

Light Harvesting and Carrier Transport in Core/Barrier/Shell Semiconductor Nanocrystals

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Excitation transfer pathways in colloidal core/barrier/shell nanomaterials were investigated in the CdSe/ZnS/CdSe system. Absorption of light in the outer CdSe shell results in emission from the band edge of the CdSe core. The CdSe quantum shell acts as a light harvester that indirectly increases the brightness of the CdSe quantum-dot core. Spectroscopic evidence suggesting that the CdSe core and shell are coupled by tunneling of excitons through the ZnS barrier is provided. Competition kinetic analysis shows that charge transport competes effectively with hole capture by pyridine at the outer CdSe shell and exciton relaxation within the outer CdSe shell.

1. Introduction

To extend the functionality of colloidal semiconductor quantum dots, modifications involving epitaxial growth of additional layers of semiconductors have received considerable attention. By controlling material composition across the radial coordinate, one introduces the ideas of band-gap engineering into the fabrication of colloidal quantum dots.¹ Initially, inorganic shells were grown onto quantum-dot cores to better passivate the surface of the core.^{2–5} Subsequently, variations on layering schemes were introduced, including creation of spherical quantum wells,^{6,7} type II core/shell structures,^{1,8} and inverted core/shell structures.^{9,10} These structures are generating interest because they might introduce novel functionality such as increased brightness, localization of carriers, charge separation, and emission at new wavelengths.

An early example of core/shell-type structures in which the shells perform a charge localization function is the CdS/HgS quantum-dot/quantum-well system.^{6,7} In the CdS/HgS system, carriers can directly relax into the low-gap HgS quantum well on an ultrafast time scale.¹¹ Recently, an interesting variation has been developed in which the core and the outer shell are separated by a wide-gap semiconductor tunneling barrier.¹² In this CdSe/ZnS/CdSe system, the inner ZnS shell serves as a tunable tunneling barrier offering a unique material geometry with which to probe charge carrier dynamics in coupled quantum-dot-based materials. This material was developed by Peng and co-workers, who showed that there was electronic coupling between the CdSe core and the outer CdSe shell that could be tuned by varying the number of layers in each phase of the shells.¹²

These colloidal systems offer a parallel to the developments of quantum-well superlattices and multiple quantum wells. In this form of core/barrier/shell material, the shell can perform a function such as light harvesting with energy or charge transfer to the lower-energy core. Such a scheme might find use for indirect pumping of the quantum-dot cores¹³ and also for increasing their brightness for imaging applications.¹⁴

Here, we focus on the mechanism underlying the electronic coupling between the core and the shell. We employ steady-state spectroscopic experiments to suggest a mechanism of

tunneling-based carrier transport between the core and the outer shell through the ZnS barrier. Following Peng and co-workers, two-color photoluminescence was observed from the CdSe core and the CdSe outer shell. The steady-state optical properties of this system provide clear evidence of electronic coupling between the CdSe phases through a tunneling barrier. Absorption of photons by the shell is shown to result in emission of photons by the core. Remarkably, the shell produces twice as much emission from the core via transport as is generated from the shell itself. Overall, the brightness of the core in the core/barrier/shell structure is 1.7 time greater than that of the bare core in a CdSe/ZnS core/shell structure. This value does not represent a limit to the enhancement, as other batches produced enhancements of up to 3 times. These materials hold promise for producing extremely bright cores by designing shell structures with which to harvest light.

An estimate of the time scale for the transfer process can be obtained via competition kinetic analysis. The steady-state data suggest that the exciton transport occurs on a time scale similar to those of hole capture by pyridine at the shell and exciton relaxation in the shell. These two observations suggest the presence of a carrier-transport mechanism with an energy dependence that is characteristic of tunneling, similar to quantum-well superlattices.¹⁵ Femtosecond spectroscopic experiments are under way to directly measure the processes suggested by the steady-state spectroscopic data. Charge transport and enhanced brightness for these colloidal core/barrier/shell structures hold promise for imaging¹⁴ and optoelectronic applications.^{15,16}

