Published in final edited form as:

Chemphyschem. 2016 March 3; 17(5): 731–740. doi:10.1002/cphc.201500868.

Role of the Inner Shell Architecture on Quantum Yield and Blinking Dynamics in Core/Multi-Shell Quantum Dots

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Abstract

Choosing the composition of the shell for QDs is not trivial, since both the band-edge energy offset and interfacial lattice mismatch play roles in influencing the final optical properties. One way to balance these competing effects is by forming multi-shells and/or gradient-alloyed shells. However, this introduces multiple interfaces and their relative effects on quantum yield and blinking are not yet fully understood. Here we undertake a systematic, comparative study of adding inner shells of single composition vs gradient-alloyed shells of cadmium/zinc chalcogenides onto CdSe cores, and then capping with a thin ZnS outer shell to form various core/multi-shell configurations. We show that the inner shell architecture between the CdSe core and the outer ZnS shell plays a significant role in both quantum yield and blinking dynamics but that these effects are not correlated – a high ensemble quantum yield doesn't necessarily equate to reduced blinking. Two mathematical models have been proposed to describe the blinking dynamics – the more common power-law model and a more recent multi-exponential model. By binning the same data with 1 ms and 20 ms resolution, we show that the on-times can be better described by the multi-exponential model while the off-times can be better described by the power-law model. We discuss physical mechanisms that might explain this behavior and how it can be affected by the inner shell architecture.

TOC graphic

What the Shell? Here we show that choosing the correct shell architecture is a complex problem, especially for multi-shell quantum dots. Different shell combinations, and whether they are alloyed or not, lead to different properties at the ensemble level (quantum yield) and the single particle level (blinking).

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Introduction

It is well known that adding a wide band-gap shell onto colloidal core CdSe quantum dots (QDs) significantly improves their photoluminescence quantum yield.^[1, 2] The subsequent modification of the shelling procedure to a stepwise monolayer-by-monolayer growth of shell material, termed SILAR, has led to more accurate control and higher reproducibility of the shell thickness and size distribution.^[3] Moreover, this advance allows for multiple shell materials to be easily grown leading to more advanced tailoring of QDs for wide-ranging applications in LEDs,^[4] photovoltaics,^[5] optoelectronics^[6] and chemical/biochemical sensors.^[7–9] In particular, QDs have certain advantages over molecular fluorophores for bioimaging applications due to their broad absorption spectra, narrow emission spectra, long fluorescence lifetime and their high photostability under real operating conditions.^[10–14]

CdSe/ZnS nanostructures were the first studied core/shell system^[1, 2] because ZnS offers the widest band gap energy that is compatible with CdSe, leading to the photoexcited charge carriers to better be confined inside the core materials. It was considered that reducing the accessibility of the exciton to surface states decreases non-radiative recombination pathways. However, a major limitation with this core/shell combination is that the large lattice mismatch (~12%) between CdSe and ZnS may lead to dislocations/defects at the core/shell interface if the shell is too thick that creates new non-radiative recombination pathways and limits the maximum QY.^[15] Other core/shell combinations have been investigated, such as the very low lattice mismatched CdSe/CdS (~4%)^[16] and the moderately mismatched CdSe/ZnSe (~8%).^[17] However, these combinations suffer from the fact that they do not confine the exciton to the core as well as ZnS, leading to the fact that the external environment can affect the QY if the shell is too thin and reducing wavefunction overlap and thus QY if the shell is too thick. It was then shown that using multi-shells of a lower lattice mismatch material as a thin inner shell with a higher bandgap ZnS as a thin outer shell led to higher QYs than using only single shell materials.^[15, 18]

The choice of shell material also has an effect on single QD blinking. Blinking is the phenomenon of intermittence between florescent and dark states of single fluorescence probes under continuous excitation and occurs in organic dye molecules,^[19, 20] fluorescent proteins,^[21, 22] or nanoparticles.^[19, 23] Blinking severely limits the applications of fluorophores, especially in bioimaging, optical storage and as single photon sources. Although blinking in organic dyes and fluorescent proteins is generally understood, the underlying mechanism behind blinking in QDs has remained elusive. It is generally agreed upon that trapping of charge carriers is responsible for blinking, but microscopic details as to which charge carriers are trapped and where the trap states are is still under intense investigation. It was found that adding a ZnS shell up to ~7 monolayers (ML) thick onto CdSe does not reduce blinking, although it does increase the ensemble quantum yield.^[24] Adding CdS shells to CdSe does allow blinking to be significantly reduced, but the shell must either be very thick (~15ML)^[25] or be grown at a slow rate but at high temperature to give near-perfect crystallinity.^[26] It appears that the lattice mismatch creates interfacial trap states at the core/shell interface which are involved in blinking, but mechanistic details are still lacking. Furthermore, for biological applications, it is less than ideal to have the outer shell containing toxic cadmium. Chen *et al.* reported that Multishell QDs of CdSe/CdS/ZnS

could also reduce blinking but, again, it was required to make the shells thick, producing what they called “Giant” multishell QDs.^[27] While this approach is suitable for many applications, their large size does not make them well-suited for applications where a small size is needed, such as for labeling small biomolecules or when they need to be optically coupled.

