Mechanistic Insights in Seeded Growth Synthesis of Colloidal Core/Shell Quantum Dots Supporting Information

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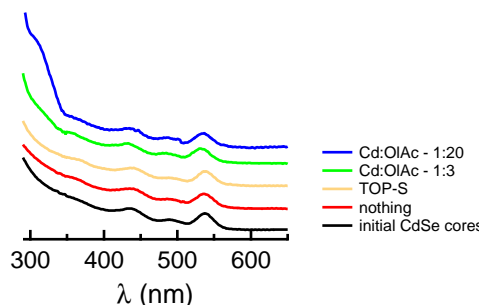
S1 Seeded growth, blank control experiments

Figure S1: Absorption spectrum of (black) CdSe cores used as seeds in blank seeded-growth reactions. The reaction mixtures contain (red) neither Cd nor S precursors, (orange) only TOP-S, (green) cadmium oleate and oleic acid in a 1:3 ratio and (blue) cadmium oleate and oleic acid in a 1:20 ratio. All reaction conditions were set as discussed in the Experimental Methods section and all spectra have been recorded on 300 s aliquots taken and have been normalized at the peak absorbance of the first exciton transition.

To evaluate possible ripening or dissolution of the CdSe cores during a seeded growth reaction, we ran a series of blank reactions. These consisted of 4 reactions in which 50 nmoles of CdSe cores where injected in reaction mixtures containing only one or none of the reactive precursors, *i.e.*, tri-octylphosphine sulfur and cadmium oleate. All remaining compounds were added in exactly the same amounts and at same conditions as described in the Methods section. We measured the absorption of unpurified aliquots taken at 300 s after the injection of the CdSe seeds. In combination with the mass of the aliquot, this enabled us to assess changes in size and concentration of the CdSe seeds. As can be seen in Figure S1, all blank reactions leave the first exciton absorption unchanged. As we found no significant change in the core concentration, we conclude that CdSe cores do not suffer from ripening or dissolution during a seeded-growth reaction.

Note that all spectra shown in Figure S1 were measured on unpurified aliquots. Especially in the case of the cadmium oleate / oleic acid 1:20 blank reaction, this leads to a pronounced additional absorbance of oleic acid at wavelengths shortern than ≈ 350 nm.

S2 Quantum Dots by Seeded Growth, Selected Area Diffraction

The crystal structure of the CdSe/CdS and CdSe/ZnSe core/shell QDs formed through seeded growth using either a zinc blende CdSe or a wurtzite CdSe core was determined using selected area electron diffraction in a transmission electron microscope. Figure S2 provides an overview of the electron diffraction patterns of all 4 core/shell systems. It can be seen that core/shell nanocrystals formed using a zinc blende CdSe core have overall a zinc blende structure. On the other hand, using a wurtzite seed results in nanocrystals with an overall wurtzite structure.
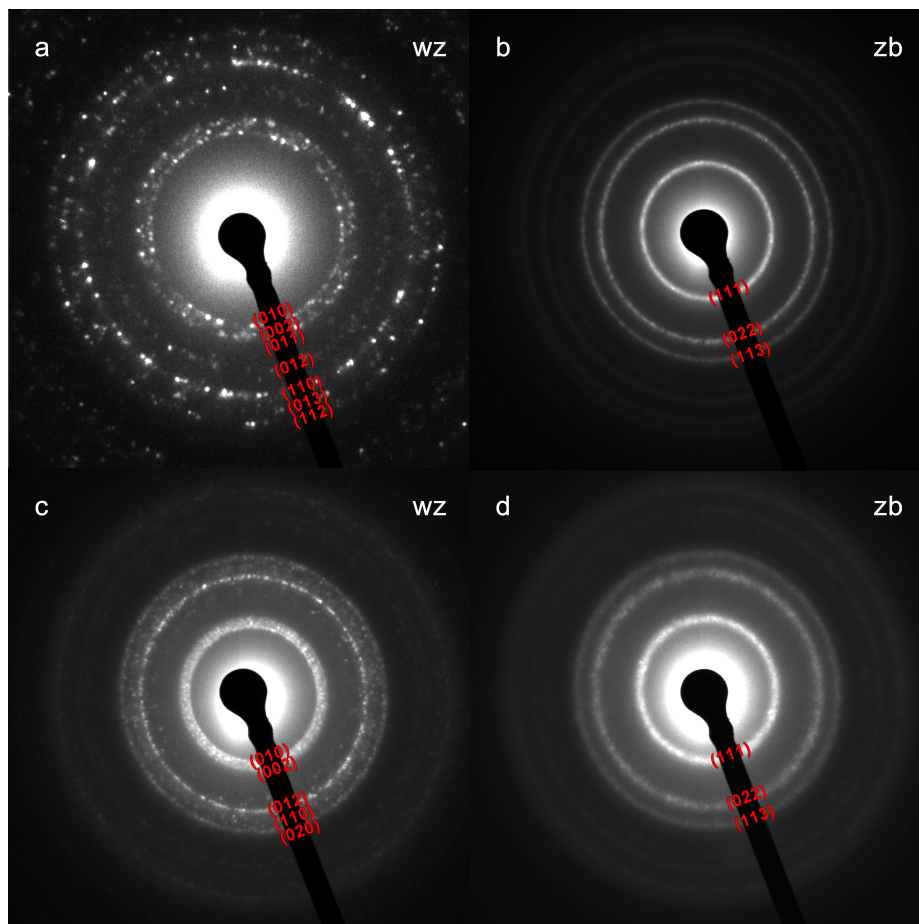