2. Experimental Methods

CdSe nanocrystal cores were prepared using the alternate precursor method developed by Peng and co-workers.¹⁷ The procedure was modified by the substitution of hexadecylamine (HDA) for octadecylamine (ODA). The CdSe nanocrystals were capped with trioctylphosphine oxide (TOPO) and HDA. The layered CdSe/ZnS/CdSe systems were prepared using the modified successive ionic layer adsorption and reaction (SILAR) method developed by Peng and co-workers.^{12,17,18} The SILAR method was recently employed by Banin and co-workers to further improve the quantum yield of InAs quantum dots.¹⁹ For this study, 3 ML of ZnS were added, followed by 3 ML of

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CdSe. For some experiments, the ligands on the CdSe cores and CdSe/ZnS/CdSe core/barrier/shells were first exchanged for pyridine. For the ligand exchange, the nanocrystals were dissolved in a small amount of neat pyridine and heated at 50 °C for 1 h. For these measurements, the nanocrystals were dissolved in toluene, with the exception of the pyridine-coated particles, which were dissolved in methanol or pyridine. The synthesis and characterization was performed four times to verify reproducibility of the results. The detailed procedures can be found in the Supporting Information.

3. Results and Discussion

Spectroscopy of the Core/Barrier/Shell Structure. One dimensionally confined structures can be grown in layers, resulting in either multiple quantum wells or quantum-well superlattices.¹⁵ The key feature is the extent to which the tunneling barrier layer isolates the wells that form the superstructure. The barrier thicknesses are ca. 4 nm, depending on the material. For three dimensionally confined structures, a direct analogy is possible in core/barrier/shell systems. Here, a tunneling barrier separates the core phase from an outer shell phase. In this work, we focus on the CdSe/ZnS/CdSe core/barrier/shell system developed by Peng and co-workers.¹² Prior work has shown that the shell layers are grown epitaxially in a controllable layer-by-layer manner. Structural data demonstrate that the growth is epitaxial and also show the quality of the shell structure.^{12,17}

The CdSe/ZnS/CdSe quantum-dot/quantum-shell structure has two low-energy CdSe phases separated by a high-gap ZnS barrier. Prior work by Peng and co-workers has shown well-resolved emission from both phases. The energies of the CdSe core and shell can be independently tuned. This work investigated variable electronic coupling of the core and shell phases by monitoring the shifting of the peak of photoluminescence for different shell structures. Figure 1 shows the relevant phases drawn to scale. Whereas the quantum mechanics of the core are well established,^{20,21} the shell is less well understood. Here, we focus on one geometry of the CdSe/ZnS/CdSe system to probe the nature of the electronic coupling between the core and the outer shell.

The band-edge absorption of the bare core has its peak at 2.1 eV, indicating a diameter of 4.2 nm, according to the sizing curve of Peng and co-workers.²² Figure 2 shows absorption, photoluminescence (PL), and photoluminescence excitation (PLE) spectra of the CdSe core and the CdSe/ZnS/CdSe core/barrier/shell system. The core/barrier/shell system was fabricated with 3 ML each of ZnS and CdSe. The PL spectra were excited at 3.10 eV. The PLE spectra were detected for band-edge emission from the core phase at 2.00 eV. Our results here reproduce the results of Peng and co-workers in which they developed and first characterized these structures.¹² The absorption spectrum dramatically shows the presence of the CdSe shell. The ZnS shell has its band-edge absorption²³ at higher energy (~4.3 eV) than the data shown here. Consistent with prior work,^{2,4} the inorganic shell slightly red shifts (0.05 eV) the band-edge absorption of the core through the slightly increased delocalization of the wavefunctions relative to the case of organic ligands.

The absorption spectrum of the core/barrier/shell system increases dramatically starting near 2.3 eV, near the emission energy of the shell. The volume of the CdSe shell is 7 times that of the core. The absorbance from the shell is also 7 times that of the core, at 3.10 eV. Although the oscillator strengths and density of states might not be identical between the cores

