Trion Decay in Colloidal Quantum Dots

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ABSTRACT Using charged films of colloidal CdSe/CdS core/shell quantum dots of ~3.5 to 4.5 nm core diameters and 0.6 to 1.2 nm thick CdS shells, the radiative and nonradiative decay of the negatively charged exciton, the trion T^-, are measured. The T^- radiative rate is faster than the exciton by a factor of 2.2 ± 0.4 and estimated at ~10 ns. The T^- lifetime is ~0.7−1.5 ns for the samples measured and is longer than the biexciton lifetime by a factor or 7.5 ± 1.7.

KEYWORDS: quantum dots · photoluminescence · cyclic voltammetry · trion · career recombination · Auger recombination

In small colloidal semiconductor nanocrystals, known as quantum dots (QDs),[1,2] the addition, or removal, of charges can have drastic effects on their optical properties.[3] These effects are significant since these materials are of interest in various applications from biology to electro-optical devices[2] where charges may be involved. In particular, the electron−hole recombination leading to fluorescence should be strongly affected by charges.[4,5] In colloidal quantum dots the negative T^- or positive T^+ trions are expected to be weakly emissive due to fast “auger” nonradiative recombination. More than a decade ago, trions were proposed to be responsible for the off-states[4,6] of the PL blinking in colloidal quantum dots. Charging QDs in solution[7] or films[8] confirmed that it diminishes the photoluminescence (PL), but films of singly and doubly charged dots had detectable PL and even a lower threshold for stimulated emission than neutral dots[8] implying that trions are not very dark. Despite being assigned a significant role in the photophysics of colloidal dots, neither the lifetime of trions nor the quantum yield have been measured in such systems. In contrast to the colloidal dots, Trion decay has been measured in Stransky−Krastanov quantum dots but, in these systems, the trions are as bright as excitons.[9,10]

In colloidal QDs, although trion decays have not been measured directly, there has been several experiments[11−13] on the recombination dynamics for multiexcitons. These confirmed that biexcitons (XX) can be much shorter lived than excitons.[11,12] It has also been proposed that the biexciton decay is separable into rates from T^- and T^+, in which case the trion lifetimes relate to the biexciton lifetime by $1/\tau_{XX} = 2/\tau_{T^-} + 2/\tau_{T^+}$.[5] Since theoretical predictions for CdSe quantum dots give similar lifetime for T^- and T^+,[5] the trions should be 4 times longer lived than the biexciton. A simple scheme showing the different relaxation routes are shown in Figure 1a. This work uses thin films of CdSe/CdS core/shell colloidal quantum dots with an electrochemical control on its Fermi level, and time-correlated single photon counting (TCSPC) measure of its PL decay to provide a first direct measure of the T^- decay. We find that the T^- decay is indeed longer than XX and also that its radiative rate is faster than the exciton radiative rate at room temperature. Taken together, the results imply a ~10 to 15% quantum yield for T^- which may be too bright for the off-state seen in blinking.

RESULTS AND DISCUSSION

Core/shell nanocrystals of CdSe/CdS are used since they exhibit good stability of the PL and fast switching with electron injection.[14] Figure 1 panels b and c show that negative charging leads to faster decays but also higher photon counts at $t \approx 0$. Qualitatively, the former is consistent with the increased nonradiative “auger” recombination rates for the trions $k_{T^-_{nr}}$. The enhanced photon counts at early times also indicates a shorter radiative lifetime of trions $k_{T^-_r}$.

Using an instrument response function (IRF) measured from the fast fluorescence

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Received for review February 5, 2009 and accepted March 20, 2009.

10.1021/nn9001177 CCC: $40.75

decay of 1% picric acid, and deconvolution, the PL decays of the charged films show an increase in the proportion of the faster component. While the PL decays from solutions require one or two exponentials to be fit with residuals smaller than the photon count noise, the films require three to four exponentials. This is likely to arise from nonradiative processes compounded with energy transfer between QDs[15] from bright to dark dots. Since the deconvolution to multiexponential does not provide a unique set of exponentials, it is impossible to directly extract the trion lifetime this way. We chose instead to simulate the ensemble of the PL decay curves with a minimum set of parameters.

