

Supporting Information for: Stranski-Krastanov shell growth in ZnTe/CdSe core/shell nanocrystals.

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Synthesis and experimental methods.

Chemicals

Diethyl zinc ($\text{Zn}(\text{Et})_2$, 96%), tellurium (Te, 99.8%), oleic acid (90%), selenium (Se, 99%) and chloroform (CHCl_3 , 99.8%) were obtained from Alfa Aesar. Cadmium oxide (CdO , 99.5%), trioctylphosphine (TOP, 97%), octadecene (ODE, 90%), methanol (MeOH , 98%), toluene (99%), phenothiazine (PTZ, 98%), and hexadecylamine (HDA, 90%) were obtained from Aldrich. TOP and ODE were purified by vacuum distillation. Oleic acid was dried by vacuum distillation with molecular sieves. Methanol, toluene, and chloroform were purified by distillation from appropriate drying agents. HDA was recrystallized from toluene before use. All other chemicals were used as received.

Precursors for shell growth

The cadmium precursor solution used for the CdSe shell growth was prepared by dissolving 0.3204 g of CdO in a mixture of 6.18 g oleic acid and 18 ml ODE at 250 °C, which gives a cadmium concentration of 0.1 M. The 0.1 M selenium stock solution was prepared by dissolving 0.1580 g of Se in 5 ml TOP and 15 ml ODE.

Synthesis of ZnTe cores and ZnTe/CdSe core/shell NCs

The synthesis of the ZnTe core NCs are performed using a procedure previously reported.¹ In a typical reaction, a 2 ml TOP solution containing 0.50 mmol Te and 0.50 mmol $\text{Zn}(\text{Et})_2$ in is quickly injected into a reaction flask loaded with 3 g HDA and 4 g ODE at 280 °C. Following injection, the reaction temperature drops to 270 °C, allowing for the growth of nanoparticles for 3 min. This produces the ZnTe NCs with a diameter of 2.6 nm.

For the growth of CdSe shell, the reaction mixture obtained above is cooled to the predefined temperature, usually 215 or 240 °C. 1.0 ml of the cadmium precursor stock solution (described above) is added dropwise, followed by addition of a same amount of the Se precursor, also added dropwise. The reaction is then run for 15 min. Subsequent shell growth is accomplished by the alternate dropwise addition of the same amounts of cadmium and selenium shell precursors. Aliquots were taken for measurements after each set of cadmium and selenium injections. Before spectroscopic analysis, the samples are precipitated by the addition of methanol and subsequently washed by several cycles of suspension in toluene, followed by precipitation by methanol and centrifugation. The washed nanocrystals are then dispersed in CHCl_3 for the spectroscopic measurements and the PL quenching experimental.

Thermal annealing

The thermal annealing of the core/shell NC is done in one of two ways; specifically, high and low temperature annealing. In the low temperature annealing, the CdSe shell is initially grown at 240 °C, following by the annealing at 215 °C. To suppress Ostwald ripening, the samples are not washed before

the annealing. Because the shelling precursors are in equilibrium with the NCs before the annealing, the annealing results in very little change the NC size. In the high temperature annealing, the CdSe shell is grown at 215 °C and then annealed at 250 °C. Before annealing, the samples are washed and about 1/3 monolayer of the shelling precursors are then replaced. This is done to avoid the further shell growth and simultaneously suppress Ostwald ripening.

Hole quenching

Samples used for the PTZ quenching studies are prepared by mixing excess PTZ dissolved in CHCl₃ with a CHCl₃ solution of the ZnTe/CdSe NCs. Prior to spectroscopic measurements, the samples are allowed to sit for more than 3 hours to ensure that the PTZ is adsorbed to the particle surfaces.

Instrumentation

Static fluorescence spectra were obtained using a Jobin-Yvon Fluorolog-3 spectrometer. The instrument consists of a xenon lamp/double monochromator excitation source and a CCD detector. Time-resolved luminescence measurements were obtained by time-correlated single-photon counting (TCSPC), using a PicoQuant PMD 50CT SPAD detector and a Becker-Hickel SP-630 board. The light source is a cavity dumped Ti:sapphire laser (Coherent Mira) operating at 410 nm with a 1 MHz repetition rate. In all cases, the fluorescence is focused through a 0.25 m monochromator with a 150 groove/mm grating. Core sizes and shell thicknesses were determined by TEM, as previously reported.¹

Calculation description.

Interdiffusion at the core/shell interface

Interdiffusion changes the composition of the core and shell materials and softens sharpness of the core/shell interface. In general, diffusion across a radially symmetric concentration gradient is described by a diffusion equation, $\frac{dC(r,t)}{dt} = D\nabla^2 C(r,t) = D \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC(r,t)}{dr} \right)$.