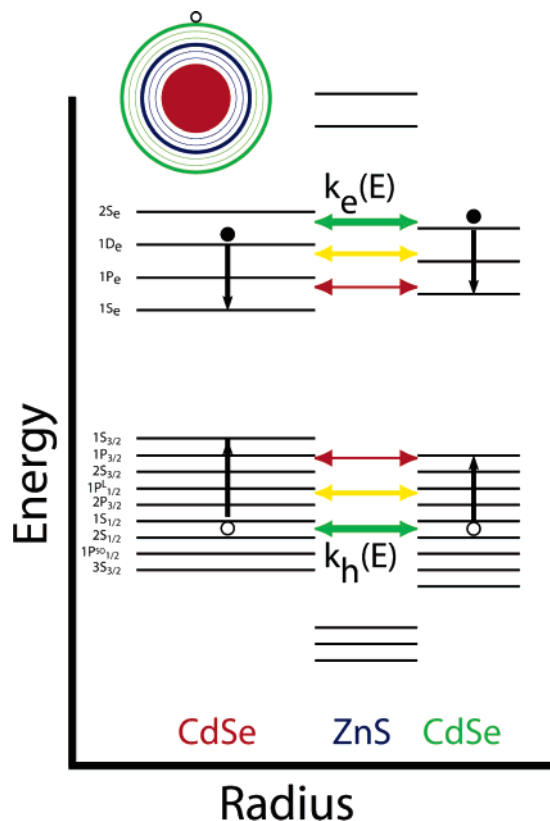


Figure 1. Schematic energy-level diagram of the CdSe/ZnS/CdSe structure. The core, shells, and pyridine ligand are drawn to scale. The core diameter is 4.2 nm, and there are 3 ML of ZnS and CdSe shells. The arrows indicate carrier paths representing carrier tunneling (horizontal) and carrier relaxation (vertical). The higher tunneling rate at higher energy is illustrated by the thickness of the arrows.

and the shells, there is remarkably good agreement between the absorption of the shell relative to that of the core and the volume of the shell relative to that of the core.

The PL spectra show two-color emission from the core (peak at 2.00 eV) and the shell (peak at 2.30 eV). The energy at which the shell emits reflects the band edge of the shell more cleanly than the absorption spectrum of the composite material. The width of the PL from the shell (214 meV, fwhm) is larger than that of the PL the core (120 meV). The PL from the original core is 89 meV fwhm. This observation is consistent with prior work on shell growth indicating that shell growth is less well controlled than core growth. The amplitude of the shell emission is lower than expected on the basis of volume, because of the lower quantum yield of organically passivated systems. The inorganically passivated cores can have quantum yields ranging from 10% to 50%, whereas the organically passivated cores can have quantum yields of 1–10% at room temperature.^{2–4} The same behavior was observed for these core/barrier/shell systems.

The PLE spectra shown in Figure 2 are for emission from the core phase. The PLE spectrum of the bare core is consistent with prior work, showing improved spectral resolution because of size selection and closely following the absorption spectrum.²⁰ The PLE of the core/barrier/shell measured by monitoring emission from the core shows a dramatic increase upon resonance with the CdSe shell at 2.3 eV. At the monitoring energy of 2.00 eV, there is <1% contribution from shell emission.

Influence of the CdSe Shell on the CdSe Core. Whereas the two-color emission in the PL spectrum is taken as evidence that we have a colloidal version of a multiple quantum-well

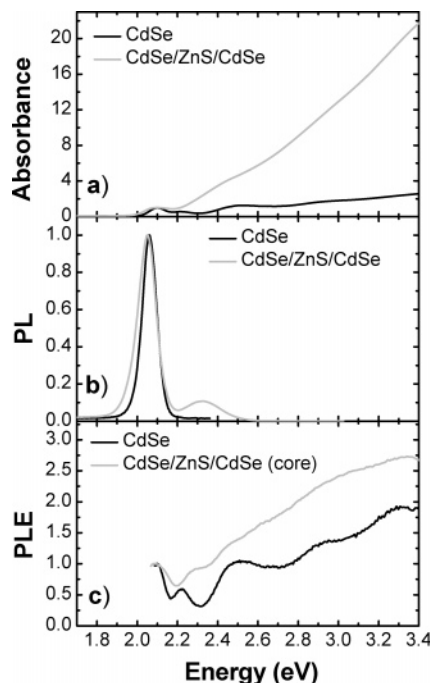


Figure 2. Spectra of bare CdSe cores and CdSe/ZnS/CdSe core/barrier/shell structures normalized to the amplitude of the core phase. (a) Absorbance normalized to the band edge. (b) Photoluminescence (PL) excited at 3.10 eV. (c) Photoluminescence excitation (PLE) spectra for the core/barrier/shell system for emission from the core phase of the structure, denoted as CdSe/ZnS/CdSe (core). The PLE spectra were monitored at 2.00 eV (core) and 2.30 eV (shell).