The simulation starts with a deconvoluted triexponential fit for the neutral film. The three components $\{A_i\}$ are not a unique choice and they arbitrarily represent three separate groups of nanocrystals with different nonradiative rates $\{k_{0i}\}$. We assume that the nonradiative rates due to charges in the quantum states of the nanocrystals can be added to the initial nonradiative rates $\{k_{0i}\}$, or in other words, the charges do not affect the preexisting nonradiative processes. Under a reducing potential these three sets are assumed to be charged with the same distribution.

A Nernst-type equation

$$\frac{\exp X + 2\exp Y}{1 + \exp X + \exp Y}$$

where

$$X = -\frac{|e|(V - V_0)}{kT^*}$$

$$Y = -\frac{2|e|(V - V_0) + E_c}{kT^*}$$

is used to fit the exciton bleach and extract three parameters which are the redox potential V_0 for the singly charged state, a charging energy E_c for the doubly charged state, and an effective broadening given by a temperature T^*. Both E_c and T^* give rise to the width of the exciton bleach *versus* potential, such that the exciton bleach alone does not allow a narrow determination of both E_c and T^*.

The trion nonradiative decay and the ratio of the T^- and X radiative rates, $k_{T_r^-}/k_X$, are the two dynamic parameters that we seek. We set the nonradiative decay rate of the doubly charged trion T^{2-} to be twice that of the T^-, as expected for an "Auger" recombination[11,16] and the radiative rate of T^{2-} to be the same as T^- since it is limited by the common hole. With the initial triexponential fitted PL decay for the neutral dots, the two dynamic parameters for the charged dots, and the charging distribution fitted to the optical bleach, all the PL decay curves are calculated and convoluted with the IRF to yield a visual fit. The parameters affect separately very different aspects of the PL decays so that the manual fitting converges rapidly. This work focuses on the low charging regime, and the PL decay curves are considered when the average charging level is less than 1.5 electrons per dot, therefore below a ~75% bleach of the exciton.

