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Supporting Information

Predictable spectroscopic properties of type-II ZnTe/CdSe Nanocrystals and electron/hole quenching

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Chemicals

Cadmium oxide (CdO, 99.5%), phenothiazine (PTZ, 98%), methyl viologen dichloride (MV^{2+}, 98%), hexadecanethiol (HDT, 92%), anthraquinone (AQ, 97%), and octadecylamine (ODA, 90%) were purchased from Aldrich and used directly without further purification. Diethyl zinc ($Zn(Et)_2$, 96%), tellurium (Te, 99.8%), selenium (Se, 99%), and *p*-benzoquinone (98%) were bought from Alfa Aesar and also used directly without further purification. Technical grade 1-Hexadecylamine (HDA, 90%) was obtained from Aldrich and recrystallized with toluene before use. Trioctylphosphine (TOP, 97%) and octadecene (ODE, 90%) were purchased from Aldrich and purified through vacuum distillation. Oleic acid (90%) was purchased from Aldrich and dried by vacuum distillation with molecular sieves. Methanol (MeOH, 98%), toluene (99%), and chloroform ($CHCl_3$, 99.8%) were purified by distillation from appropriate drying agents.

Calculations for wavefunctions and conduction/valence band edge energies

By the effective mass approximation, the carriers in the solid carriers are taken to be the free electrons and holes with masses in units of the rest mass of an electron. In our cases, the effective masses of the carriers are position dependent due to its stepwise composition profiles. Specifically, to calculate the spectroscopic properties and the energies of conduction and band edges of the ZnTe/CdSe NCs, the following Schrödinger equation is resolved:

$$-\frac{\hbar^2}{2m_0}\nabla\frac{1}{m^*(r)}\nabla\psi+V(r)\psi=\left(\frac{1}{2m_0}\right)\left(\frac{1}{m^*(r)}\nabla^2\psi+\nabla(\frac{1}{m^*(r)})\nabla\psi)\right)+V(r)\psi=E\psi \quad (1)$$

Where m_0 and m^* are the electron mass and the effective masses (in units of electron mass), respectively. In the spherical coordinate, the wavefunction can be expressed in the following form:

$$\psi_{mnl} = R_m(r)Y_l^m(\theta,\varphi) \tag{2}$$

Where $Y_l^m(\theta,\varphi)$ is the Laplace's spherical harmonics. For each type of the state, the radial functions can be express in terms of the appropriate Bessel functions:

$$R_m(r) = \sum_n C_{nm} J_m(\alpha_{mn} r / R_f) \tag{3}$$

where α_{mn} is the n'th root of J_m. Unlike the case in which the mass is position independent, the radially-dependent effective mass generates off-diagonal kinetic energy matrix elements. The coefficients of C_{mn} can be obtained by diagonalizing the sum of the kinetic and potential energy operators. Specifically,

$$V_m(i,j) = \int_0^{R_f} rdrV(r)J_m(\alpha_{mi} r / R_f)J_m(\alpha_{mj} r / R_f) \tag{4}$$

$$T_m(i,j) = \frac{\pi^2\hbar^2}{2m_0R_f^2}\int_0^{R_f} rdr(1/m^*(r))J_m(\alpha_{mi} r / R_f)J_m(\alpha_{mj} r / R_f) \tag{5}$$

$$T_{1m}(i,j) = \frac{\hbar^2}{2m_0}\int_0^{R_f} rdrJ_m(\alpha_{mj} r / R_f)d(1/m^*(r))/drd\left(J_m(\alpha_{mi} r / R_f)\right)/dr \tag{6}$$

where R_f is the outerradius of the calculation. These integrals are performed numerically, with R_f taken to be sufficiently larger than the shell radius that the exact choice of R_f doesn't matter – it is larger than the extent to which the wavefunction penetrates out of the particle. The matrix to be diagonalized is the sum $V_m + T_m + T_{1m}$. The eigenvalues are the electron or hole energies and the eigenvectors are the C_{nm} coefficients of the electron or hole wavefunctions. This approach gives continuity of the wavefunction and of probability current without explicitly considering the core/shell boundary conditions. Electron-hole coulombic is considered as a perturbation.