system, the PLE and new data provide evidence of charge-transport mechanisms akin to those occurring in quantum-well superlattices. The key feature in the PLE data is that the emission from the CdSe core clearly shows a spectral response similar to that of the CdSe shell. Prior work by Peng and co-workers had proposed the possibility of Förster-type energy transfer from the shell to the core.¹² Here, we provide evidence that verifies prior work showing electronic interactions between the CdSe phases. We furthermore show evidence for a tunneling mechanism for the charge-transport process, quantify its efficiency, and relate its time scale to those of other relevant dynamical processes.

The PLE spectra are informative for illustrating the effects of the shell excitation on core emission. Figure 2c shows that the PLE for emission from the core is dramatically different for the core/barrier/shell structure. By monitoring the PL and PLE at 3.10 eV, one can see that the shell is actually twice as likely to produce emission from the core as it is to generate emission itself (Supporting Information).

To further quantify the effect of the shell on the core, Figure 3 shows the Δ PLE spectrum. The Δ PLE spectrum represents the difference in PLE between the core/barrier/shell at the core emission wavelength and the core alone. The notation of core/shell (core) reflects emission from the core phase, upon excitation of the core/barrier/shell structure. This spectrum shows a clear peak at 2.3 eV, matching the onset of absorption from the shell phase. The Δ PLE spectrum directly reflects the influence of shell excitation on core emission. Further verifying this relationship, the PLE for emission from the shell phase qualitatively tracks the Δ PLE spectrum.

When the excitation energy is >2.3 eV, both core and shell phases are excited. In principle, the core and the shell can mutually influence each other. In practice, the shell has ~ 7 times the volume and ~ 7 times the absorption of the core. Thus, the

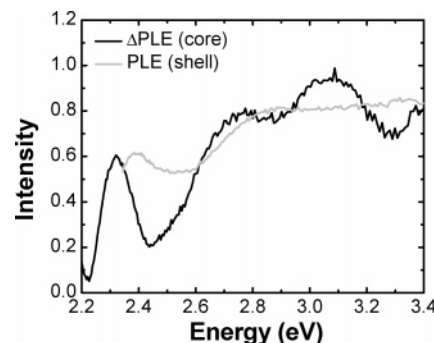


Figure 3. Influence of the shell on the core. Δ PLE refers to emission from the core phase in the core/barrier/shell system, minus emission from the bare core. The Δ PLE spectrum follows the spectral response of emission from the shell.

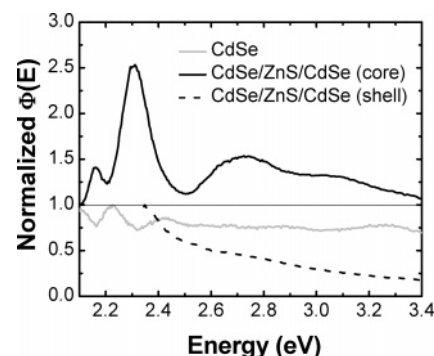


Figure 4. Normalized quantum yield spectra. The quantum yield spectrum is proportional to the PLE spectrum divided by the absorption spectrum. The anomalous behavior of the core/shell (core) is due to the influence of the excitation of the shell on the emission of the core via tunneling. The PLE spectra were monitored at 2.00 eV (core) and 2.30 eV (shell).

effect of the shell on the core is much larger than the effect of the core on the shell. Hence, we focus only on the shell effect to investigate the nature of coupling between the phases. The data in Figures 2c and 3 show that excitation of the shell phase contributes to emission from the core phase.

To probe the energy dependence of emission and light harvesting through charge transport, we also show the quantum yield spectra of the relevant phases in Figure 4. The quantum yield is proportional to the emission intensity divided by the absorbance. The data shown here are normalized to the band edge to illustrate the spectral shape. The normalized quantum yield spectrum, $\Phi(E)$, for the core drops slightly at higher energy, as was previously established.^{20,24} The $\Phi(E)$ spectrum drops off much more rapidly for the shell. This behavior likely relates to the poorer quality of the shell relative to the core.

