

Type-II Quantum Dots: CdTe/CdSe(Core/Shell) and CdSe/ZnTe(Core/Shell) Heterostructures

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Semiconductor nanocrystal quantum dots (QDs) have been the subject of great scientific and technological interest, with promising applications that include display devices,¹ biological tagging materials,² photovoltaics,³ and lasers.⁴ The colloidal synthesis of QDs is well suited to the fabrication of engineered heterostructure nanoparticles such as CdSe/CdS(core/shell (c/s)),⁵ CdSe/ZnS(c/s),⁶ and InAs/CdSe(c/s)⁷ QDs. Thus far, these have been type-I QDs, where the band offsets are such that the conduction band of the shell (the higher band gap material) is of higher energy than that of the core (the lower band gap material), and the valence band of the shell is of lower energy than that of the core. As a result, both electrons and holes are confined in the cores. A type-II QD, in contrast, has both the valence and conduction bands in the core lower (or higher) than in the shell. As a result, one carrier is mostly confined to the core, while the other is mostly confined to the shell. Type-II QDs are expected to have many novel properties that are fundamentally different from the type-I QDs because of the spatial separations of carriers. Type-II structures can allow access to wavelengths that would otherwise not be available with a single material. In addition, the separation of charges in the lowest excited states of type-II nanocrystals should make these materials more suitable in photovoltaic or photoconduction applications, where the QDs are the chromophores and one of the photocarriers is injected from the QD into a matrix before recombination can occur. The type-II QDs that have been reported thus far, GaSb/GaAs⁸ and Ge/Si⁹ heterostructures, have been grown by molecular beam epitaxy. Colloidal QDs have the distinction that they can be further processed and incorporated in a variety of media. We report here a synthetic route to two type-II colloidal heterostructures: CdTe/CdSe(c/s) QDs (CdTe/CdSe QDs) and CdSe/ZnTe(c/s) QDs (CdSe/ZnTe QDs).

Potential energy diagrams for CdTe/CdSe and CdSe/ZnTe QDs are shown in Figure 1. A simple modeling of the radial wave functions for the electron and hole in their lowest energy levels shows the expected separation of carriers.^{6b,10} For CdTe/CdSe QDs, the hole is mostly confined to the CdTe core, while the electron is mostly in the CdSe shell. In CdSe/ZnTe QDs, the band offsets are reversed, so that the electron resides mostly in the CdSe core, while the hole is mostly in the ZnTe shell.

CdTe and CdSe cores are prepared as described previously.¹¹ CdSe and ZnTe shells are grown by a method similar to other overcoating procedures.⁵⁻⁷ The detailed procedures can be found in the Supporting Information. Figure 2 shows the absorption and emission spectra of CdTe and CdSe cores and corresponding CdTe/CdSe and CdSe/ZnTe type-II QDs grown from those initial core particles. The distinctive peaks in the absorption spectra of the initial cores are replaced in the overcoated type-II structures with a featureless absorption tail into the red and near-infrared. This is because type-II QDs effectively behave as indirect semiconductors near the band edges. We expect that excitons created in the higher excited states have both carriers delocalized over the core and the shell. Relaxation to the band edge results in the spatial separation

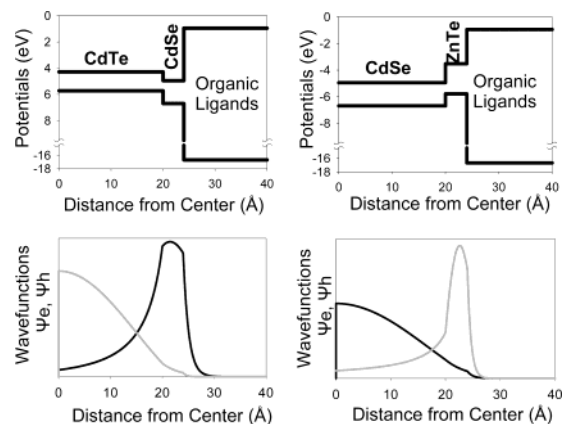


Figure 1. Potential diagrams (top) and modeled electron (gray) and hole (black) radial wave functions (bottom) for CdTe/CdSe(core/shell) QD (left) and CdSe/ZnTe(core/shell) QD (right). Potentials are referenced to the vacuum level. A 20-Å core radius and a 4-Å shell thickness are used in the modeling.

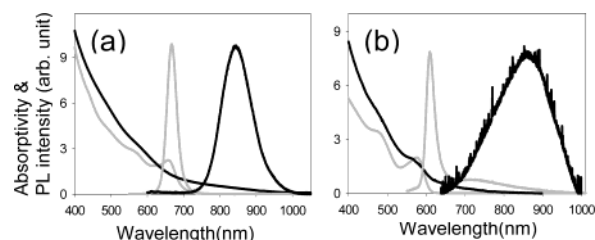


Figure 2. Absorbance and normalized photoluminescence spectra of 32 Å radius CdTe QD (gray lines on (a)), CdTe/CdSe(32 Å radius core/11 Å shell) QD (black lines on (a)), 22 Å radius CdSe QD (gray lines on (b)), and CdSe/ZnTe (22 Å radius core/18 Å shell) QD (black lines on (b)).