A major question that remains is whether the choice of inner shell material and whether it is alloyed or not can be systematically chosen to reduce blinking and increase QY without the detrimental side effects of too large a size or using CdS as the outer shell. To reach this goal it is necessary to more thoroughly understand the role of the inner shell architecture on such properties. In this work, we have synthesized four different QD architectures on the basis of their lattice mismatch and band gap energy offset parameters. We started with a high quality CdSe core (QY = 30–50%) and varied the inner shell material up to 5ML of CdS, ZnSe or their gradient alloy analogs ($\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ and $\text{ZnSe}_{(1-x)}\text{S}_x$, respectively, with x increasing by 0.2 per ML), followed by up to 3 ML of ZnS. We found that CdSe/CdS/ZnS showed lower blinking QDs but also had a lower ensemble QY (~20%) while CdSe/ZnSe/ZnS had a 3-fold higher ensemble QY (~60%) but more blinking, although still blinking less than the core-only CdSe. Gradient alloys of CdZnS were generally worse than just using CdS, but gradient alloys of ZnSeS led to higher QYs than ZnSe (up to 80%), although blinking remained the same as when using ZnSe. While these are among the highest QY reported for core/shell/shell QDs, it is interesting to find that ensemble QY isn't necessarily a good indicator of the blinking behavior. We fit the distribution of on and off times to two models – a truncated power-law and a multi-exponential model – and discuss the relative merits of current blinking models to explain our data.

Materials and Methods

Chemicals

Cadmium oxide (CdO, 90%, Sigma-Aldrich), selenium powder (Se, 99.99%, Alfa Aesar), zinc oxide (ZnO, 99%, Sigma-Aldrich), sulfur powder (S, 99.9%, Alfa Aesar), oleic acid (OA, tech. grade, Alfa Aesar), 1-octadecene (ODE, 90%, Alfa Aesar), octadecylamine (ODA, 95%, Acros Organics), tri-butylphosphine (TBP, 95%, Alfa Aesar), Sulforhodamine 101 dye (S 101 dye Invitrogen), poly(methyl methacrylate) (PMMA, Sigma Aldrich) and tri-octylphosphine oxide (TOPO, Sigma-Aldrich) were used as prepared without further purification. Solvents: All solvents were purchased from VWR international. Methanol, hexane and acetone were of pure grade. Toluene was of high purity HPLC grade.

CdSe Core Synthesis

CdSe core samples were synthesized by modification of the literature methods.^[28] Briefly, 0.04 M cadmium (Cd) precursor was prepared by degassing under vacuum and then heating a mixture of 0.02565 g CdO, 0.4452 g OA and 2 g ODE to 200°C under argon flow until the solution became clear. The temperature was then reduced to 50°C and then 1.5092 g ODA and 0.5026 g of TOPO was added. The reaction mixture was degassed again and heated to 300°C under argon flow. Once at this temperature, 0.04 M Se precursor solution (made from 0.01579 g Se, 0.4653 g TBP and 1.37 g ODE) was rapidly injected and, within a few

seconds, the heating mantle was removed and reaction was quenched by adding hexane to avoid further growth of particles. After cooling the solution to room temperature, it was purified by washing with approximately equal amounts of hexane and methanol. The mixture was centrifuged for about 5 minutes at 7K rpm and the process was repeated 2 more times.

Core/shell/shell synthesis

The shelling of CdSe core was accomplished by applying successive ion layer absorption and reaction (SILAR) with thermal cycling (TC).^[3] Generally, 0.08 M Cd or Zn and 0.4 M Zn precursors (depending on the amount of precursor needed for each injection) were prepared by the same method as the Cd precursor while 0.08 M or 0.4 M S precursor was prepared in the same way as that of Se. The starting CdSe core solution for the shelling process was prepared by mixing together 3 mL of CdSe in hexane, 1.5 g ODA and 3 mL of ODE in a 3 necked reaction flask. Now, calculated amounts of Se or S and Zn or Cd were injected alternately one monolayer (ML) at a time at a temperature of 180°C, allowed to equilibrate for 5 minutes each, followed by crystallization of the shell by raising the temperature to 210°C for CdS or to 230°C for ZnSe or ZnS shell for 20 more minutes. The S or Se precursor was always injected first. Approximately 1 mL aliquots were taken out and dissolved in hexane after the growth of each ML before lowering the temperature and used for characterization. The first 5 ML injections were for either CdS or ZnSe shell while the last 3 ML injections were for the ZnS shell. All sample syntheses were performed twice to ensure reproducibility in the resulting optical and structural properties.

