

Surface-Related Emission in Highly Luminescent CdSe Quantum Dots

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ABSTRACT

We report our experimental studies of surface-related emission in highly luminescent CdSe quantum dots (QDs) with controlled quantum yield and photooxidation by time-resolved photoluminescence measurements. This kind of surface-related emission, with a radiative lifetime of tens of nanoseconds, implies the involvement of surface states in the carrier recombination process of such highly luminescent CdSe QDs.

Colloidal semiconductor quantum dots (QDs) are a class of nanocrystals intermediate between single molecules and bulk solid-state materials and are of great interest for both fundamental research and technical applications.^{1,2} One of the best-studied semiconductor quantum systems is the CdSe quantum nanostructure. Its 3D quantum confinement of both electrons and holes leads to strongly size- and shape-dependent optical and electronic properties,^{3–5} which make them ideal candidates for tunable emitters in such applications as biological imaging⁶ and single-photon sources.⁷ One important concern in these applications is the radiative lifetime, which, for example, determines the average time interval between two consecutive emitting photons from the single-photon source and, consequently, the speed of optoelectronic devices. Compared with the typical ~ 1 -ns radiative lifetime in bulk materials, the radiative lifetime of CdSe QDs usually ranges from several to tens of nanoseconds.^{6–10} One interesting feature of the photoluminescence (PL) decay of colloidal QDs is the almost universal occurrence of a biexponential time distribution in the radiative lifetime. Typically, a shorter lifetime is on the time scale of several nanoseconds, and a longer one is tens of nanoseconds. The shorter lifetime can be attributed to the intrinsic recombination of initially populated core states,^{8,9,11,12} but the possible origin of the longer lifetime is still in question.

One distinct feature of colloidal QDs is the large surface-to-volume ratio due to the decreasing particle size, and it has long been believed that the surfaces of colloidal QDs play important roles in carrier relaxation and recombination processes.^{8,11,13} For example, a femtosecond broad-band transient absorption technique was used to show that electron relaxation was controlled by surface passivation, compared

to surface-independent hole relaxation.⁸ One direct way to understand the role of the surface in the PL decay dynamics fully is to change the surfaces of QDs systematically while monitoring the corresponding PL decay. Recently, we successfully realized the control of quantum yield (QY) from a few percent to as high as 86% in colloidal CdSe QDs via surface reconstruction.¹⁴ This controllable high QY of QDs using the new synthesis procedure¹⁴ provided us with a rare opportunity to study the correlation between the surface quality and the PL decay dynamics systematically.

In this letter, we investigate the biexponential distribution of the radiative lifetime in colloidal CdSe QDs with changing surface quality realized either by controlling the QY in synthesis or by introducing photooxidation with laser irradiation. The amplitude ratio of the longer (15–25 ns) to the shorter (2–5 ns) lifetime components in the PL decay-time distribution increases with increasing QY, as measured in vacuum. We also observed a decreasing amplitude ratio of the longer to shorter lifetime components when monitoring the PL decay in the process of photooxidation. Using previously established models of photooxidation,¹⁵ it can be concluded that the recombination of electrons and holes on the surface gives rise to this surface-related emission with longer lifetime, which likewise implies the involvement of surface states.

The method of synthesizing CdSe QDs with controlled high QY was described in detail elsewhere.¹⁴ It was found that under a largely biased initial Se/Cd ratio of precursors in solution the PL QY of CdSe QDs during their growth increases to a certain maximum value and then decreases, as shown in the inset of Figure 1. A series of samples with increasing diameters from 3.5 to 5.0 nm and different QYs ($>30\%$) were taken from the solution during the growth process. For comparison, another QD sample with a QY of $\sim 8\%$ was prepared by the common method without using a

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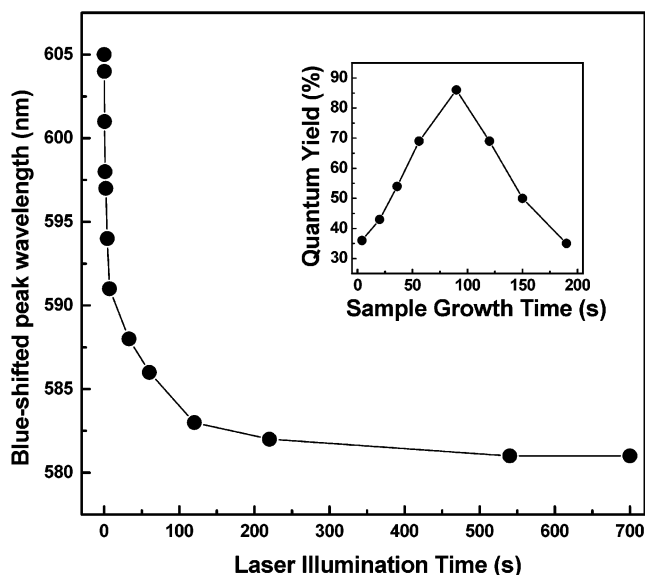