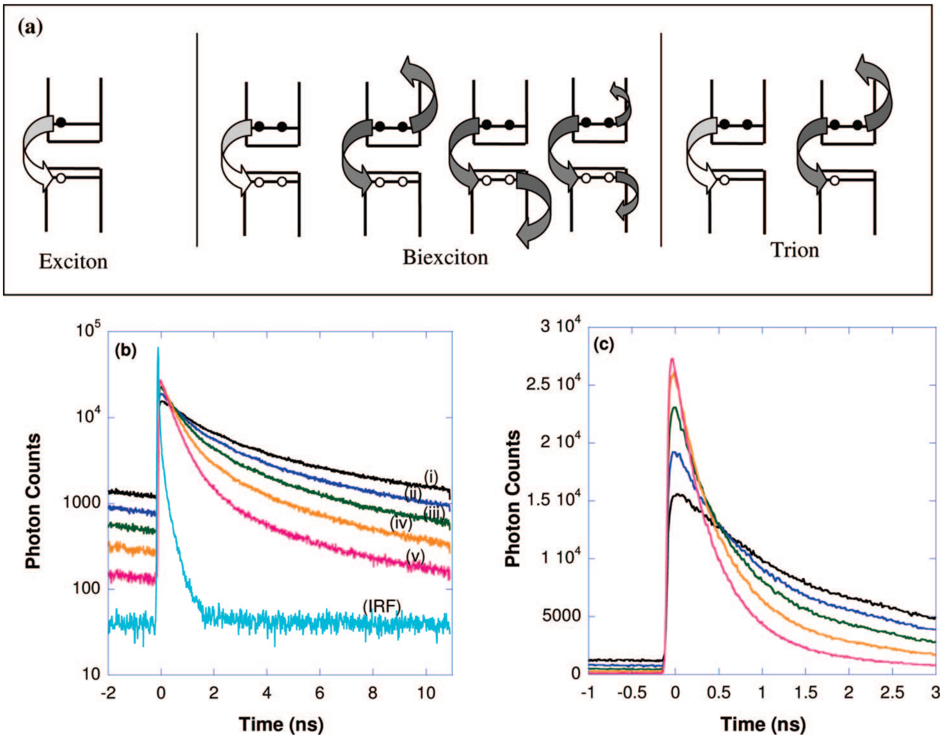

Figure 1. (a) A cartoon of the radiative (white arrows) and nonradiative (gray arrows) recombination are shown for an exciton, biexciton, and a negative trion. PL decays of CdSe/CdS quantum dots at different charging levels from neutral (i) to most negatively charged (~1.5 electrons/dot,(v)) are shown on a log (b) and linear scale (c). The long lifetime component of the films (Table 1) and the rapid laser periodic excitation every 13.2 ns also give rise to a "wrap-around" in the photon counts.

TABLE 1. Decay Lifetimes and Fit Parameters Obtained for the Four Samples Investigated in This Work

sample	diameter (nm)	τ_{XX} (ps)	τ_{T^-} (ps)	$k_{T_r^-}/k_X$	kT^* (meV)	E_c (V)	k_{ET}^{-1} (ns)
I	5.3 ± 0.4	100 ± 25	700	2.25	0.086	0.1	200
II	5.7 ± 0.2	150 ± 25	950	2.55	0.068	0.01	100
III	5.6 ± 0.2	160 ± 30	1300	2.25	0.053	0.03	100
IV	6.7 ± 0.4	200 ± 25	1500	1.8	0.082	0.023	50

The model works well for times shorter than ~3 ns which is the relevant time scale for the trion decay. However it deviates significantly at longer times because the longest lifetime of the neutral dots remains fixed in the model while, experimentally, the long time component gets faster at more reducing potential, typically from ~10 to ~5 ns. In neutral films, the dots having the longest lifetime are likely to be bright dots with only bright dots as nearest neighbors so that energy transfer does not alter the PL decay. However, when some of the nearest neighbor dots are charged, energy transfer should now lead to faster decay kinetics. This can be captured by introducing an energy transfer rate k_{ET} between neutral dots and singly charged dots, noting that there can be no energy transfer to the doubly charged dots. The overall rate is proportional to the number of singly charged dots within the 12 nearest neighbor shell with a binomial distribution. With three dynamic parameters ($k_{T_r^-}/k_X$, $k_{T_{nr}^-}$, and k_{ET}) the experimental PL decays are well reproduced over the full 13 ns acquisition time as shown in Figure 2a. The simulation also captures the PL peak signal as shown in Figure 2b (inset). Note that the addition of the energy transfer parameter, k_{ET}, affects $k_{T_r^-}/k_X$, $k_{T_{nr}^-}$ by less than 10% since these capture the earlier part of the decays.

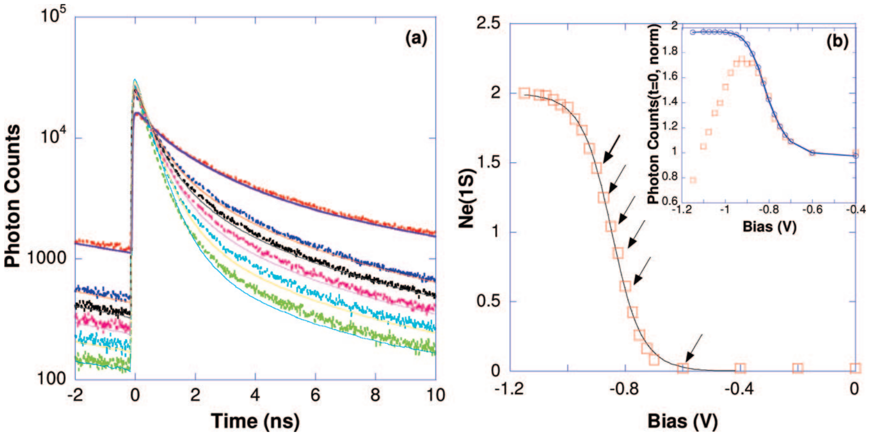

Figure 2. (a) Simulated (solid lines) and experimental (dots) PL decays for sample I. The faster decays are in order of increasingly reducing potentials. (b) The 1S optical bleach (squares) and the corresponding Nernst fit (solid line) with the arrows corresponding to the reducing bias for the displayed PL decays. The photon burst upon pulse arrival determined experimentally (red squares) and from simulation (blue circles) are shown in the inset of panel b.