Figure S2: SAED of the different core/shell nanocrystal samples used for TEM analysis: (a) wz-CdSe/CdS. (b) zb-CdSe/CdS. (c) wz-CdSe/ZnSe. (d) zb-CdSe-ZnSe.

S3 Reaction simulations

S3.1 Model equations

The modeling approach used here is based on a kinetic scheme where injected precursors P react to form a solute or monomer M, which precipitates to form QDs:

$$P \longrightarrow M \longleftrightarrow QD \tag{S1}$$

Following this scheme, the central quantities in the modeling are (1) the concentration distribution $c(r, t)$ of QDs where the product $c(r, t)dr$ yields the concentration of QDs with a radius between r and $r + dr$ at time t (2) the supersaturation $S(t)$, which is defined as the ratio between the actual concentration of the solute or monomer and its equilibrium concentration $[M]_0$ and (3) the precursor concentration $[P]$. For simplicity, the model assumes a single precursor. The concentration distribution $c(r, t)$ changes with time since new QDs nucleate (index N) and existing QDs grow (index G):[1]

$$\left.\frac{\partial c}{\partial t}\right|_N + \left.\frac{\partial c}{\partial t}\right|_G = J_N \delta(r - r_c) - \frac{\partial (j_G c)}{\partial r} \tag{S2}$$

In the above expression, we describe nucleation as the formation of QDs with the critical radius r_c at a rate J_N , both given by classical nucleation theory:

$$r_c = \frac{2\gamma V_m}{RT \ln S} \tag{S3}$$

$$J_N = \frac{2D}{v_0^{5/3}} exp\left(-\frac{16\pi \gamma^3 V_m^2 N_A}{3(RT)^3 (\ln S)^2}\right) \tag{S4}$$

Here, D stands for the monomer diffusion coefficient; v_0 is the monomer volume; γ is the surface tension of the QD; V_m is the molar volume of the QD material; N_A is Avogadro's constant; R is the gas constant, and T is the absolute temperature The growth term in Eq S2 is written in terms of the QD growth rate j_G, which is defined as the change of the QD

radius with time (i.e., $j_G = dr/dt$). In this work, we use the expression for the growth rate as proposed by Talapin et al.:[2]

$$j_G = \frac{dr}{dt} = DV_m \left[M\right]_0 \left\{ \frac{S - exp\left(\frac{2\gamma V_m}{rRT}\right)}{r + \frac{D}{k_g^\infty}exp\left(\alpha\frac{2\gamma V_m}{rRT}\right)} \right\} \tag{S5}$$