Figure 1. Time evolution of the blue-shifted emission peak wavelength for the sample with the highest QY (~86%) during photooxidation. Inset: Time evolution of QY for the colloidal CdSe QDs during their growth. The lines are guides for the eye.

largely biased Se/Cd ratio. Each sample for PL and PL decay measurements was prepared by spin-coating a clean fused-silica coverslip with a solution of QDs in chloroform followed by a 1 wt % PMMA solution. The average distance between proximal QDs in the as-prepared film was kept >200 nm purposely to minimize the possibility of energy transfer between proximal QDs. The samples were placed inside a small vacuum chamber, which could be either in the ambient air environment or pumped to a vacuum of 10^{-6} Torr. PL decay measurements were taken at room temperature by using a time-correlated photon-counting system.⁹

Upon laser light illumination in air, all samples with high QY ($>30\%$) showed significant blue shifts in their emission peak wavelengths, indicating that the sizes of QDs were getting smaller because of photooxidation. Figure 1 shows the time evolution of the blue-shifted emission peak wavelength for the sample with the highest QY (86%) during the process of photooxidation, which reaches a maximum value of 23 nm after 200 s of photooxidation. In contrast, nearly no blue shift was observed in the QD sample with ~8% QY. Previous experiments have shown that the surface selenium atoms in CdSe QDs will be oxidized to selenium oxide during photooxidation, which requires the presence of oxygen and holes at the surface.¹⁶ Additionally, according to one model for electron-active photooxidation established for both bulk silicon and germanium nanostructures,¹⁵ the presence of electrons on the surface can moderate the dissociation of molecular oxygen to facilitate the oxidation process. Therefore, one can conclude that, after laser excitation, the probability for the electrons and holes to be present on the surface until photooxidation occurs is increased in the QD samples with high QY, which was further verified by the surface-related emission discussed next. In fact, this increased probability for the carriers to be present on the surface of these QDs with high QY is a direct consequence of the

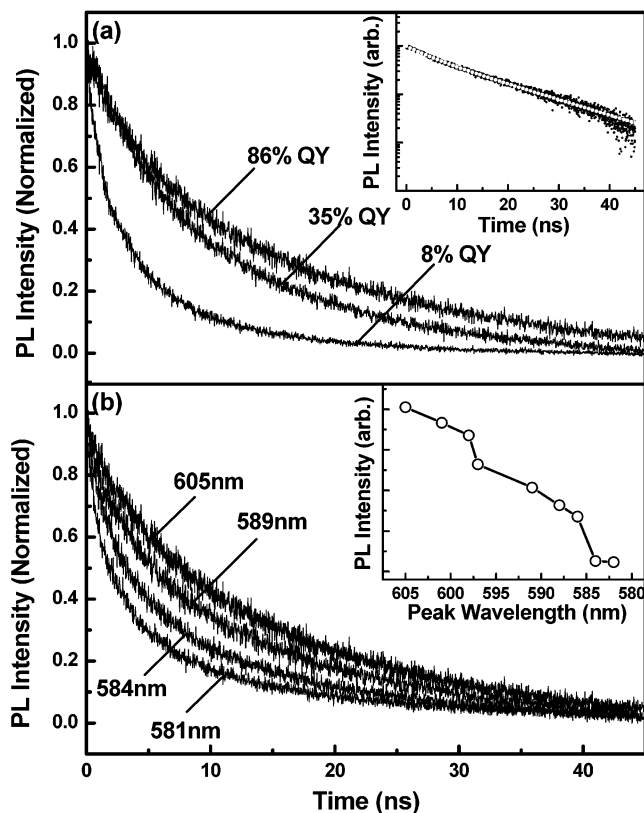


Figure 2. (a) Three representative PL decay spectra for QDs with QYs of 86, 35, and 8%. Inset: PL decay curve for the QD sample with a QY of 35% plotted on a logarithmic scale. The dotted line is a biexponential fit to the data. (b) Four representative PL decay curves for the QD sample with the highest initial QY (86%) in the process of photooxidation. Inset: Decreasing spectrally integrated PL intensity with blue-shifted peak wavelengths for the process of photooxidation. The lines are guides for the eye.

optimal surface reconstruction in the sample growth process, which efficiently removes the carrier-quenching defects from the surface.¹⁴