Core/gradient-alloyed shell/shell synthesis

The growth of 5 ML of alloyed $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ or $\text{ZnSe}_{(1-x)}\text{S}_x$, was carried out by varying the ratio of x from 0 to 1 in increments of 0.2 per ML. The synthesis is exactly similar to the core/shell/shell synthesis except 0.08 M Cd and Zn precursors or 0.08 M Se and S precursors, with exact volumes varying depending on the required alloy composition for that ML, were injected together at 180°C and heated at 220°C for CdZnS and at 230°C for ZnSeS. All sample syntheses were performed twice to ensure reproducibility in the resulting optical and structural properties.

Fluorescence and Absorption Spectroscopy

Photoluminescence (PL) and absorbance of the aliquots for different monolayers were measured with a Perkin Elmer LS 55 luminescence spectrometer and Hitachi U-3900H spectrophotometer, respectively. PL percentage quantum yields (PL QYs) were measured by comparing the integrated areas of the PL spectra of QDs dissolved in hexane to that of the dye standard, Sulforhodamine 101 in ethanol, with the same optical density of 0.05 at the excitation wavelength of 530 nm.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were performed using a Tecnai G2 F20-TWIN (TF20, FEI, Hillsboro, OR). To prepare TEM

samples, 200 μL of thoroughly washed/purified samples were deposited on a thin film of carbon-coated grids. The QDs diameter was measured using the ImageJ software.

Blinking

A MicroTime 200 scanning confocal fluorescence microscope (PicoQuant GmbH, Berlin, Germany), which is based on Olympus IX71 equipped with PicoHarp 300 TCSPC controller, was used.^[29] It utilizes a 485 nm laser (PDL 485, Picoquant) operating in continuous wave mode at a power of 10 μW for excitation of QD samples. A dichroic mirror (500dxcr, Chroma, McHenry, IL) sends the light through a water immersion objective (Olympus, Apochromat 60 $\times$, NA 1.3) to a diffraction-limited laser focus. The same objective collects the fluorescence and sends it through the same dichroic mirror and a 100 μm pinhole. To reject background fluorescence and scattered laser light, a fluorescence filter that best matches the emission wavelength of the QDs (HQ560/40M for CdSe cores, HQ620/60M for CdSe/CdS/ZnS and CdSe/CdS_(1-x)S_x/ZnS, HQ585/65M for CdSe/ZnSe/ZnS and HQ605/55M for CdSe/ZnSe_(1-x)S_x/ZnS, Chroma) is placed in front of Single Photon Avalanche Diode Detector (SPAD, MPI, Microphotonic devices, Bolano, Italy). To perform blinking experiments, 50 μL of a diluted quantum dot solution containing $\sim 3\%$ (W/V) Poly(methyl methacrylate) (PMMA) in toluene was spin coated onto a clean No. 1 glass coverslip to make a thin film of immobilized single QDs in a PMMA matrix. The objective is positioned on a sub-nanometer precision 3D piezo scanning stage (PI, Berlin, Germany) and fluorescence images of 20 $\times$ 20 μm were recorded. Then, from the recorded fluorescence images, the diffraction-limited focus was focused onto the individually well-isolated bright spots to collect fluorescence time traces for up to 5 minutes. The collected photons were binned at 1 ms resolution or 20 ms resolution and the intensity-time data extracted for analysis of on and off time distributions using homemade analysis software written in Igor. All blinking data is the average of two separate preparations for each sample to ensure that the observed differences were reproducible.

