Controlling photo-induced spectral changes in CdSe/ZnS quantum dots by tuning inter-dot energy transfer

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We study photo-induced spectral changes in films containing two sizes of chemically synthesized CdSe/ZnS quantum dots (QDs) using static and time-resolved spectroscopies. As the concentration of the smaller (donor) QDs is varied over two orders of magnitude relative to the larger (acceptor) dots, we find that with decreasing proportion of donors, the photo-oxidation rate increases in acceptors but slows down in donors. We conclude that these differences originate from the variations in the amount of inter-dot energy transfer from donors to acceptors, and this tunability can be used to enhance the shelf-life of QD based opto-electronic and photovoltaic devices. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4721808]

The flexibility associated with the size-tunability of optical and electronic properties have made chemically synthesized semiconductor quantum dots (QDs) very appealing for a variety of applications. These include opto-electronic,[1,2] biochemical sensory,[3,4] and photovoltaic applications.[5,6] However, many of the devices designed for these applications are operated under ambient conditions, which bring up the issue of short QD photo-stability. Generally, QDs display photoluminescence (PL) quenching following exposure to light and oxygen.[7–9] A number of other factors also influence the photo-degeneration of QDs, including QD core diameter,[7] thickness,[10] and composition[11] of passivation layer(s). An additional factor is inter-particle interactions, which result in energy transfer (ET) from the smaller to the larger QDs in an ensemble. Prior work[12] has shown that although increasing the packing density of single-size QDs with a modest dispersion distribution reduces the rate of photo-oxidation and darkening, this trend is reversed in the limit where the QDs form a close-packed film. Then, the spectral stability substantially worsens. Typical QD based devices may require high density of dots that will most definitely have considerable ET,[13] which makes this a problem worth investigating. In this letter, we study the extent and nature of ET influence on photo-oxidation and quenching rates in mixed-size CdSe/ZnS QD films. We tune the efficiency and amount of ET by preparing samples with the ratio of donors (smaller QDs) and acceptors (larger QDs) varying over two orders of magnitude, and follow their spectral dynamics during prolonged periods of photo-excitation.

For our samples, we use octadecylamine capped CdSe/ZnS core-shell QDs (purchased from Ocean Nanotech). In solution, the donor QDs (4.1 nm core diameter) have emission centered at 580 nm and the acceptors (5.8 nm core diameter) at 620 nm. The ligands add an extra 2 nm to the total diameter. The mixed-size samples are prepared as solutions by combining the different proportions of donor and acceptor QDs in a vial, followed by sonicating the mixture for 30 min. The donor-to-acceptor ratios are varied between from 0.1:1 to 10:1, while maintaining a net molar concentration in the range of 17–19 μM. To form the close-packed QD films, we drop-cast the solution on clean glass slides and allow the solvent to evaporate. For control measurements, we create similar samples using exclusively donor and acceptor QDs. All measurements are performed using a custom-designed, motorized, scanning confocal microscopy system with diffraction-limited optical resolution (600 nm). The photo-excitation is tuned to 420 nm using the frequency-doubled output of a tunable Ti:sapphire laser. It has a 76 MHz (13 ns) repetition rate and pulse width of 150 fs. The excitation power density is kept constant at 45 W/cm^2. For the spectral analysis, the data are collected by a 0.3 m spectrometer and dispersed onto a thermo-electrically cooled CCD (resolution, 0.18 nm). Time-resolved data are collected with a single photon avalanche detector via the spectrometer coupled to a time-correlated single photon counting system (PicoHarp 300) with an instrument response function of 12 ps. All measurements are done at room temperature under ambient conditions.

Figures 1(a) and 1(b) compare the emission spectra of our samples before and after forming the films. As seen in Fig. 1(a), in solution the peak emission wavelength (λ_{PEAK}) is unaltered for both donors and acceptors (labeled "D" and "A") as their concentrations are varied. The relative emission intensities are proportional to the amount of each type of QD. In the films, close packing of QDs allows ET via inter-dot dipolar coupling and the extent and efficiency of ET is reflected in the modified emission spectra. For all three samples the acceptor emission intensity is enhanced compared to that in solution, indicative of ET from the donors.[14] The 10:1 sample additionally shows an increased λ_{PEAK} (red-shift) of the donor emission, implying significant ET between the donors themselves.[15] This is expected since the typical coordination number of donors for each acceptor is in the range 4–5, which means that in this sample there are regions in the film where each donor is surrounded exclusively by other donors. To quantify ET in the initial state of the system before the photo-excitation is started, we carry out spectrally resolved, time-resolved measurements in the range 550–650 nm in 10 nm steps. For this data collection, we