The $\Phi(E)$ spectrum for the core/barrier/shell (core) is particularly informative. This spectrum is the PLE from the core/barrier/shell (core) divided by the absorption spectrum from the core only. This spectrum serves to further present the effect of the shell on the core. Here, we see anomalous behavior in which there is higher quantum yield at higher energy. This behavior is particularly pronounced at 2.3 eV, where the core has low absorption but the shell has its band-edge absorption. The main portion of this spectrum is from 2.4 to 3.4 eV, which reflects electronic coupling between the shell and core. This anomalous quantum yield spectrum reflects the effect of absorption of photons by the shell on emission of photons by the core.

Evidence of Tunneling of Carriers between CdSe Phases. Electronic coupling between phases involving colloidal quantum dots has previously been described in terms of Förster-type

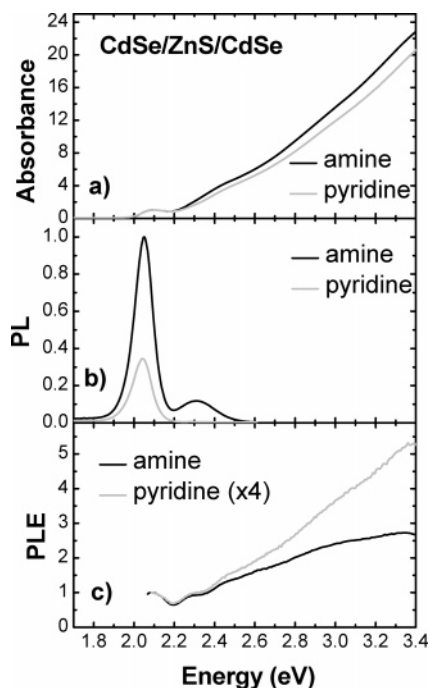


Figure 5. Effect of pyridine passivation of the CdSe shell phase of the CdSe/ZnS/CdSe core/barrier/shell structure. Pyridine is a hole acceptor that attenuates emission. (a) Absorption spectra normalized to the band edge of the core phase. (b) PL data at 3.10 eV excitation (not normalized). (c) PLE data for emission from the core phase of the core/barrier/shell structure, rescaled as indicated to illustrate the spectral differences. The PLE spectra were monitored at 2.00 eV (core) and 2.30 eV (shell). Pyridine passivation attenuates emission from the core at all excitation wavelengths.

processes for quantum-dot/quantum-shell structures,¹² as well as for quantum dots adjacent to quantum dots^{25,26} or wells.¹³ The second set of configurations are different from ours in that organic ligands separate the quantum dots. The configuration of quantum dot/barrier/quantum shell is more akin to a quantum-well superlattice. In quantum-well superlattices, tunneling is considered the active mechanism of charge transport over distances of ~ 2 nm.¹⁵

The data in Figures 2–4 show evidence of electronic coupling between the CdSe phases. The mechanism can be established through the use of hole acceptors. A control experiment that shows the coupling mechanism can be performed by varying the organic ligands that passivate the shell. Pyridine is a known hole acceptor that quenches emission from cores.²⁷ The time scale of pyridine transport from cores was measured as ~ 400 fs using transient absorption spectroscopy and intraband modulation spectroscopy.²⁸ The time scale has not yet been established for shells, however.

Figure 5 shows the effects of pyridine on the absorption, PL, and PLE spectra. Pyridine produces a negligible effect on the absorption spectra. The PL spectra (excited at 3.10 eV) clearly show that emission from the shell is completely quenched, whereas emission from the core is merely attenuated. Similar behavior was observed for CdSe/CdS core/shell quantum dots in which the presence of the CdS shell maintained emission from the core, albeit attenuated by a factor of about 15 for a shell of ~ 1 nm.⁴ This observation is the first key point to understanding the mechanism of coupling. That emission from the core is affected at all provides evidence that the holes created in the core are trapped by pyridine by tunneling through ~ 1 nm of ZnS and ~ 1 nm of CdSe.