Results and discussion

Both the band-edge offsets and the lattice strain between the different materials are important contributors to the optical and structural properties of heteronanostructured QDs. A schematic showing the relative differences in these parameters for the material combinations used in this study is shown in figure 1a. The key difference between using CdS/ZnS and ZnSe/ZnS on CdSe cores is the relative degree of confinement and the lattice strain at each interface. The conduction band offset for CdSe/CdS is very small, leading to a high probability for the electron to tunnel into the inner shell, but the lattice mismatch between these materials is also very small leading to fewer trap states closer to the core. When ZnS is then added to the CdS, a larger lattice mismatch at this interface is likely to cause trap states to form. For ZnSe, the opposite is true; the higher lattice strain is moved from the shell/shell interface to the core/shell interface, but the electron and hole wavefunctions have less penetration into the inner shell. When the inner shell is changed from pure CdS or ZnSe to gradient-alloyed analogs that gradually change the composition to ZnS, the confinement potential changes from a step function at the interface to a more gradual change with each ML (Figure 1b). Furthermore, the lattice strain between the inner

and outer shell is eliminated, but is instead spread out through the inner shell. The main goal of this study is to determine how these parameters affect the optical and structural properties.

The change in PL λ_{max} and the PL QY upon shelling with each ML of each material combination is shown in figure 2. The data is the average of 2 separate preparations of each sample. The error bars (1σ in width) show that the λ_{max} shifts are highly reproducible. There is some variation in the exact PL QY values, but we found that the actual trends were very reproducible. As expected, upon shelling there is a red-shift in the λ_{max} , with CdS showing a larger shift than ZnSe due to the smaller band-gap of CdS compared to ZnSe that results in weaker confinement of the exciton to the CdSe core. Once 5 ML of either shell is added, adding 3 ML ZnS causes very little change in the λ_{max} . The PL QY changes, however, are more complex. We start from a relatively high QY core then, for CdS, it increases with the first ML, then decreases between ML1 and ML3, and increases again up to 5 ML. Adding ZnS to this high QY CdSe/CdS then causes a significant decrease in the QY to eventually become lower than even the original core. Using a gradient-alloy $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$, where x changes by 0.2 per ML, shows the same trend, although the increase in QY is much less than using the pure CdS. On the other hand, shelling with ZnSe causes a slight decrease in QY until adding the 5th ML, at which point the rise is fairly large. For shelling with $\text{ZnSe}_{(1-x)}\text{S}_x$ there is a slight increase in QY until the 5th ML at which the rise is, again, fairly large. Interestingly, when ZnS is added to CdSe/ZnSe, there is a decrease in QY, whereas when ZnS is added to CdSe/ $\text{ZnSe}_{(1-x)}\text{S}_x$ the QY continues to rise. It appears that the lattice strain at the ZnSe/ZnS shell/shell interface causes the introduction of additional non-radiative pathways, which is eliminated by forming the gradient from ZnSe to ZnS over the 5ML of inner shell. It is important to point out at this point that these trends and QY fluctuations are all reproducible at each ML using different CdSe core batches of about the same QY. It has been suggested that there is an inverse relationship between the core quality and the final maximal QY of the core/shell system,^[30] although in that study the core QYs were much lower than those used in our study. The ability to grow good quality shells onto cores appeared to be facilitated by the presence of defects in the core. Our data suggests that this complex behavior may also extend to the quality of the inner shell architecture when using core/multi-shell systems. Still, using the gradient-alloyed inner shell of $\text{ZnSe}_{(1-x)}\text{S}_x$, we are able to synthesize QDs with a very high 80% QY and with a less toxic composition than using CdS, which are attractive for a number of applications where toxicity is important, such as for biological labeling or for use in consumer devices such as LEDs in TVs.

To ensure that the SILAR/thermal cycling process grows the shells as anticipated, TEM was used to monitor the increase in size of QDs after shelling with each material combination, as shown in figure 3. For CdSe cores, the average size was 4.6 ± 0.6 nm. Upon shelling with CdS/ZnS or ZnSe/ZnS, the average size was 12.7 ± 1.4 nm and 12.4 ± 1.6 nm, respectively. When gradient-alloyed inner shells were used, the increase in size was about 1.5 – 2 nm less in both cases, 11.3 ± 1.4 nm and 10.4 ± 1.0 nm respectively. It is interesting to note that using $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ caused the final shape to be less spherical than just CdS while using $\text{ZnSe}_{(1-x)}\text{S}_x$ caused the final shape to be more spherical than using just ZnSe. This could indicate that Cd and Zn are less amenable to alloying than S and Se, with Zn causing more lattice strain in the inner shell when it replaces Cd than when S replaces Se. This is in

agreement with the QY results of figure 2, where adding ZnS to $\text{ZnSe}_{(1-x)}\text{S}_x$ caused the QY to continue increasing, where adding ZnS to $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ caused the QY to decrease.