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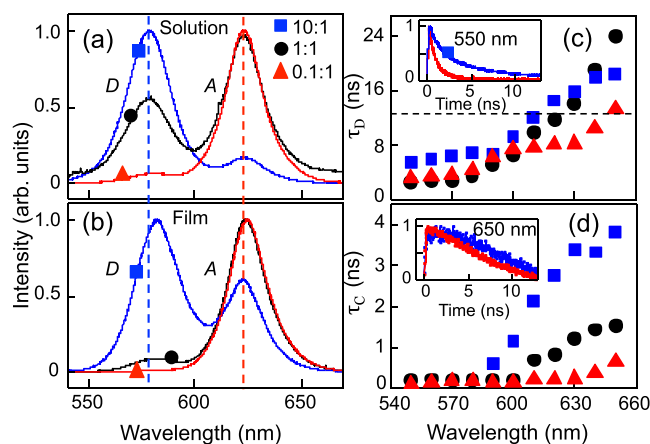
FIG. 1. (a) Emission spectra of QD solutions with 10:1 (square), 1:1 (circle), and 0.1:1 (triangle) donor to acceptor ratios. (b) Emission spectra of QD films with the same ratios. Both emission spectra are normalized. The dashed lines represent the emission peaks of the solution samples. (c) Long decay times τ_D for 10:1 (square), 1:1 (circle), and 0.1:1 (triangle) samples. (d) "Charging" time τ_C for the same samples. Insets: time-resolved PL data for the 10:1 and 0.1:1 samples at 550 nm (c) and 650 nm (d).

reduce the excitation power by a factor of 10 and use an integration time of 20 s to ensure measurements are completed before any photo-excitation related effects begin. Two representative recombination curves are shown in the insets of Figs. 1(c) and 1(d), at 550 and 650 nm, respectively. Their changing shapes are testimony to the effect ET has on the dynamics of the mixed-size QD ensemble emission. We analyze the time-resolved curves using exponential fits and the general trend for all samples is the presence of three time scales: a short decay time, a longer decay time τ_D, and a rise time τ_C. The short decay occurs on the scale of ~1 ns and is indicative of intra-ensemble ET, so we concentrate on the other two in the rest of our discussions. Figure 1(c) shows τ_D for the samples, and the recombination time in solutions in shown as a dashed line for comparison. τ_D in all the films is less than the decay time in solution for the donor emission ($\lambda < 600$ nm). We can quantify the efficiency of ET in the donors as $1 - \tau_D/\tau_S$, where $\tau_{D,S}$ are the recombination times of the donors in the film and solution, respectively.[16] In the 10:1 sample at 550 nm, the donors have ET rates as high as 60% but by 580 nm it is reduced to 49% and by 590 nm, to 44%. By contrast, both 1:1 and 0.1:1 samples have ET rates ~90% at 550 nm which decreases with increasing wavelength but does not fall below 80% until 590 nm. In the acceptor emission range ($\lambda > 600$ nm), the recombination time is longest in the 10:1 sample (with the exception of the very long end), which appears counter-intuitive to the observation above that it shows least efficient ET. This can be understood by dissociating the efficiency of energy transfer from its exhibited impact.[16] Although the 10:1 sample has less efficient ET, due to the large proportion of donors relative to acceptors, the effects are clearly observable, resulting in an average longer acceptor recombination time. Similarly, while the 0.1:1 sample has higher ET rates, they have less of an impact when averaged over the acceptor ensemble. The 1:1 sample with most efficient ET also prolongs the acceptor recombination times. We also note that the effects of ET in the 10:1 sample appears to reach a plateau, but the 1:1 sample shows an unsaturable increase in τ_D with increasing

acceptor emission wavelength, resulting in it surpassing the 10:1 sample's lifetimes for $\lambda > 640$ nm. The short rise time τ_C is not observed in the solutions, but is present in all the films exclusively in the acceptor emission range ($\lambda > 600$ nm). This is typical of ensembles with ET,[17] and is attributed to the time scale over which the acceptors receive energy from the nearby donors. We refer to it as a "charging" time and observe in Fig. 1(d) that it increases with acceptor wavelength and is consistently longer with increasing donor concentration in the mix.

