Photoluminescence dynamics of ensemble and individual CdSe/ZnS quantum dots with an alloyed core/shell interface

Daniel Ratchford, Konrad Dziatkowski, Thomas Hartsfield, Xiaoqin Li, Yan Gao, and Zhiyong Tang

Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA
National Center for Nanoscience and Technology, Beijing, People’s Republic of China

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A comprehensive study of the photoluminescence dynamics in newly developed CdSe/ZnS quantum dots with alloyed core/shell interfaces is presented. Time-correlated single photon counting is used to measure the decay of exciton luminescence from both the ensemble and individual quantum dots. For decreasing emission wavelength (i.e., for smaller dots), the ensemble data reveal increasing total decay rates with greater variation. This systematic change is expected for emitters with stronger quantum confinement and more influenced by the surface/interface trap states. In experiments performed on single quantum dots, the photoluminescence trajectories exhibit two-state blinking behavior. The distributions of the “off”-state probability density are described by an average power-law exponent of 1.5 ± 0.2, while the average decay rate of emission from the threshold-discriminated “on”-states is estimated to be 0.035 ± 0.004 ns⁻¹. We suggest that in core/shell quantum dots with a large bandgap offset, the compositionally graded energy profile at the interface may not be smooth enough to suppress nonradiative Auger recombination and prevent blinking. © 2011 American Institute of Physics. [doi:10.1063/1.3587168]

I. INTRODUCTION

The sustained and extensive study of colloidal semiconductor nanocrystals over the past decade has been driven by their promising applications in such areas as biological labels, photovoltaic devices, and light emitting diodes. Colloidal quantum dots (QDs) are desirable for these applications because of their unique optical properties, which include broad absorption spectrums, tunable emission wavelengths, large electric dipole moments, and long term photostability in comparison to dye molecules. In addition, the solution based synthetic approach of colloidal QDs is compatible with inexpensive and high-throughput fabrication processes such as spin-coating and jet-printing. However, unresolved issues remain with the optical characteristics of colloidal QDs, and continued research has been targeted toward optimizing their properties. For example, multilayer dots were developed to reduce lattice strain and increase the quantum yield of photoluminescence (PL). Fluctuations of the PL intensity (so called “blinking”) is perhaps one of the most important obstacles to broader technological utilization of QDs. The blinking phenomenon has been observed in virtually all types of single emitters including molecules, polymer segments, fluorescent proteins, and nanorods. The luminescence statistics are particularly striking in the case of QDs as the power-law probability distributions for “on” and “off” states extend over a wide range of time scales from milliseconds to tens of seconds. Although numerous common features of PL intermittency have been observed repeatedly, the underlying mechanism of blinking remains obscure. Various microscopic models have been proposed and summarized in the recent review of Frantsuzov et al., yet no single theory accounts for all observations. In general terms, when a QD is charged, a rapid nonradiative process (e.g., Auger recombination) quenches the emission, making the QD appearing dark. The charging events are often associated with surface/interface trap sites. These speculations seem to be supported by reduced blinking in surface modified QDs and QDs with thicker shells. Diminishing of Auger recombination and suppression of blinking has also been reported by Wang and coworkers in selenium-based ternary QDs, even though these QDs possess extra charge. According to a recent theoretical study, this particular observation is expected to be a general feature of quantum emitters in which a softened confinement potential results in a reduction of the transition matrix element for the Auger process. Thus creating a smoothed confining profile (e.g., via chemical-composition gradient) may be a general and promising approach to reduce blinking in QDs and deserves further investigation.

Chemical synthesis techniques were recently employed to make core/shell QDs where graded ternary (CdZnSe) or quaternary (CdZnSeS) alloys were introduced to soften the abrupt structural interface between the core and the shell. Such QDs exhibited a relatively high quantum yield of up to 80%. We have followed the approach from Ref. 25 to synthesize CdSe/ZnS QDs with a modified core/shell interface. In this paper, a comprehensive PL study of exciton dynamics in chemically graded CdSe/ZnS QDs is presented, employing both ensemble and single QD emission decay measurements. The ensemble PL decay is shown to follow a multi-exponential dependence with the individual total decay rates distributed log-normally. Both the most frequent decay rate and the width of log-normal distribution of
total decay rates increase with decreasing QD diameter. The PL experiments conducted on single QDs reveal familiar blinking behavior, and the probability density distribution for durations of off-states follows a power law $P(t_{\text{off}}) \propto t_{\text{off}}^{-\gamma}$ with average $m_{\text{off}} = 1.5 \pm 0.2$. Finally, the application of a threshold that discriminates photon-counting events originating from on and off periods reveals purely single-exponential decays of emission from bright QD states with an average decay rate of about $0.035 \pm 0.004 \text{ ns}^{-1}$ (decay lifetime $\sim 29$ ns).