Here, $\left[M\right]_0$ is the solubility of the monomer, k_g^∞ is the monomer adsorption rate constant for a flat surface and α is the transfer coefficient of the monomer adsorption reaction. Regarding the supersaturation S, we assume that its time-dependence is governed by the generation of monomers from the precursors and by their consumption through the nucleation and the growth of nuclei. Writing the monomer generation rate as G_M, dS/dt thus reads:[1]

$$\frac{dS}{dt} = \frac{1}{\left[M\right]_0} \left\{ G_M - \frac{4\pi r_c^3}{3v_0}J_N + \int_0^\infty \frac{4\pi r^3}{3v_0}\frac{\partial(j_G c)}{\partial r}dr \right\} \tag{S6}$$

Finally, the monomer generation rate G_M also determines the change of the precursor concentration [P] with time. For simplicity, we assume here a first order rate equation which agrees with the experimental CdSe synthesis under conditions of a large Se excess:

$$\frac{d\left[P\right]}{dt} = -G_M = -k_1\left[P\right] \tag{S7}$$

S3.2   Reaction simulations and parameter values

The coupled differential Equations S2, S6 and S7 were implemented in COMSOL Multiphysics. A one-dimensional simulation domain for the nanocrystal radius ranging from 0 to 8 nm was divided in 1274 elements. From 0 to 0.2 nm an absorbing boundary condition was implemented to account for nanocrystal dissolution into monomers. The nucleation term was implemented as a Gaussian function with a width of 0.01 nm, centered 0.03 nm above the critical radius. The monomer diffusion coefficient D was chosen according to measured values for cadmium oleate in toluene at room temperature. The monomer volume was taken

as the volume of a single spherical CdSe unit in the zincblende CdSe unit cell. The term $RT/2\gamma V_m$ and the monomer solubility $[M]_0$ was adjusted to yield a realistic nucleation radius of ≈ 0.5 nm and a final QD concentration and radius comparable to what is obtained in the experiments. The monomer adsorption rate constant k_g^∞ was chosen to be in the diffusion-limited growth regime. The magnitude of the first order monomer generation rate constant was set equal to the experimental value for the product $k_2 [P_{Se}]$ obtained from the experimental yield development. Especially in terms of reaction speed, the values for k_1 (0.03333 s^{-1}) and $[M]_0$ $(2 \, 10^{-11} \text{ mol/L})$ imply a fast reaction with a low monomer solubility.

Table S1: Overview of the different parameters in the reaction simulations and their respective value used for the reference simulation.

Symbol	Parameter Description	Value	Unit
D	Monomer diffusion coefficient	$0.5 \, 10^{-9}$	m^2/s
v_0	Monomer volume	$1.33 \, 10^{-29}$	m^3
$[M]_0$	Monomer solubility	$2 \, 10^{-8}$	mol/m^3
T	Absolute temperature	553.15	K
γ	Surface tension	0.24	N/m
α	Transfer coefficient	0.5	–
V_m	Molar volume of CdSe	$3.367 \, 10^{-5}$	m^3/mol
k_g^∞	Monomer adsorption rate constant	$5 \, 10^{-7}/[M]_0$	m/s
k_1	Monomer generation rate constant	0.03333	1/s
$[P]_0$	Initial precursor concentration	0.01667	mol/L

S3.3   Seeded growth modifications

The effects of seeded growth were included in the reaction simulations by imposing an initial concentration distribution $c(r, t = 0)$. No additional modifications of the model formalism are needed, however the one-dimensional simulation domain must be chosen large enough to accomodate the growth of the seeded nanocrystals which compete with nucleation for monomer consumption. The initial distribution was chosen as a Gaussian expression:

$$c(r,0) = \frac{c_0}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{r-\mu}{\sigma}\right)^2} \tag{S8}$$

where c_0 is the total concentration obtained when integrating the distribution, μ the average seed radius and σ the size dispersion of the seed distribution. c_0, μ and σ were chosen to be 10 μM, 1.54 nm and 6 % respectively during the simulations used for Figures 4 and 5 of the main article.

References

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