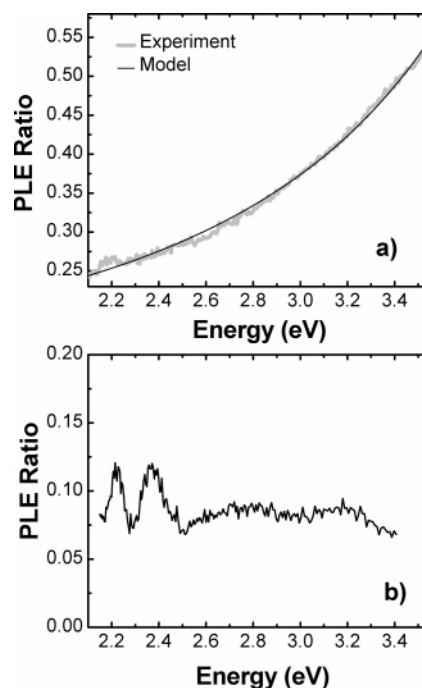


Figure 6. (a) PLE ratio showing the effectiveness of pyridine in quenching emission of the core in the core/barrier/shell structure. The energy dependence is well fit by a tunneling model characterized by an energy-dependent rate. Hole capture becomes less effective relative to tunneling as the tunneling rate increases at higher photon energies. (b) In comparison, the attenuation effect of pyridine is spectrally flat when in contact with a bare core.

A more detailed analysis is provided by the PLE spectra. Excitation at 3.10 eV excites both the core and the shell, which can complicate the analysis. Emission from the core is attenuated by a factor of 4.2 when excitation occurs at the band edge of the core (2.16 eV), whereas it is attenuated by a factor of only 2.9 when excitation occurs at 3.10 eV, where both phases absorb. The key observation is that emission from the core is attenuated by hole capture by pyridine even when excitation occurs *below* the band edge of the shell. Thus, hole transport must proceed across 6 ML of spacer layers. This process would not happen by the Förster mechanism because excitation at 2.16 eV is subresonant with either the shell or pyridine. Thus, the hole must tunnel through the 6 ML of spacer (~ 2.0 nm). Similar results were obtained by Alivisatos and co-workers in which there was ~ 4 times more hole capture through a thinner and lower tunneling barrier.⁴ Quenching experiments using hole acceptors are useful for investigating the mechanism and time scales for coupling between the shell and the core. The hole-capture experiments show that tunneling of holes can proceed over distances of 2 nm. With a smaller effective mass, electrons should tunnel with still more efficiency.

To further rule out other mechanisms such as defects or Förster energy transfer, Figure 6 is useful. Here, the PLE of the core/shell (core) is shown as a ratio for pyridine passivation relative to amine passivation (hexadecylamine; Supporting Information). There is a clear energy dependence of PL attenuation on hole capture. The effectiveness of pyridine in attenuating emission diminishes at higher energy. One might consider the presence of pinholes that allow pyridine to sit close to the core, but such a situation is unlikely for 6 ML of inorganic spacer layers. Furthermore, proximity of pyridine would not show an exponential energy dependence. In the case Förster energy transfer, efficiency scales with the spectral overlap between the donor and the acceptor. Instead, the ratio is well

fit with a model function characteristic of tunneling (Figure 6a). In a tunneling mechanism, the energy dependence of the rate scales as the square of the matrix element coupling the two states. Thus, $k(E)$ should scale as an exponential of the square root of the difference between the energy and the tunneling barrier. Figure 6a shows that the tunneling model fits the experimental data well.

To rule out any energy dependence of pyridine capture, PLE spectra of bare cores passivated with pyridine were compared to those of bare cores with amine passivation. This control experiment was performed with sufficient pyridine to attenuate 92% of the emission from the bare core, but allow sufficient emission to detect the spectral profile of the PLE. The PLE spectra were compared by taking the ratio between the PLE spectra with pyridine passivation and with amine passivation. Figure 6b shows that the PLE ratio exhibits no energy dependence from 2.4 to 3.4 eV, the region of shell absorption. Thus, the energy dependence shown in Figure 5 is due to the transport process rather than any energy dependence of hole capture by pyridine.