Besides assisting photooxidation in the ambient air environment, another important role of the surface-charge carriers can be illustrated by the following experiment. The PL decay curve was measured in the respective emission peak wavelength for each QD sample with QY ranging from 8 to 86% under vacuum to prevent photooxidation. The PL decay curve for each sample has a biexponential form of

$$A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

with τ_1 equal to 2–5 ns and τ_2 equal to 15–25 ns. Figure 2a shows three representative PL decay curves for QD samples with different QYs, and the inset plots one of the PL decay curves on a logarithmic scale, which is well fit by a biexponential function. Other PL decay curves are all well fit by such a biexponential function with different τ_1 and τ_2 values. It should be noted that carrier transfer to the quenching defects on the surface usually happens on a time scale of several to tens of picoseconds,⁸ so it should not contribute to the two lifetime components measured here.

The radiative nature of the shorter-lifetime component of several nanoseconds has been extracted in our previous experiments,^{9,12} and it can be attributed to the initially populated core-state recombination. This is also consistent with the theoretically calculated value of ~ 3 ns when the screening of the radiating field inside the QD is taken into account.¹⁷ As for the longer-lifetime component in the PL decay curves, it is definitely due to the radiative recombination of carriers because it accounts for more and more of the total PL when the QY of QDs is increased. In the QD sample with 8% QY, the amplitude of A_1 with a shorter lifetime accounts for nearly 76% of the total PL. Conversely, in the QD sample with 86% QY, it is the amplitude A_2 with a longer lifetime that accounts for nearly 80% of the total PL. In the sample with 35% QY, A_2 still accounts for nearly 60% of the total PL. As discussed above, the increased probability for the electrons and holes to be present on the surface of QDs with high QY contributes unambiguously to this surface-related emission with a longer lifetime.

To verify this surface-related emission with the longer radiative lifetime further, we measured the PL decay for the QD sample with the initial 86% of QY during the process of photooxidation. After measuring the first PL decay curve for the starting wavelength in vacuum, the laser was turned off, and the chamber was vented to room air. After exciting the sample by laser irradiation for a fixed time interval according to Figure 1 to introduce some degree of photooxidation, the high-vacuum environment was then resumed, and the corresponding PL spectra were measured and the PL decay curves were recorded at the blue-shifted wavelengths. The inset of Figure 2b shows a decreasing spectrally integrated PL intensity with the blue-shifted peak wavelength, which implies that more and more quenching defects are generated on the surface of QDs in the photooxidation process. Several typical PL decay curves for this sample with different blue-shifted peak wavelengths are presented in Figure 2b. We can see that once photooxidation takes place the PL decay curve is significantly modified. Figure 3 plots the PL amplitude ratio of the shorter-lifetime component A_1 to the longer-lifetime component A_2 , which indicates that the longer-lifetime component accounts for less and less of the total PL when the surface is continuously undergoing photooxidation. This decreasing amplitude of the longer-lifetime component agrees well with that from decreasing the QY described earlier and represented in Figure 2a. Because in both cases more and more quenching defects would be formed on the surface as the surface quality becomes worse, the change in the amplitude ratio of the longer- to the shorter-lifetime components truthfully reflects this trend of decreasing surface-related emission. Our results are consistent with those from the recent experiment on the fluorescence decay time of single ZnS/CdSe semiconductor QDs.¹⁰ It was found that in single ZnS/CdSe QDs there exist fluctuations of nonradiative decay channels leading to variable dynamic quenching processes of the excited state, whereas a high fluorescence intensity (or high QY) is always correlated with a long fluorescence decay time of around 20 ns.¹⁰

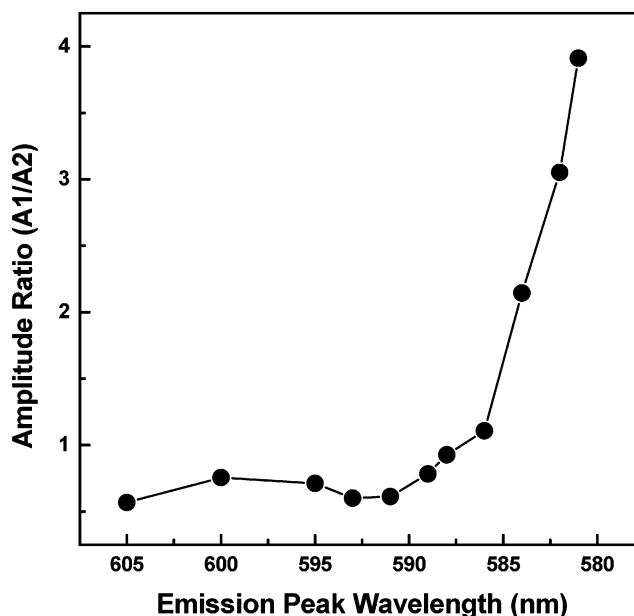


Figure 3. Emission peak wavelength dependence of the amplitude ratio for the shorter- and longer-lifetime components A_1/A_2 . Here we conveniently choose the blue-shifted emission peak wavelength to represent the degree of photooxidation. The lines are guides for the eye.