One potential application for QDs in biological labeling is for single molecule studies, due to their higher brightness and photostability over organic dyes.^[31–33] However, a major hurdle for such studies is fluorescence blinking. As discussed in the introduction, several reports on suppressing blinking *via* the shell have been published, but none are yet ideal for biological imaging applications. Either they have a CdS outer shell, which leaves toxic Cd exposed to the biological system,^[25, 26] and/or they are very large.^[25, 27] Using multishells provides more flexibility over where the lattice strain is placed while reducing potential toxicity by using a ZnS outer shell. In order to investigate the role of where the lattice strain resides in these materials on blinking, we performed single particle fluorescence experiments. Fluorescence traces of single QDs embedded in a PMMA matrix were recorded of each different structure as shown in figure 4a and 4b, which gave a high signal to noise ratio (>80) with easily distinguishable on and off states. Therefore, we could directly apply a fluorescence threshold to the fluorescence traces to obtain on-time and off-time distributions as shown in figure 4c and 4d. Figure 4e shows how the fraction of time that a QD spends in the on state depends on the shell architecture. Overall, figure 4 shows that shelling with multi-shells significantly reduced the blinking of quantum dots, but that the inner shell architecture determines by how much.

As was already mentioned, shelling helps to reduce the surface traps of core QDs but may also introduce new trap states due to induced lattice strain.^[24] When CdS or $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ is used as the inner shell, blinking is reduced significantly more than with ZnSe or $\text{ZnSe}_{(1-x)}\text{S}_x$, even though the ensemble quantum yield of $\text{CdSe}/\text{ZnSe}_{(1-x)}\text{S}_x/\text{ZnS}$ is by far the highest. In fact, although there is a significant difference in the quantum yield of $\text{CdSe}/\text{ZnSe}_{(1-x)}\text{S}_x/\text{ZnS}$ and $\text{CdSe}/\text{ZnSe}/\text{ZnS}$, their blinking dynamics are similar. This result shows that a high ensemble QY is not necessarily a good indicator for reduced blinking. One reason for this is that the dark fraction plays a significant role in the ensemble QY and the fraction of QDs visible for blinking analysis, as we had previously identified.^[29, 34] In those studies, we identified a relationship between increased blinking and dark fraction formation. One possibility that may explain this result is that the QDs that blink the most will become part of the dark fraction when using CdS or $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ as the inner shell, lowering QY, but allowing the QDs that blink the least to remain so. On the other hand, using ZnSe or $\text{ZnSe}_{(1-x)}\text{S}_x$ will reduce blinking of all QDs (when compared to the core), but not switch the worse-blinking QDs into the dark fraction. In fact, using this shell may even switch some of the dark fraction back into on-but-blinking QDs, having the effect of increasing ensemble QY. The physical reasons for this behavior at this point would be somewhat speculative, but is likely affected by where the lattice strain is placed in the QD – at the core/shell interface vs the shell/shell interface. The dark fraction is likely only part of the explanation for the lack of correlation between ensemble QY and blinking. Changes in radiative and non-radiative recombination rates directly affect the ensemble QY but may not show up in the blinking statistics. Multiple on states have been observed in some QD reports, with each having a different QY.^[35, 36] Differences in these states would not show up in the blinking statistics when analyzed using a threshold but will directly affect the ensemble QY. Quantifying the differences in various on states is beyond the scope of this manuscript, but

will be the subject of future studies. One other possible source for the lack of correlation between ensemble PL QY and blinking is the different environment of the QDs in the two experiments. For PL QY measurements, the QDs are dissolved in organic solvent and blinking is performed in PMMA film. Quantifying the ensemble PL QY of QDs in PMMA film is technically very difficult due to film inhomogeneity, although the PL QY of *single* QDs in such an environment has been previously measured.^[37] While not an exact comparison, we did compare the ensemble PL QY of QDs in toluene to those in 12% (w/v) PMMA in toluene (we used toluene instead of hexane here due to the higher solubility of PMMA in toluene) and found no difference (results not shown), suggesting that PMMA quenching is not a major problem, although we cannot completely rule it out when QDs are cast in a film. At this point, we would like to note that the TEM images (figure 3) show that CdSe/ZnSe/ZnS particles are the least spherical and CdSe/ZnSe_(1-x)S_x/ZnS are the most spherical, although they show similar blinking statistics. This indicates that, when there is sufficient lattice strain at the core/inner-shell interface, the overall shape of the QD and the strain at the inner-shell/outer-shell interface play less important roles in blinking.