II. METHODS

The QDs were synthesized from cadmium oxide (0.2 mmol), zinc acetate (2 mmol), and oleic acid (OA, 5.5 ml) dispersed in 20 ml 1-octadecene. Subject to heating at about $300^\circ \text{C}$, the mixture yielded a clear solution of Cd(OA)$_2$ and Zn(OA)$_2$. At the elevated temperature, 0.1 mmol selenium and 1.5 mmol sulfur—dissolved in advance in 1.5 ml trioctylphosphine—were added to the solution. The heating continued for 10 min at $310^\circ \text{C}$, promoting the crystallization of QDs. The growth was interrupted by cooling down the solution to about $60^\circ \text{C}$, at which temperature the QDs were purified with hexane and acetone. Finally, the QDs were dispersed in chloroform for further treatment. The procedure described in the preceding text only marginally differs from the approach described in Refs. 9 and 25. In previous studies, this synthesis method was shown to result in QDs with a graded Cd$_{1-y}$Zn$_y$Se$_{1-x}$S$_x$ core-to-shell transition region verified by combined studies of high resolution–transmission electron microscopy (HR–TEM) and inductive coupled plasma–atomic emission spectroscopy (ICP–AES). 25

For ensemble measurements, the width of the input slit of the spectrograph was set to 200 $\mu$m, providing a spectral resolution of about 2.5 nm. After using the CCD to acquire the ensemble spectrum, the exit of the spectrograph was switched to the APD port. The PL decay rate was determined as a function of wavelength by rotation of the spectrograph grating to direct different portions of the spectrum to the APD. This spectral selectivity allows us to study a group of QDs with similar diameters within the ensemble.
The solid curves were fit according to the single-exponential (10 ms resolution) for acquiring blinking trajectories and on a short time scale (500 ps resolution) for PL decay measurements.

III. RESULTS AND DISCUSSIONS

The ensemble PL measurement in Fig. 2(a) shows an emission spectrum centered at 557 nm with a full width at half maximum of approximately 38 nm. Figure 2(b) displays a typical PL decay curve collected for the arbitrarily chosen spectral position of 545 nm. The nonlinear shape of the decay plotted on a semilog scale is apparent and confirmed by the unsuccessful fit of the experimental data with a single-exponential decay function. Fluorescence decays that deviate from the single-exponential behavior are frequently described with use of Kohlrausch’s stretched-exponential model, where the luminescence intensity at time \( t \) is proportional to:

\[
\begin{align*}
  f(t) &= \frac{\beta}{(\Gamma t)^\beta} \exp \left[ -\left( \frac{\Gamma t}{\bar{\Gamma}} \right)^\beta \right].
\end{align*}
\]

Here \( \Gamma \) is the total decay rate and \( \beta \) is the stretch parameter. Although no explicit distribution of decay rates is used to derive Eq. (1), the value of \( \beta \) different than 1 is often regarded as a signature that the system in question decays in a multi-exponential way. For quantum-confined systems like QDs, different microscopic explanations for \( \beta \neq 1 \) have been proposed, e.g., distribution of sizes and shapes, disorder-induced trap states, and inter-nanocrystal coupling. It should be noted, however, that the physical basis of this phenomenological approach remains controversial. In particular, it is not clear whether the stretched-exponential model can be validly imposed on fluorescent systems with realistic quantum yields of less than 100%. As seen in Fig. 2(b), the application of Kohlrausch’s equation to the ensemble data brings only slight improvement as compared to the single-exponential behavior.

In view of the failure of single- and stretched-exponential decay functions, the proper explanation of the ensemble measurements requires a model with an explicitly defined distribution of decay rates. Such a model has been proposed and successfully employed in the quantum efficiency studies of core-shell CdSe/ZnS colloidal QDs. The decay function is given by

\[
\begin{align*}
  f(t) &= \int_0^\infty \sigma(\Gamma) \exp\left[-\Gamma t/\bar{\Gamma}\right] d\Gamma,
\end{align*}
\]

where different total rates \( \Gamma \) are distributed log-normally according to

\[
\sigma(\Gamma) = \frac{1}{\Gamma_{\text{mf}} w \sqrt{2\pi \exp[w^2/4]}} \exp\left[-\left(\frac{\ln\Gamma - \ln\Gamma_{\text{mf}}}{w}\right)^2\right].
\]

Note that \( f(t) \) is parameterized by two adjustable quantities: \( \Gamma_{\text{mf}} \) denotes the most frequent decay rate, while \( w \) is directly related to the width of log-normal function at 1/e of its height, i.e., \( \Delta \Gamma = 2 \Gamma_{\text{mf}} \sinh(w) \). Because \( \Gamma_{\text{mf}} \) and \( \Delta \Gamma \) have a straightforward statistical interpretation, as opposed to the phenomenologically derived parameter \( \beta \) of Kohlrausch’s approach, they can be correlated to the physical features of a system in study.