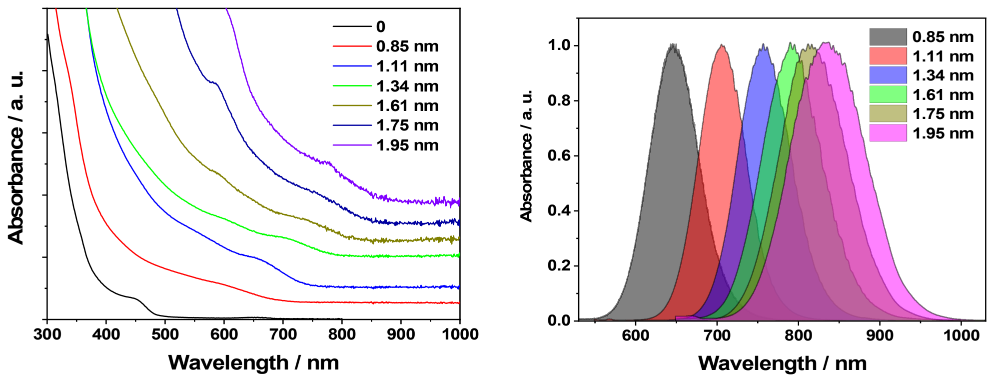

Figure S1. (a) Absorption spectra of bare ZnTe cores of 3.42 nm and ZnTe/CdSe NCs with various shell thicknesses. (b) Photoluminescence spectra of the ZnTe/CdSe NCs of various shell thicknesses on a 3.42 nm core.

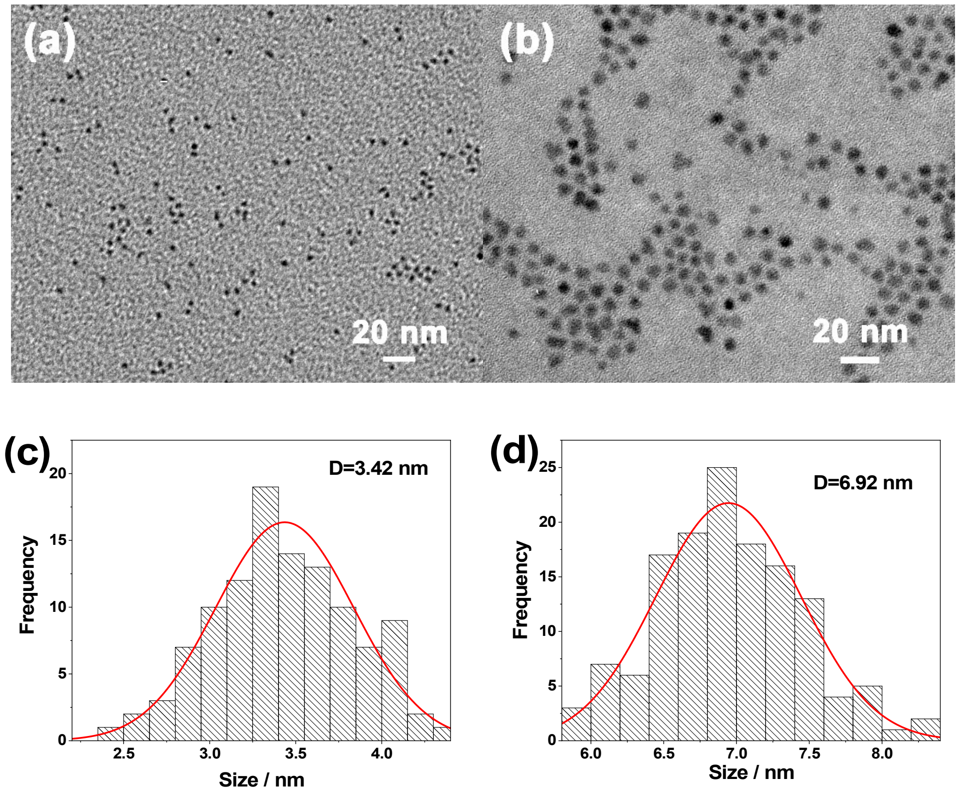

Figure S2. TEM image of (a) the ZnTe NCs of 3.42 nm core and (b) the ZnTe/CdSe NCs with a 1.75 nm shell. Size distribution histogram of (c) the ZnTe NCs and (d) the ZnTe/CdSe NCs.

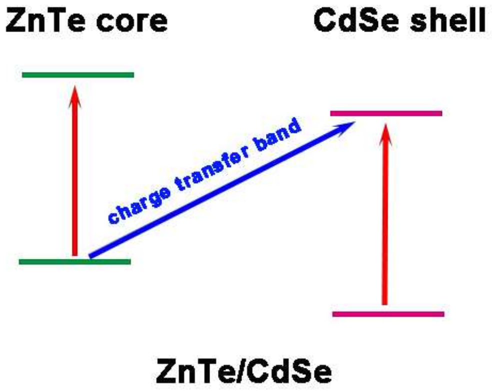

Figure S3. Schematic illustration of the charge transfer band absorption.