The majority of QD literature to date has analyzed the blinking dynamics as being power-law distributed in the duration of both the on and off events.^[38–42] Some extensions have also been added to explain deviations in this behavior such as the exponential cutoff in observing long on times^[24, 43, 44] and changes in the power-law slope at short time-scales.^[34, 45] Further deviations from power-law behavior have been reported upon varying the QD local environment, such as changing the immobilization matrix and the proximity of silanol groups leading to exponential terms in the on-times distribution function.^[46, 47] Recently, a multiple recombination centers model has been proposed^[48] to describe blinking in which the on times can be fit to a multi-exponential decay function rather than a (truncated) power law.^[35] These recent studies have brought into question whether the blinking dynamics are indeed power-law distributed, as was generally thought.

In light of this new debate, we decided to examine our blinking dynamics in more detail to ascertain if the shell architecture affects which model best describes blinking. We fitted our blinking data to each of the two general models (truncated power law vs. multi-exponential) in figure 5 for the on-times distributions and in figure 6 for the off-times distributions. For the on times, fitting CdSe cores, CdSe/ZnSe/ZnS and CdSe/ZnSe_(1-x)S_x/ZnS to the multi-exponential model required only 2 exponentials while CdSe/CdS/ZnS and CdSe/Cd_(1-x)Zn_xS/ZnS required 3 exponentials. Fitting the on times to a power law required an exponential cutoff time for all samples. Fitting the distributions of off times to a multi-exponential model required 3 exponentials to reasonably fit the data for all samples. For the power-law fit to off times, CdSe cores and the Zn-based inner shells, CdSe/ZnSe/ZnS and CdSe/ZnSe_(1-x)S_x/ZnS, show an exponential cutoff time. A cutoff time for the off states was proposed from ensemble experiments to exist at much longer timescales than the on states,^[44] and our data provides additional evidence for this. On the other hand, the Cd-based inner shells, CdSe/CdS/ZnS and CdSe/Cd_(1-x)Zn_xS/ZnS, did not require an exponential cutoff time, probably a result of shifting to even longer timescales, outside of our analysis window. Clearly, for either model, the fit parameters are highly dependent on the inner shell architecture.

Schmidt *et al.* recently used a change-point analysis method to resolve the various exponential dwell time components based on their varying on intensity.^[35] In their case, they uncovered up to 5 exponentials for CdSe/ZnS core/shell particles, with their longest on-state dwell time of ~120 ms. For CdSe cores, CdSe/ZnSe/ZnS and CdSe/ZnSe_(1-x)S_x/ZnS, our timescales are in general agreement with Schmidt *et al.*,^[35] although we do not recover as many exponentials due to using a threshold rather than change-point analysis algorithm. However for CdSe/CdS/ZnS and CdSe/Cd_(1-x)Zn_xS/ZnS, the longest component is an order of magnitude longer than the CdSe/ZnS particles of Schmidt *et al.*^[35] Differences in the QD architecture (core/shell vs core/multi-shell) may be the reason for this variation, but differences in the excitation mode is also a possibility; Schmidt *et al.*^[35] used a pulsed laser with an average power of 500 nW and a 100× 0.9 NA objective, while our setup used an average power of 10 μW with a 60× 1.2 NA objective.

From visual inspection of the data in figures 5 and 6, it appears that the multi-exponential model fits some of our on-times data better, although the difference is small, but that both models seem to fit the off-times equally well. Normally, the relative goodness of fit is quantified by calculating a reduced chi-squared value. However, this is difficult due to not knowing the exact uncertainty for each point in the distributions of number of events. The uncertainty in the number of events comes from two sources: incorrectly assigning an on (or off) state due to noise crossing the on-off threshold and particle-to-particle variations. The first source of uncertainty is likely to be very small due to the high signal:noise ratio separating the on and off events (as shown in figure 4) and, even if it did occur, would not lead to a state of longer than just a few bins (i.e. < ~5 ms). The second source of uncertainty is more difficult to estimate. We collected long traces from many QDs (at least 30 traces of 300 s each) to reduce the uncertainty as much as we could but there is still likely to be some. We can overcome this problem by using the Pearson chi-squared test in which we do not need to know the variance in the experimental value, but assume that the model (fit) value is the exact value and calculate the deviation of the experimental value from it. This data is reported in table 1 as a ratio, calculated as $\chi^2_{\text{multi-exp}}/\chi^2_{\text{power-law}}$. If this ratio is greater than 1 it suggests that power-law is a better fit, if it is less than 1 then a multi-exponential fit is better and, if it is close to 1 the two models cannot be easily distinguished. From the data in table 1, the ratio for the on times are consistently less than 1, although the cores are only slightly below 1. For the off times, the ratios are more variable, but are generally either above 1 or closer to 1 than are the on times. While this data is not conclusive, it does suggest that the on times might fit better to the multi-exponential model, while the off times are much more difficult to assign to a model.