Table 1 shows the results for four samples of different core sizes and shell thicknesses. The T^- radiative rates are larger than for the exciton by a factor of 2.2 ± 0.4 while the T^- lifetimes get systematically longer for larger dots. The effective broadening kT^* for the different samples stays within a narrow range, (0.086−0.053 eV), that arises from size distribution. The charging energy covers a range (0.1−0.01 eV) that seems wide but it may reflect different coupling between dots for the different films. The energy transfer rate from neutral to charged dots obtained from the model is slow compared to the estimated energy transfer between two nearest neighbor resonant nanocrystals.[17] This may be due to the weaker and red-shifted absorption of charged quantum dots[18] compounded by the fact that the charged dots would also be the largest. The low value of k_{ET} also results from assuming 12 nearest neighbors. The cross-linking process may instead create a local environment with a smaller numbers of nearest neighbors, such that k_{ET} would be correspondingly larger. A further study of energy transfer in films would require characterizing energetic and structural disorder but, as mentioned above, it does not affect the conclusions on the trion decays.

For self-assembled dots, changes in the wave functions due to Coulomb interactions have been proposed to explain different radiative rates of trions and exciton.[10] With the more strongly confined colloidal dots, degeneracy between bright and dark states for the exciton already justifies a faster trion radiative rate.[8] Angular momentum considerations for CdSe colloidal dots have explained the 3−6× faster radiative lifetime of the biexciton compared to the exciton.[13,19] The neutral band edge exciton has a total of eight excitons, with five dark states ($F = 2$) and three bright states ($F = 1$),[1,20] while all four T^- states ($F = {}^3/_2$) should be bright with a negative charged ground state ($F = {}^1/_2$). Assuming equally populated states would give a ratio of $k_{T_r^-}/k_X = (4/4)/(3/8) = 2.6$ consistent with our experimental results. At low temperature, the ratio $k_{T_r^-}/k_X$ should get larger since the lowest excitonic state is a dark state[21] and this will be tested in future work.

The trion lifetimes are then compared to biexciton lifetimes that are directly measured on the same samples but in solution using transient absorption (TA) pump−probe spectroscopy.[22] For one sample, this was measured in a film as well to confirm that the dot−dot interactions do not change the biexciton decay appreciably. The high fluence PL decay was also recorded for the film and, after deconvolution with the IRF, the fast rate was again found to be similar to the one obtained by transient absorption. Since biexciton decay measured from three different techniques are consistent, we use the biexciton decay times obtained from transient absorption in solutions to compare with the trion lifetimes from PL decay in films. For the samples investigated here, the biexciton decay increased from 100 ps for the smaller nanocrystals (5.4 nm diameter) to 200 ps for the larger ones (6.4 nm diameter). The T^- lifetime also increases from 700 to 1500 ps, with a nearly constant ratio of 7.5 ± 1.7. This is larger than the expected 4-fold discussed earlier. Assuming the additivity of rates $1/\tau_{XX} = 2/\tau_{T^-} + 2/\tau_{T^+}$, would give T^+ lifetimes about 3× shorter than T^-, or ~ 2.5× longer than XX. We note that the additivity of rates neglects more than two-particle Coulomb interaction, that is, the fourth scheme of biexciton recombination in Figure 1. We cannot verify its validity in our system, since we cannot positivily charge the CdSe-based QDs and directly measure the T^+ lifetime. It is also noteworthy that the T^- quantum yields are calculated to be between 10% and 15%, taking exciton radiative and biexciton lifetimes of ~20 ns and ~200 ps, respectively. Thus although the singly charged quantum dots would be dimmer than the neutral dots in single dot microscopy experiments, they may not be dark enough for the off-state.