The above two experiments have shown that the distribution of radiative lifetime components in PL decay dynamics is mainly determined by the surface quality of the QDs. We should also note that, although the strong surface-related emission may account for as much as 80% of the total PL, it can be realized only in the environment of high vacuum. Once illuminated with laser light in air, the QDs cannot maintain the high QY with a large portion of the total PL from the surface due to photooxidation. This may also be the main reason that this surface-related emission has not been previously discussed and reported. In QD samples with QYs of only a few percent (which is true for commonly used colloidal QD samples), this surface-related emission contributes only a small portion of the total PL (in our case, $\sim 20\%$ for the sample with a QY of 8%).

This kind of surface-related emission due to the recombination of electrons and holes on the surface strongly implies the involvement of surface states in the recombination process in colloidal QDs, which is a topic of current interest.^{11,18} Because the electron has a much smaller effective mass than the hole in a QD, once generated, it has a much greater chance of going to the surface rather than staying inside the core of the QD.^{19,20} This “delocalized” feature of the electrons can be further confirmed by the fact that the PL QY of colloidal QDs can be increased from a few percent to more than 50% by proper passivation of the surface utilizing a core/shell structure.²¹ Compared with the electron, the “heavy” hole is usually considered to be located at the center of a QD after generation.¹⁹ However, previous research on the surface structure of CdSe QDs has shown that most surface Se atoms are not passivated, which supports the existence of surface-localized Se lone-pair orbitals that can trap an optically excited hole.¹³ It was proposed that the hole

could be excited on the picosecond time scale to these surface-localized states at the *same* energy as that of the internal core states because of their strong mixing.¹¹ The surface reconstruction of QDs in our experiments may also drive surface states out of the band gap and into *resonance* with the internal core states.²² After laser excitation, the delocalized electrons have the possibility of recombining with the holes from the internal core states as well as from the *resonant* surface-localized states to give emissions with the same wavelength, so we cannot spectrally resolve them. It is well established that once the carriers have been trapped by the surface states the radiative lifetime can be increased to more than 10 ns because of the poor overlap of the carrier wave functions,¹¹ from which we can attribute the origin of the longer radiative lifetime to the involvement of surface states. In this sense, the time-resolved measurements, as shown in Figure 2, can provide at least one *indirect* way to probe the existence of surface states in these highly luminescent CdSe QDs used in our experiment.

Recently, up-converted photoluminescence (UCPL), the observation of luminescence with energies higher than those of the excitation photons, has been experimentally observed in colloidal InP,²³ CdSe,^{23,24} and CdTe²⁴ QDs. The observations of UCPL have provided more *direct* proof of the existence of surface states in colloidal QDs because the demand of intermediate states in the UCPL process can be fulfilled only by the existence of surface states. In the case of colloidal InP QDs, theoretical calculations²⁵ have been used to predict the energy positions of both electron and hole surface states on the basis of the In and P surface dangling bonds, which have been perfectly reproduced by the experimental observations of UCPL in these colloidal InP QDs, as mentioned above.²³ In the same report, the authors also observed UCPL signals from colloidal CdSe QDs similar to that of the colloidal InP QDs, so it can be proposed for colloidal CdSe QDs that the surface states mainly result from the surface Cd and Se dangling bonds. However, a detailed atomic/molecular model needs to be established theoretically for colloidal CdSe QDs to address the real origin of such surface states fully.

In summary, we have addressed the issue of how the surface characteristics (via QY) influence the dynamic behavior of charge carriers in colloidal CdSe QDs (i.e., the relative distribution of radiative lifetime components is mainly determined by the surface quality). The shorter lifetime can be attributed to the intrinsic recombination of initially populated core states, and the longer lifetime can be attributed to the involvement of surface states in the carrier recombination process. We have gained a good understanding of the radiative PL decay processes in the time range from several to tens of nanoseconds in these highly luminescent

CdSe QDs. Our experimental results not only help us to gain a clear picture of the carrier recombination dynamics in colloidal QDs, especially the influence of the surface states, but also provide useful guidance for the applications of colloidal QDs involving the properties of their radiative lifetimes.

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