Another way of distinguishing between the two mathematical models is to re-bin the blinking data at 20 ms resolution rather than 1 ms resolution. If the data are power-law distributed, the power law exponent and cutoff time (which are all longer than 20 ms) should not vary upon re-binning. If the data are indeed multi-exponential, one would expect re-binning to change the recovered fit parameters, since at least one of the exponential lifetimes is on this 1–20 ms timescale. Figure 7 shows the effect of re-binning the data for both on-times and off-times. The off times are generally unaffected by the re-binning whereas the on-times are significantly affected. One must be careful with this type of analysis, however, as was discussed by Crouch *et al.*^[49] It is necessary that a large enough number of events are

analyzed (at least 3000) and that there is a good separation of on and off intensities to avoid artefacts in the data analysis. In our data, we analyzed between 50,000 and 200,000 events for each sample (except for the cores, which had 10,000 – 30,000 events, still well in excess of the minimum criteria needed, as discussed by Crouch *et al.*). Most of our traces also showed excellent separation of on and off intensities, as highlighted in figure 4, with average on intensities higher and lower dark (off) noise than those in Crouch *et al.*^[49]. While we cannot completely exclude the possibility, we feel that the data in figure 7 adequately avoids the pitfalls discussed by Crouch *et al.*^[49] Figure 7 thus indicates that re-binning at 20 ms causes very short off events to be missed, leading to a shift to longer on-times. This is not true for short on events. In other words, if the particle is on, it is possible for the particle to quickly turn off and back on again whereas if the particle is off, the recovery on the on state is more long-lived (at least longer than 20 ms). This observation indicates that the mechanisms underlying switching on and switching off behaviors are different in origin. The change in behavior upon re-binning, taken together with the goodness of fit data from table 1, supports the conclusion that the off-times are best fit to a power law distribution while the on-times are best fit to a multi-exponential model that underlies a multiple recombination centers explanation for blinking. In this case, the recovered exponentials will depend on the binning time, and this must be taken into account when comparing different blinking reports. Importantly, our data further suggests that switching from the high-to-low quantum yield recombination centers (that determines the on-time distributions) is influenced strongly by lattice strain at the core/shell interface, but that moving the lattice strain to the shell/shell interface in core/multi-shell quantum dots reduces the high-to-low switching probability. Switching from the low-to-high quantum yield recombination centers (that determines the off-time distributions) is also affected by the shell architecture, but to a lesser extent, and is likely to be influenced by random processes that underlie a power-law distribution. The exact mechanism(s) of these processes is still unclear but could be related to random static and/or dynamic heterogeneity in the environment of the quantum dot such as ligand dynamics, surface reorganization or fluctuations in the external, local environment. A recent report used a variable pulse rate approach to show that surface trap states can vary with light flux, which they postulated to be related to photoinduced ligand reorganization.^[50] A subsequent paper used the slightly different approach of vary the number of pulses at a fixed repetition rate.^[51] Together these studies showed that both fast and slow decay processes are affected via multiphoton absorption on varying timescales. Our continuous wave excitation at 10 μ W power can certainly lead to multiphoton processes, especially when long-lived trap states are involved to produce trion states that may be affected by both the interfacial trap states and the surface ligands. In this case, it is likely that trapping of the charge carrier to one of these surface traps depends on the number of traps at the core/shell interface and, to a lesser extent, at the shell/shell interface. Then, ligand re-organization back to an emitting state could be a more random process (i.e. resulting in power law behavior) that is not light-induced. This could allow for the ability for both slow recovery and fast recovery. The fast recovery processes leads to very short off times being missed by binning at 20 ms rather than 1 ms, which, in turn, pushes the on-times distribution towards longer times (as figure 7 shows). More work on systematically changing the environment is needed to thoroughly evaluate this mechanism but, in any case, our results show that both of these processes – trapping and recovery – are affected by the inner shell architecture.

Summary and Conclusions

We systematically synthesized a range of multi-shell QDs containing CdSe cores, ZnS outer shells with various inner shells to determine the role of the inner shell architecture on the QY and blinking properties. For the inner shell, we used CdS, ZnSe and the gradient alloys $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ and $\text{ZnSe}_{(1-x)}\text{S}_x$ where x changes by 0.2 per monolayer to slowly change the inner shell composition to ZnS. We found that the QY depends strongly on the inner shell thickness and composition. Upon adding ZnS, the maximum QY of ~80% is reached when a gradient-alloy of $\text{ZnSe}_{(1-x)}\text{S}_x$ is used as the inner shell. For all other inner shell architectures, adding ZnS reduces the QY. On the other hand, blinking is reduced more when CdS is used and using a gradient-alloy does not improve blinking over using just the single-component inner shell. This result highlights that a high QY is not necessarily a good indicator for reduced blinking. The connection between blinking and the dark fraction formation^[29, 34] is one likely candidate for this lack of correlation between QY and blinking, and the inner shell architecture could play a role in whether the worse blinking QDs are turned off or not. Another possibility is that the inner shell architecture could lead to variations in radiative and non-radiative rates of the on state(s). Future work will further investigate the contributions from these possibilities.