The log-normal distribution approach provides significantly better description of the experimental data. The exceptional goodness of the fit in Fig. 2(b) is evident in both the reduced \( \chi^2 \) value close to 1 as well as the random distribution of the weighted residuals around zero [bottom panel of Fig. 2(b)]. This procedure has been applied to the series of PL decay curves collected at different photon wavelengths in the range 535–605 nm, and derived values of \( \Gamma_{\text{mf}} \) are plotted in Fig. 3(a). Clearly, the most frequent decay rate decreases with increasing wavelength \( \lambda \) of emitted photons, i.e., with increasing diameter of QDs. \( \Gamma_{\text{mf}} \) is a measure of the total decay rate \( \Gamma \), and its dependence on \( \lambda \) agrees with the prior PL studies performed on CdSe and CdTe nanocrystals as well as core-shell CdSe/ZnS QDs where the analogous decrease of \( \Gamma \) with wavelength was observed. The total decay rate, \( \Gamma \), has two components: the radiative decay rate, \( \Gamma_{\text{rad}} \), and the nonradiative decay rate, \( \Gamma_{\text{nrad}} \). It follows from Fermi’s golden rule that the rate of spontaneous radiative decay in two-level system is proportional to \( |p|^2/\lambda^3 \), where \( p \) is the transition dipole moment. \( \Gamma_{\text{rad}} \) has been shown to decrease monotonically with \( \lambda \) even for nonspherical QDs. It is harder, however, to predict a dependence of...
\( \Gamma_{\text{rad}} \) on \( \lambda \) because it depends on the microscopic mechanisms of the dominant nonradiative pathways. The surface-interface trap states are often regarded as the most important factor in this regard, thus nonradiative recombination should be reduced for QDs of smaller surface-to-volume ratio, i.e., with larger diameter. Consequently, \( \Gamma_{\text{rad}} \) should decrease with \( \lambda \). Although based on the ensemble measurements one cannot separate \( \Gamma_{\text{rad}} \) and \( \Gamma_{\text{nrad}} \) components of the total decay rate, the downward trend revealed in Fig. 3(a) is consistent with theoretical expectations.

Figure 3(b) demonstrates a \( \lambda \)-dependent decrease of the second parameter of log-normal distribution, \( \Delta \Gamma \). This means for smaller QDs the total decay rates are distributed more broadly than for the larger dots. The change in the width of distribution is depicted in the inset of Fig. 3(b) where the plots of \( \sigma(\Gamma) \) for the two peripheral cases are presented. At each \( \lambda \), the emission was collected from the spectral window that was narrow enough to minimize the contribution from different radiative decay rates due to different sized QDs. Then the almost fourfold decrease of \( \Delta \Gamma \) with \( \lambda \) reflects mainly the change in the distribution of \( \Gamma_{\text{nrad}} \). For colloidal QDs, nonradiative recombination often arises from disorder-induced trap sites,\(^{33,43,45,46}\) e.g., those in the core-to-shell transition region. Any effect of composition fluctuations in a core-to-shell transition should be more pronounced for small QDs due to the large surface-to-volume ratio. Consequently, the excitons will be more diversely affected by the trap states, leading to the broader distribution of the decay rates at shorter emission wavelength.

Whereas the ensemble measurements provide insight into the statistical behavior of the QDs, some of the intrinsic optical properties cannot be extracted from such averaged data. As compared to red light emitting QDs, those with luminescence at shorter wavelengths tend to be less stable under continuous optical illumination.\(^5\) Yet the QDs investigated in this paper were stable enough to permit measurements on the individual dot level. Single dot measurements were performed to characterize the blinking behavior and to approximate the radiative decay rate of the QDs. Shown in Fig. 4(a) is a typical emission trajectory of a single QD constructed by binning the photon counts into 10 ms bins. The characteristic intensity fluctuations with distinct on and off states can be clearly seen both in the emission trajectory as well as in the bimodal distribution of the histogram of count rates [right panel in Fig. 4(a)]. Recently the suppression of blinking in ternary CdZnSe/ZnSe semiconductor nanocrystals has been reported and related to the softening of the confinement potential.\(^{23}\) The latter is expected to arise when the
purportedly core/shell structure is indeed a graded alloy of CdZnSe and ZnSe. Because Auger recombination is suppressed in the absence of steep potential changes that relax momentum conservation rules,14 the smooth band profile will in principle suppress the PL intensity fluctuation even for charged emitters.23 Despite the intentionally introduced alloying of the core-to-shell transition region, the QDs investigated in this study revealed clear blinking. These modified CdSe/ZnS QDs, however, are composed of semiconductors with significantly larger offset in the core/shell band gaps as compared to the work of Wang et al., where ZnSe ($E_g \approx 2.7$ eV) instead of ZnS ($E_g \approx 3.7$ eV) was used. Consequently, the carriers of a single emitter with a ZnS shell are subject to a stronger quantum confinement within a steeper band profile, and the Auger process may remain an efficient path of nonradiative recombination. This speculation corroborates a recent quantitative analysis performed in the framework of the ionization energy theory, where the relation between the chemical gradient and PL blinking in QDs composed of different binary and ternary compounds was discussed.48