Once we establish the initial parameters and ET related effects in the mixed-size samples, we begin the process of photo-excitation, which consists of continuous illumination of the films for a 120 min period and collecting emission spectra every 30 s. The two well-known effects of photo-exposure on any QD ensemble are irreversible PL quenching, and a corresponding spectral blue-shift.[7] These two are normally linked because oxidation of the core creates surface states where carriers get trapped, resulting in the emission being quenched. It also causes the QD core to shrink in size, which increases the quantum confinement and hence, the band gap. As mentioned earlier, ET between QDs can also promote PL quenching of the dots in the "acceptor" subset. This mechanism manifests itself differently from the photo-oxidation effect, as it does not create an oxide shell and is therefore not accompanied by spectral changes, a useful distinction that allows us to identify the origin of photo-darkening. We begin by analyzing our control samples. In Figs. 2(a) and 2(b), we plot the PL intensity and λ_{PEAK} as functions of photo-excitation time for films formed using only donors and acceptors (long and short dashed lines, respectively). The trends we observe are typical, including the photo-brightening[18] and increase in λ_{PEAK} (red-shift)[19] during the initial 20 min. These are followed by the expected quenching and decrease in λ_{PEAK} (blue-shift). Exponential fits to the intensity curves of Fig. 2(a) suggest a 1/eth decay time of approximately 120 min for the acceptors and only 20 min for the donors. The donors not only exhibit a faster intensity quench rate (quantified as inverse of the 1/eth decay time) but λ_{PEAK} blue-shifts much more than in the acceptors.
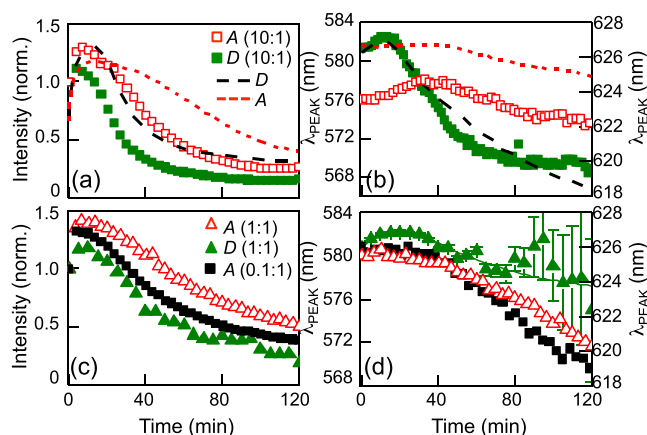

FIG. 2. (a) Emission intensity and (b) emission peak (λ_{PEAK}) as functions of photo-excitation time for donors and acceptors in the 10:1 sample. The comparative curves for films with only donors (long dashes) and acceptors (short dashes) are also shown. Equivalent results for (c) emission intensity and (d) λ_{PEAK} for the 1:1 sample and the 0.1:1 sample.

These are most likely a result of their smaller comparative sizes.[7]

Next, we subject the mixed-size films to a similar protocol of photo-excitation and observe very different trends for donors and acceptors. Focusing solely on the photo-induced changes in the acceptors, we notice that in the 10:1 sample (Fig. 2(a), hollow squares), PL intensity decays much faster than in the single-size control sample, with a decay time ∼30 min. But the magnitude and rate of the spectral shift surprisingly remains unchanged (Fig. 2(b), hollow squares). In the other two samples with fewer donors, the acceptor intensity quench rate slows down (Fig. 2(c), hollow triangles and solid squares) although it never recovers to the single-size sample's rate. Conversely, the spectral shift in Fig. 2(d) shows larger blue-shifts than the 10:1 sample. It appears therefore, that in the mixed-size samples, the photo-excitation impacts acceptor PL quenching and λ_{PEAK} variation in an opposite sense. In the same figures, the donor behavior appears more consistent. When the proportion of acceptors is small (10:1), the PL quench (Fig. 2(a), solid squares) and λ_{PEAK} blue shift (Fig. 2(b), solid squares) are very similar to the donor-only sample, with the minor difference that the rate of blue-shift is faster. However, the donors are significantly impacted in the 1:1 sample where the donor PL decay is slower by about a factor of 2, and the spectral blue-shift is smaller by a factor of 5. To recapitulate the results so far, addition of donors cause faster PL quenching in acceptors, but has a more complicated effect on their λ_{PEAK}. From the perspective of donors, both emission intensity and λ_{PEAK} evolution appear more stable in the mixed-size samples than in the unmixed ones. Clearly, there is an inter-play of ET and photo-oxidation effects in the mixed-size films, which make understanding the observations complicated. However, the behavior of the 10:1 sample can be explained with reasonable ease—there is a large amount of energy transfer from the donors to the acceptors, with almost every acceptor completely surrounded by donors. As a result of this continuous ET, the acceptors rapidly darken. But the rate of photo-oxidation is not affected by ET, which is why the magnitude and rate of shift of λ_{PEAK} remain unaffected. The donor emission quench rate is unperturbed, although they appear to oxidize and blue-shift slightly faster. Overall, it appears this ratio of donors and acceptors is not beneficial to either in terms of photo-stability.