We analyzed the blinking statistics according to 2 mathematical models: the more common truncated power-law and the more recent multi-exponential model. By comparing the fit qualities as well as how the blinking data changes with binning at 1ms vs. 20 ms, we proposed that the off-times are best described by the power law model while the on-times can be best described by the multi-exponential model. The key result from this work is that both are affected by the inner shell architecture.

Acknowledgments

Generous financial support by the NSF (CHE-1255440), the NIH (COBRE P30 GM103450), and the Arkansas Biosciences Institute is gratefully acknowledged. TEM instrumentation access is provided by the Arkansas Materials Characterization Facility (Funded in part by the NSF) and the Institute of Nanoscience and Engineering at the University of Arkansas.

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Figure 1.
(a) Schematic of band gap offset and lattice mismatch values of semiconductor materials specific to our work. (b) Schematic highlighting difference in band-edge offsets between core/shell/shell (left) and core/gradient-alloyed shell/shell (right) architectures.

Figure 2.

a) PL peak maximum and b) photoluminescence quantum yield as a function of shell composition and thickness. Red: CdSe/CdS/ZnS; Green: CdSe/Cd_(1-x)Zn_xS/ZnS; Blue: CdSe/ZnSe/ZnS; Magenta: CdSe/ZnSe_(1-x)S_x/ZnS. Points are average values of 2 samples and the error bars are 1 standard deviation wide to show the reproducibility.

Figure 3.
TEM Images and size distributions of core/multi-shell samples.

Figure 4.

(a) A 60-second section of a typical fluorescence trace highlighting blinking behavior (b) 5-second section of the trace showing well-resolved on and off events using a threshold. Log-log plots of P_{on} (c) and P_{off} (d) distributions for CdSe cores (black) CdSe/CdS/3ZnS (red) and CdSe/5Cd_(1-x)Zn_xS/3ZnS (green) and CdSe/5ZnSe/3ZnS (blue) and CdSe/5ZnSe_(1-x)S_x/3ZnS (magenta). (e) Fraction of time a QD spends in the on state as a function of the shell architecture (the gradient alloy shells are labeled as CdZnS and ZnSeS rather than Cd_(1-x)Zn_xS and ZnSe_(1-x)S_x due to space limitations).

Figure 5.

(a–c) Power law fitting of on-times and extracted parameters plotted as a function of shell architecture. (d–f) Multi-exponential fitting of on-times and extracted parameters plotted as a function of shell architecture. Color scheme is the same as for Figure 4. In (b, c, e, f), the gradient alloy shells are labeled as CdZnS and ZnSeS rather than $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ and $\text{ZnSe}_{(1-x)}\text{S}_x$ due to space limitations.

Figure 6.

(a–c) Power law fitting of off-times and extracted parameters plotted as a function of shell architecture. (d–f) Multi-exponential fitting of on-times and extracted parameters plotted as a function of shell architecture. Color scheme is the same as for Figure 4. In (b, c, e, f), the gradient alloy shells are labeled as CdZnS and ZnSeS rather than $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ and $\text{ZnSe}_{(1-x)}\text{S}_x$ due to space limitations.

Figure 7.

Overlay of on-times distributions (circles) and off-times distributions (triangles) from 1-ms binned data (open symbols) and 20-ms binned data (filled symbols) for each shell architecture. On and off data are offset relative to each other on the y-axis for visualization, so the y-axis has been relabeled as relative occurrence to reflect this fact.

Relative goodness of fit tests to power law and multi-exponential models for the data in figure 5 (on times) and figure 6 (off times). Data are reported as χ^2 ratios (multi-exponential/power-law) using the Pearson χ^2 test. A ratio less than 1 indicates that the multi-exponential model is a better fit and a ratio greater than 1 indicates that a power-law model is a better fit.

Table 1

	CdSe core	CdSe/CdS/ZnS	CdSe/CdZnS/ZnS	CdSe/ZnSe/ZnS	CdSe/ZnSeS/ZnS
On times χ^2 ratio	0.8863	0.6111	0.1603	0.1080	0.1205
Off-times χ^2 ratio	1.1629	0.8229	2.5919	0.3206	0.8857