CONCLUSIONS

We provide the first measurements of the trion radiative and nonradiative lifetimes in colloidal nanocrystals. The problem of deconvoluting the ensemble PL dynamics into sums of multiexponential decays with meaningful physical interpretations was circumvented by simulating the PL decay at different charging levels with a minimum number of parameters. The trion radiative lifetimes are (2.2 ± 0.4) times shorter than the exciton at room temperature, and the trion lifetimes are found to be (7.5 ± 1.7) fold slower than the biexciton. The results are relevant to electrically generated light from colloidal dots as well as for the models of blinking.

METHODS

The CdSe/CdS core/shell are synthesized as reported earlier.[14,23] In a typical reaction, 0.026 g of cadmium acetate is converted to cadmium myristate by heating it with 0.060 g of myristic acid in 6 mL of octadecene (ODE) at 235 °C in an inert atmosphere. The mixture is brought down to room temperature and 0.0078 g of selenium is added. After degassing for a few minutes, the temperature is raised rapidly to 235 °C. When the solution turns orange-red, 1 mL of trioctylamine is added dropwise to the reaction mixture. The absorption spectrum is monitored by taking small aliquots of the product at regular intervals. The flask is quickly cooled to room temperature when the first absorption peak reaches the desired wavelength. The cores were then cleaned and redispersed in 4 mL ODE with 1.5 g octadecylamine (ODA). The CdS shell is grown by the dropwise addition of 0.1 M cadmium oleate in ODE (0.1 M) and sulfur in ODE (0.1 M) each at 220 °C. CdS shells of only one to two ML are grown to allow distinct charging of the $1S_e$ and $1P_e$ states.[24] The size range of dots investigated is *ca.* 3.5−4.5 nm for the core diameters with 0.6−1.2 nm thick CdS shells, emitting in the 590−615 nm range. Excess ligands are removed by redispersing the dots in toluene and reprecipitating with ethanol a few times. The clean quantum dots are stored in tetrachloroethylene. Clear films are made on transparent indium tin oxide (ITO) coated glass electrodes by dropcasting the nanocrystals from a 9:1 hexane/octane solution. The film is then exposed to ethanol with 0.1 M 1,7-heptanediamine, to cross-link[25] the dots and allow fast electrochemistry. The electrochemical cell consisting of the ITO (working electrode), a platinum wire (counter-electrode), and silver wire (pseudoreference electrode) is assembled inside a glovebox with the oxygen content <5 ppm. The lower half of the cell is a glass test tube, allowing optical measurements on the films. The electrolyte is 0.1 M tetrabutylammonium perchlorate (TBAP) in propylene carbonate (PC).

The PL decay is measured by exciting a spot on the film using a coherent Verdi pumped Mira 900 (Ti:Sapphire, 76 MHz, <200 fs pulse width) laser frequency doubled to 425 nm and recording the photon arrival time statistics by a Picoquant MPD avalanche photodiode at 16 ps time resolution. To compare the lifetimes of differently charged films, the integration time for the system is fixed in each experiment. The optical bleach of the film is measured at each electrochemical potential using an USB 4000 Ocean Optics spectrometer with the white light beam focused at the same spot as the 425 nm excitation source. Biexciton PL lifetimes of films are measured by focusing the excitation with a 10× objective. Biexciton lifetimes of the dot solutions as well as films are measured by transient absorption using a separate ps pulsed laser system.[22]

Acknowledgment. We would like to thank Anshu Pandey for transient absorption spectroscopy and the U.S. National Science Foundation NSF under Grant No. DMR-0706268 for funding. The authors made use of shared facilities supported by the NSF MRSEC Program under DMR-0820054.

Supporting Information Available: Simulated and experimental PL for the samples under different conditions. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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