The two samples with lower donor-to-acceptor ratios appear more favorable in this respect. In both of these, the reduced amount of donor-to-acceptor ET is responsible for the acceptors quenching slower. This also allows the donors to oxidize slowly in the 1:1 sample as following ET over 1–2 ns, they can remain "dark" for a prolonged period between excitation pulses. The acceptors' faster blue-shift is due to a more mundane reason. In the 10:1 sample each acceptor is surrounded completely by smaller donors, whereas in the 1:1 sample they are instead surrounded by other acceptors. In a close-packing scenario, smaller spheres enclosing a larger one expose less of the surface of the latter to oxygen.[20] Therefore, in the 1:1 sample photo-oxidation rate increases for the acceptors. For the same reason, the acceptors quench and oxidize slightly faster in the 0.1:1 sample.
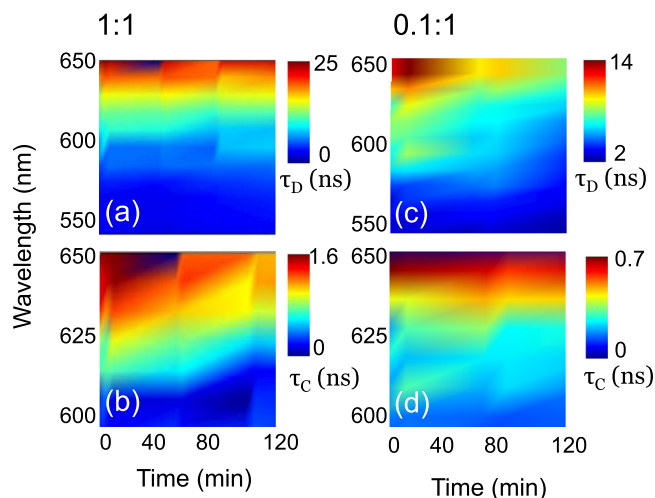

FIG. 3. (a) τ_D and (b) τ_C for the 1:1 sample mapped out with varying emission wavelength and 120 min of photo-excitation time. (c) τ_D and (d) τ_C for the 0.1:1 sample.

The signal-to-noise makes it impossible to follow the donor emission in the 0.1:1 sample using static spectroscopy. Instead, we turn to studying how the recombination dynamics of both donors and acceptors change over the photo-excitation period for this, and any additional characteristics not revealed so far. Photo-oxidation creates surface trap states, which introduce a channel of non-radiative recombination for the photo-generated carriers. Consequently, the recombination decay time decreases as oxidation progresses with time. In Figs. 3(a) and 3(b), we plot τ_D and τ_C for the 1:1 sample extracted from time-resolved PL data at different emission wavelengths and photo-excitation times. τ_D is unaltered in the donors ($\lambda < 600$ nm) and this ties in with Fig. 2(d), which indicated small photo-oxidation induced blue-shift. τ_D over the acceptor emission regime shows a small (∼5%) decrease only at very long wavelengths ($\lambda > 640$ nm). This indicates that photo-oxidation begins with the largest acceptor QDs, as we would expect using the geometrical argument outlined earlier. As the overall emission of the acceptors shifts to lower wavelengths, the charging time τ_C decreases, seen in Fig. 3(b) and in agreement with the trend observed in Fig. 1(d). Analyzing the 0.1:1 sample, we see that in the range $\lambda > 620$ nm, there are indications of substantial photo-oxidation where τ_D decreases by almost 40% over the 120 min of photo-excitation. Again, this is expected as now the acceptors have greater exposed surface area vulnerable to oxidation, and is supported by Fig. 1(c). The donor emission shows decay times that decrease very slightly over the 120 min period, which indicates that while at this concentration donors oxidizing slowly, they are less stable than in the 1:1 sample. This time though there is no corresponding change in τ_C for the acceptors, shown in Fig. 3(d), which may not have any fundamental implications, since those times were very small to begin with. It does establish the continuation of ET throughout the photo-excitation process.

In conclusion, we have shown that ET between different sized QDs is a vital factor in determining their long-term stability. Varying the relative proportions of each size allows us to tune the effect of ET on the ensemble, and by choosing a suitable ratio of different sized QDs, it is possible to inhibit

rapid photo-degradation of the smaller QDs in the mixture. From our studies, we suggest that a mixture with excessive donors is detrimental while a 1:1 ratio is most beneficial in achieving optimal performance.

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