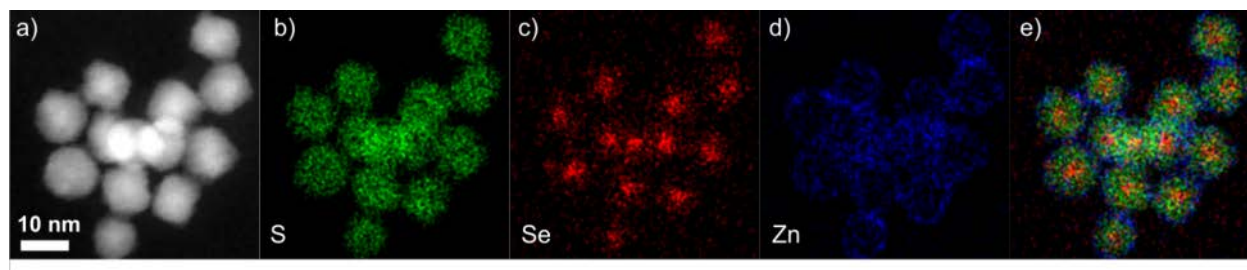


Figure S4. Chemical mapping of the multi-shell quantum dots. (a) HAADF-STEM image (high angle annular dark field scanning transmission electron microscopy) of several individual quantum dots. (b–d) Quantified STEM-EDS chemical maps for the elements (b) S, (c) Se, and (d) Zn. (e) Overlay image of panels b–d.

References

- [1] Kloper, V.; Osovsky, R.; Cheskis, D.; Sashchiuk, A.; Lifshitz, E. Suppressed Blinking in CdTe/CdSe Core-Shell Quantum Dots. *Phys. Status Solidi C* **2009**, *6*, 2719–2721.
- [2] Van Embden, J.; Jasieniak, J.; Mulvaney, P. Mapping the Optical Properties of CdSe/CdS Heterostructure Nanocrystals: The Effects of Core Size and Shell Thickness. *J. Am. Chem. Soc.* **2009**, *131*, 14299–14309.
- [3] Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots. *Science* **2000**, *287*, 1011–1013.
- [4] Park, Y.-S.; Bae, W. K.; A. Padilha, L. A.; Pietryga, J. M.; Klimov, V. I. Effect of the Core/Shell Interface on Auger Recombination Evaluated by Single-Quantum-Dot Spectroscopy. *Nano Lett.* **2014**, *14*, 396–402.