of the carriers. Excitation into the red absorption tail directly creates spatially separated carriers. The overcoated dots show a small increase in relative absorptivity over the cores in the blue region of the spectrum as a result of the higher effective density of states expected there due to their larger size, as seen in Figure 3. Type-II QDs have relatively small absorptivities near the band edge because of the weaker oscillator strength that results from the decreased wave function overlap.¹² Photoemission from CdTe/CdSe and CdSe/ZnTe QDs is observed at longer wavelengths than that from the corresponding cores. This type-II emission is not the “deep trap” luminescence often observed in cores. In Figure 2b, “deep trap” luminescence of the initial CdSe cores is observed around 750 nm, which does not match the emission peak of the corresponding CdSe/ZnTe type-II QDs. This excludes the possibility that the deposition of shells merely quenches the band-edge luminescence while the “deep trap” luminescence remains. Type-II emission originates from the radiative recombination of the electron–hole pair across the core–shell interface. The energy of the emission thus depends on

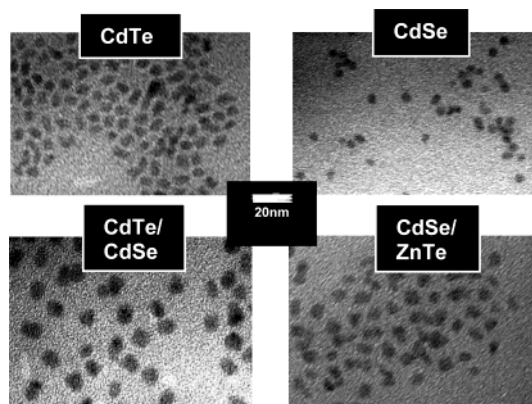


Figure 3. Bright field TEM images of the samples used for Figure 2: 32 Å radius CdTe QD (upper left), CdTe/CdSe (32 Å radius core/thickness of 11 Å shell) QD (lower left), 22 Å radius CdSe QD (upper right), and CdSe/ZnTe (22 Å radius core/thickness of 18 Å shell) QD (lower right). Size histograms can be found in the Supporting Information.

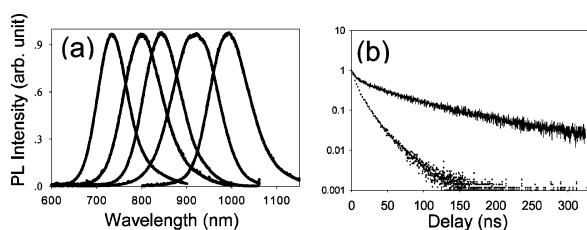


Figure 4. (a) Normalized room-temperature photoluminescence spectra of different CdTe/CdSe(core/shell) QDs. The CdTe core radii and CdSe shell thicknesses are 16 Å/19 Å (core radius/shell thickness), 16 Å/32 Å, 32 Å/11 Å, 32 Å/24 Å, and 56 Å/19 Å from left to the right in the spectra. (b) Normalized photoluminescence intensity decays of CdTe/CdSe (32 Å radius core/thickness of 11 Å radius CdTe) QD (dotted line, quantum yield 40%).

the band offsets of the two materials making up the core and the shell. Type-II QDs can thus emit at energies that are smaller than the band gap of either material. This is demonstrated in Figure 2, where CdTe/CdSe QDs (CdSe/ZnTe QDs) emit at a wavelength longer than the band gap of either CdSe or CdTe (CdSe or ZnTe). Type-II QDs can be thought to have effective band gaps that are then determined by the band offsets. This creates the potential for flexible band gap engineering, since many possible combinations of semiconductor materials can be used to tailor these effective band gaps. In type-II QDs, the thickness of the shell and the core size both control the effective band gap through quantum confinement effects. By changing the two variables of shell thickness and core size, the emission of type-II QDs can be easily and widely tuned. Figure 4a shows emission spectra from CdTe/CdSe QDs that range from 700 nm to over 1000 nm simply by changing the core size and shell thickness. Type-II QDs are expected to have longer exciton decay times than type-I QDs⁸ because of the spatial separation of charges. Figure 4b shows room-temperature PL decays of CdTe/CdSe QDs and the corresponding CdTe QDs. The experimental decay data are fit using stretched exponentials to account for the distribution of nonradiative decay rates.¹³ We find mean decay lifetimes of 9.6 ns for CdTe QDs and a much larger value of 57 ns for CdTe/CdSe QDs. Given the quantum yields of the samples, the average radiative and nonradiative lifetimes of CdTe/CdSe QDs are 120 times and 3.6 times larger than those of CdTe QDs, respectively. The longer radiative lifetime results from the slow electron–hole recombination of the excitons in type-II structures. The longer nonradiative lifetime may arise from the

suppression of hole-trap-mediated nonradiative channels on the QD surface, since the CdTe/CdSe structure confines holes away from the surface.

We have demonstrated control of carrier distributions within QDs. We have engineered a QD heterostructure where the hole is distributed near the center of the dot, while the electron is distributed toward the edge, and vice versa. This degree of control can be especially important in applications where rapid carrier separation followed by charge transfer into a matrix or electrode is important, for example in photovoltaic or photoconducting devices. The type-II QDs described here have PL QY lower than 4%. Type-II QDs with carrier distributions that have better overlap (for example, with a thin shell) can give rise to type-II QDs with higher QYs. The spatial separation of carriers and the long radiative lifetimes that this implies means that nonradiative decay channels dominate. This hinders type-II QDs from achieving high QYs. We have found, however, that a ZnTe layer grown onto CdTe/CdSe QDs can raise QYs up to 20%. The band offsets between CdSe and ZnTe help contain the electron within the dot, without affecting the hole wave function, which is still constrained to the core.

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Supporting Information Available: Detailed synthetic procedures of type-II QDs and modeling of the carrier wave functions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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