In quantum-well superlattices, the tunneling lengths are similar to those employed here to separate the CdSe phases. The energy dependence of the transfer rate is consistent with tunneling of the carriers through the ZnS barrier. In principle, the electrons and holes can be decoupled by alignment of the energy levels of the relevant phases. In this specific material, we monitor radiative recombination of the exciton, so that both carriers must tunnel across the barrier. Furthermore, because the outer shell has the same composition as the core, the levels will be aligned in type I form. The present experiment cannot distinguish electron and hole transport; it can show only that both carriers are transferred from the shell to the core under these conditions. For the present purposes, we focus on transport of the exciton.

The exciton transport can be further analyzed in relation to competing processes. Competing processes for tunneling from the outer shell to the core include hole capture by pyridine, electron and hole relaxation, and radiative recombination. These processes have been measured for CdSe cores, but remain to be measured for the shell phases of core/shell structures. The time scale for hole capture by pyridine was measured as ~ 1 ps for CdSe cores.²⁸ The time scale for electron relaxation is < 1 ps, whereas that for hole relaxation is > 1 ps.²⁹ Emission from the shell is completely extinguished by hole capture (Figure 5), consistent with the expectation that hole capture is faster than radiative processes. Yet, excitations in the shell still contribute to emission from the core (Figure 6), showing that tunneling proceeds on a time scale similar to that of hole capture.

The energy dependence of the quenching process can also be understood in terms of competition kinetics. If the tunneling rates were much lower than the exciton relaxation rates, transport would happen only from the band-edge state of the shell. The energy dependence shown in Figure 6 shows that the tunneling is faster at higher energy, thereby competing more effectively with hole capture. Thus, tunneling competes with exciton relaxation in addition to hole capture. Because the tunneling rate, $k(E)$, can be modeled as an exponential with square-root energy dependence, one can estimate the energy dependence from the height of the barrier and the energies of the initial and relaxed states in the core phase. From the energy differences, the unrelaxed rate should be ~ 10 times higher than transport from a fully relaxed exciton in the shell. The energy dependence of the rate is noted in Figure 1. This energy dependence is exactly what is observed in Figure 6 when comparing the rate

at an unrelaxed 3.5 eV to that at a fully relaxed 2.3 eV. The data in Figure 6 show that tunneling competes with hole capture near 3.5 eV, but hole capture dominates near the band edge of the shell at 2.3 eV. The control experiment on pyridine-passivated cores shows that hole capture does not contribute to the observed energy dependence (Figure 6b). At high energy, exciton transport competes effectively with hole capture because of the higher rate from the lower barrier. At lower energy, the tunneling rate slows by a factor of ~ 10 and hole capture dominates. The presence of an energy-dependent rate shows that the transport proceeds in competition with relaxation of the exciton in the shell. Further work will be needed to directly monitor the relevant processes in the time domain.

4. Conclusions

The nature of the electronic couplings between barrier-separated CdSe quantum dots and CdSe quantum shells was investigated. CdSe/ZnS/CdSe core/barrier/shell structures were fabricated using solution-phase epitaxial methods (SILAR).¹² Prior work by Peng and co-workers has provided evidence of electronic coupling between the CdSe core and the outer CdSe shell.¹² This material was further investigated by steady-state spectroscopy and quenching experiments.

Absorption of photons by the shell has a clear influence on emission of photons by the core. Excitation of the shell produces twice as much emission from the core as from the shell itself. Quenching experiments using pyridine capping groups provide evidence of tunneling of holes through the 6 ML of shells. By considering competition kinetics, we show that tunneling of carriers proceeds on a time scale similar to those of hole capture by pyridine and exciton relaxation within the manifold of quantized states. Experiments are under way to directly measure these processes using femtosecond spectroscopic experiments.

Incorporating quantum shells might also be an effective way to increase the effective oscillator strength of the core by utilizing the large volume of the shell and subsequently transferring its excitons to the core. In this manner, one can envisage quantum shells as light harvesters with quantum dots as emitters. Such a geometry might be fruitful for quantum dots in imaging, lasing, and charge-separation applications.

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Supporting Information Available: Details on synthetic procedures and spectroscopic analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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