For the specific case that the ions isotropically interdiffuse across an initially sharp interface with a spherical particle of a radius (R), the composition function of the materials can be expressed as:²

$$C(r,t) = \sum_i \left[\int_0^R \rho^2 d\rho j_0(z_i \rho / R) C(\rho, 0) \right] \exp \left(\frac{-D z_i^2}{R^2} t \right) j_0(z_i r / R) \quad (1)$$

where r and ρ are radial distances, j_0 is a spherical Bessel function and z_i is the i 'th zero of the j_0 . D is the interdiffusion constant. $C(\rho, 0)$ is the composition profile of the core/shell NCs before the interdiffusion. This approach amounts to expanding the initial radially dependent concentration in a Fourier-Bessel series, with each term having its own relaxation time. In the present case, both cation and anion interdiffusion are considered, but the rate of anion interdiffusion is very small, because of the anions' larger sizes and low mobilities.^{3, 4}

Radial and tangential stresses and strains

The radial dependent strain and stress caused by the core/shell lattice mismatch is calculated from elastic continuum theory.⁵ For the spherical core/shell NCs with a coherent interface, the interior pressures are dependent on the core size and the shell thickness, the extent of lattice mismatch, and the elastic properties of the materials. Due to the composition variation along the radial NC coordinate caused by

the interdiffusion, the radially dependent pressures in the spherical NCs are calculated by a concentric method, in which the core/shell NCs are considered to be composed of n concentric shells with the shell radii given by evenly spaced values of r_i . The radially dependent displacements for the i 'th and $i+1$ 'th shells in the NCs can be expressed by:²

$$u_i(r_i) = P_{i-1} A_{i,+} + P_i B_{i,+} \quad (2)$$

$$u_{i+1}(r_i) = P_i A_{i+1,-} + P_{i+1} B_{i+1,-} \quad (3)$$

$$A_{i,+} = \frac{r_i(1+\nu)}{E_i} \left(\frac{1-2\nu}{1+\nu} + \frac{1}{2} \right) \left/ \left(\left(\frac{r_i}{r_{i-1}} \right)^3 - 1 \right) \right.,$$

$$B_{i,+} = \frac{r_i(1+\nu)}{E_i} \left(\frac{1-2\nu}{1+\nu} + \frac{1}{2} \left(\frac{r_{i-1}}{r_i} \right)^3 \right) \left/ \left(\left(\frac{r_{i-1}}{r_i} \right)^3 - 1 \right) \right.,$$

$$A_{i+1,-} = \frac{r_i(1+\nu)}{E_{i+1}} \left(\frac{1-2\nu}{1+\nu} + \frac{1}{2} \left(\frac{r_{i+1}}{r_i} \right)^3 \right) \left/ \left(\left(\frac{r_{i+1}}{r_i} \right)^3 - 1 \right) \right., \text{ and}$$

$$B_{i+1,-} = \frac{r_i(1+\nu)}{E_{i+1}} \left(\frac{1-2\nu}{1+\nu} + \frac{1}{2} \right) \left/ \left(\left(\frac{r_i}{r_{i+1}} \right)^3 - 1 \right) \right.$$

where ν is the Poisson's ratio, which is taken to be ~ 0.33 .⁶⁻⁸ This value of ν is a good approximation for the most II-VI semiconductors. In the above equations P_i is the pressure in the i 'th shell and E is the Young's modulus, which is taken to scale linearly with the composition. That is, for an alloy with a composition of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Te}_y\text{Se}_{(1-y)}$, E is given as:

$$E = xyE_{\text{ZnTe}} + (1-x)yE_{\text{CdTe}} + x(1-y)E_{\text{ZnSe}} + (1-x)(1-y)E_{\text{CdSe}} \quad (4)$$

The Young's modulus for the different semiconductors is given in Table S1. With the boundary condition that $u_i(r_i) - u_{i+1}(r_i) = \varepsilon_{i,i+1}r_i$, where $\varepsilon_{i,i+1}$ is the difference in the lattice constants between the i 'th and $i+1$ 'th shell, $\varepsilon_{i,i+1} = (x_i - x_{i+1})\varepsilon$, where ε is the total relative lattice mismatch, gives $P_{i-1} A_{i,+} + P_i (B_{i,+} - A_{i+1,-}) - P_{i+1} B_{i+1,-} = \varepsilon_{i,i+1}r_i$. Here, we may define vectors of the pressures, \mathbf{P} , and lattice mismatches, $\boldsymbol{\varepsilon}$. This equation may be written in terms of the matrix \mathbf{D} , such that:

$$\mathbf{D}\mathbf{P} = \boldsymbol{\varepsilon} \quad (5)$$

where \mathbf{D} is tri-diagonal: $D_{i,i-1} = A_{i,+}$, $D_{i,i} = B_{i,+} - A_{i+1,-}$, and $D_{i,i+1} = -B_{i+1,-}$. In combination with the boundary condition that the pressure at the surface of the NCs is zero, $P_n = 0$, the solution of this matrix equation gives the radially dependent pressures, P_i , for the NCs with any radial composition profile. The radial and tangential stresses are given in terms of the pressures,

$$\sigma_r = -P_i, \text{ and } \sigma_\theta = \sigma_\varphi = \frac{P_i \left(\left(\frac{r_{i+1}}{r_i} \right)^3 + 2 \right)}{2 \left(\left(\frac{r_{i+1}}{r_i} \right)^3 - 1 \right)} - \frac{3P_{i+1}}{2 \left(1 - \left(\frac{r_i}{r_{i+1}} \right)^3 \right)}$$

The radially dependent displacements, u_r , can be obtained from Equation 2. Radial (ε_{rr}) and tangential ($\varepsilon_{\theta\theta}$ and $\varepsilon_{\phi\phi}$) strains are then obtained from the displacements, and are given by

$$\varepsilon_{\theta\theta} = \varepsilon_{\phi\phi} = u_r / r \quad \text{and} \quad \varepsilon_{rr} = \frac{du_r}{dr} - \frac{r}{a_0} \frac{da}{dr},$$

where a is the zero-pressure lattice parameter and a_0 is the lattice parameter in the core. The second term is the radial expression accounts for the change in displacement due to the radial dependence of the composition of the material and hence the zero-pressure lattice parameter. The strain energy density is then given by $E = (\sigma_r \varepsilon_r + \sigma_\theta \varepsilon_\theta + \sigma_\phi \varepsilon_\phi) / 2$.

Table S1. Parameters of different bulk semiconductors used for the spectroscopic calculations in this work.

parameter	ZnTe	ZnSe	CdTe	CdSe
lattice mismatch ^a	0	-0.07 ^{9, 10}	0.064 ¹¹	-0.003 ¹²⁻¹⁴
bulk modulus (GPa)	51.0 ¹⁵	62.4 ¹⁵	42.4 ¹⁵	53.0 ¹⁵
α (eV)	5.25 ^{16, 17}	4.54 ¹⁷	3.7 ²	2.3 ¹⁸
conduction band edge (V vs. NHE)	-1.52 ^{14, 19}	-1.16 ²⁰	-0.56 ¹⁴	-0.30 ^{21, 22}
valence band edge (V vs. NHE)	0.73 ^{14, 19}	1.58 ²⁰	0.87 ¹⁴	1.44 ^{1, 21, 22}
electron effective mass (m_0)	0.12 ^{13, 14}	0.14 ²⁰	0.10 ²³	0.13 ^{1, 14}
hole effective mass (m_0)	0.60 ^{13, 14}	0.53 ²⁰	0.40 ²³	0.45 ^{1, 14}

^a Lattice mismatch used in the calculations. These are the relative lattice constants compared to ZnTe. Negative values indicate a smaller lattice parameter than ZnTe.

Conduction band potential

In semiconductor heterostructures, the strain induced pressure changes the unit cell volume, which leads to shifts in the conduction band potential. However, the calculation of the conduction band potential shift is complicated by the anisotropic nature of the strain. Specifically, one needs to consider the effects on conduction band potentials by the radial and tangential components of the strain tensor. In this case, the strain induced shifts of conduction band potentials should be given by $\Delta E = \alpha(\varepsilon_r + \varepsilon_\theta + \varepsilon_\phi)$, where ε_r , ε_θ and ε_ϕ are the radial, theta and phi components of the strain tensor, respectively. α is the volume dependence of the bandgap change, defined as $\alpha = -(dE_{cb}/d \ln V)$. For the NCs with a composition of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Te}_y\text{Se}_{(1-y)}$, the conduction band potential can be given by:

$$\begin{aligned} E_{cb}(r) = & xy(E_{cb}(\text{ZnTe}) + (\varepsilon_r + \varepsilon_\theta + \varepsilon_\phi)\alpha_{\text{ZnTe}}) + x(1-y)(E_{cb}(\text{ZnSe}) + \\ & (\varepsilon_r + \varepsilon_\theta + \varepsilon_\phi)\alpha_{\text{ZnSe}}) + (1-x)y(E_{cb}(\text{CdTe}) + (\varepsilon_r + \varepsilon_\theta + \varepsilon_\phi)\alpha_{\text{CdTe}}) + \\ & (1-x)(1-y)(E_{cb}(\text{CdSe}) + (\varepsilon_r + \varepsilon_\theta + \varepsilon_\phi)\alpha_{\text{CdSe}}) \end{aligned} \quad (6)$$

The α values for the ZnTe, ZnSe, CdTe and CdSe are given in Table S1. In the present case, a is taken to scale linearly with the composition, i.e.,

$a = xy a_{\text{ZnTe}} + x(1-y) a_{\text{ZnSe}} + (1-x)y a_{\text{CdTe}} + (1-x)(1-y) a_{\text{CdSe}}$, in which the lattice mismatch parameters for ZnSe, CdTe, CdSe with respect to ZnTe are given in Table S1.

Valence band potential

The semiconductor alloys are known to have a valence band nonlinearly dependent upon their composition, a phenomenon termed “optical band bowing”.²⁴⁻²⁶ The band bowing greatly changes the energy gap of the semiconductor composites, and therefore has an effect on the spectroscopic properties of the NCs. The composition profile of the NCs markedly changes with the interdiffusion time and band bowing effects therefore need to be incorporated into the calculation.

The valence band potential of semiconductor alloys having a composition of $\text{MSe}_y\text{Te}_{(1-y)}$ (M represents the cations) can typically be given by:^{24, 26}

$$E_{vb} = yE_{vb}(\text{MSe}) + (1-y)E_{vb}(\text{MTe}) + by(1-y) \quad (9)$$

Where E_{vb} is the valence band potential and b is the band bowing parameter. For the NCs with the composition of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Te}_y\text{Se}_{(1-y)}$, therefore, the valence band potential is:

$$E_{vb} = xyE_{vb}(\text{ZnTe}) + x(1-y)E_{vb}(\text{ZnSe}) + b_1xy(1-y) + (1-x)yE_{vb}(\text{CdTe}) + (1-x)(1-y)E_{vb}(\text{CdSe}) + b_2xy(1-y) \quad (10)$$

Where b_1 and b_2 are the band bowing parameters of $\text{ZnTe}_y\text{Se}_{(1-y)}$ and $\text{CdTe}_y\text{Se}_{(1-y)}$, respectively. Values of b depend only weakly on whether M is Cd or Zn, and b_1 and b_2 are both taken to be 1.27 eV.^{24, 27} The E_{vb} values for the ZnTe, ZnSe, CdTe and CdSe are given in Table S1.

Electron and hole wave functions

The determination of the conduction and valence band profiles along the NC radial coordinate allows the calculation of the electron and hole wave functions and the spectroscopic properties of the ZnTe/CdSe NCs. The electron and hole wavefunctions and energetics are calculated using an effective mass approximation. However, the present case is complicated by the radially varying composition. In this case, the Schrödinger equation can be written as:^{2, 28}

$$-\frac{\hbar^2}{2} \left(\frac{1}{m^*(r)} \nabla^2 \Psi + \nabla \left(\frac{1}{m^*(r)} \right) \cdot \nabla \Psi \right) + V(r) \Psi = E_e \Psi \quad (11)$$

where $m^*(r)$ is the location dependent effective mass. In the present case, the effective mass is taken to linearly change with the composition of the NCs. That is, for a local composition of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Te}_y\text{Se}_{(1-y)}$, the effective mass is:

$$m^* = xym_{\text{ZnTe}}^* + x(1-y)m_{\text{ZnSe}}^* + (1-x)y m_{\text{CdTe}}^* + (1-x)(1-y)m_{\text{CdSe}}^*$$

The electron and hole effective masses for ZnTe, ZnSe, CdTe and CdSe are all given in Table S1. Equation 11 is solved by expanding the wavefunctions in a series of spherical Bessel functions. The Hamiltonian is diagonalized using the conduction or valence band potential described above, giving the zero'th order electron and hole wave functions. The electron-hole coulombic interaction is then considered as a perturbation to calculate the final electron and hole wavefunctions and the exciton energies.

There are several approximations and uncertainties involved in these calculations. The wavefunction and exciton energy calculations used the effective mass approximation, which has limitations that are well known. However, for these relatively large particles, this is not a severe problem. Probably the biggest limitation in the accuracy of the exciton energy calculations is from the bulk material band offsets. One commonly sees literature values for the bulk material conduction and valence band energies that differ by as much as 100 mV, which is not completely insignificant compared to the band offsets. We have chosen what appear to be the most reasonable and accepted set of values (see Table S1) and used them in a self-consistent way. By doing this, any errors enter into the calculations enter into all of them in the same way and therefore tend to offset.

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