Among the various semiconducting systems studied, the CdSe/ZnS combination was identified as the least likely for gradient-induced suppression of blinking due to the large difference of the atomic ionization energies between the core and shell. The same conclusion can be drawn from calculations based on a two-band, effective mass Kane model. It was shown that the nonradiative Auger decay rate is substantially reduced in heterostructures with a smooth confining energy profile.24 For a given functional form of the potential, however, the efficiency of Auger recombination increases with the confinement height, i.e., with the difference of the fundamental band gaps of the core and shell. Interestingly, it was predicted that the most efficient (2-3 orders of magnitude) quenching of Auger recombination should only be expected for emitters which diameters belong to a series of “magic” sizes.

Because the QDs under study reveal distinct, two-state blinking of fluorescence, the probability density distributions for durations of on and off periods should be addressed. In order to separate the on and off states, a cutoff threshold value of 2 standard deviations above the background was applied to each emission trajectory [solid horizontal line in Fig. 4(a)]. Time periods for which the emission rate is higher than the threshold are considered on-times, while those time periods for which the emission rate is lower than the threshold are off-times. To analyze blinking events, one typically fits these distributions with the following power laws:

$$p(t_{on}) \propto t_{on}^{-m_{on}} \exp \left[ \frac{-t_{on}}{\tau_{on}} \right],$$

$$p(t_{off}) \propto t_{off}^{-m_{off}},$$

where $m_{on}$ and $m_{off}$ are the characteristic exponents of on-time and off-time distributions, and $\tau_{on}$ is a truncation (or saturation) time. It has been shown recently that the value of the on-time power law exponent derived from a QD emission trajectory depends on the particular binning period and threshold used.50 We restrict the following analysis to the off-time probability density distribution to ensure the reliability of the extracted exponent. Continuous probability density distributions can be produced with the method used by Kuno et al., where the $k$-th element of the off-time histogram is weighted with an algebraic average $(t_{off,k+1} + t_{off,k-1})/2$ of time distances to the two nearest neighbors.51 Then one plots the normalized probability density distribution according to the following formula:

$$p(t_{off,k}) = \frac{N(t_{off,k})}{N_{tot}} \frac{2}{t_{off,k+1} + t_{off,k-1}},$$

where $N(t_{off,k})$ is the number of off-events of duration $t_{off}$, and $N_{tot}$ is the total number of all off-events. In the particular set of data presented in Fig. 4(b), this distribution obeys Eq. (4b) with an exponent of $1.6 \pm 0.1$, and the average of the results obtained for many single QDs yields a value of $m_{off} = 1.5 \pm 0.2$. These values are consistent with the ones reported for other single emitters that have off exponents ranging from 1.2 to $2.15,16,51$

We emphasize that the apparent PL decay is often multi-exponential, even if it is measured on a single QD. This multi-exponential behavior clearly cannot be attributed to size or shape variations. Instead it may arise from fluctuating charging events. The PL decay from a single QD becomes single-exponential if one considers only photons detected during the on periods.33 Therefore lifetime decays were constructed using only those photons emitted when the emission rate exceeded the cutoff threshold. In these on-state lifetime decays, the contribution from dark (off) periods is minimized, and the resulting decays can be well fit with single exponentials, as shown in Fig. 4(c). The single decay rate was estimated to be about $0.029$ ns$^{-1}$ ($\chi_r^2 = 0.97$). Averaged over data collected from multiple single QDs, the mean on-state decay rate of $0.035 \pm 0.004$ ns$^{-1}$ was obtained. Noteworthy, this on-time decay rate is smaller than any of the most frequent decay rates $\Gamma_{mf}$ extracted from the ensemble measurements [see Fig. 3(a)]. This difference can be explained as follows. When the QD is in the off-state, recombination is dominated by a fast nonradiative process, which corresponds to a large decay rate. By application of a threshold, these fast nonradiative events are eliminated and a decay rate obtained from the single-exponential fit is expected to be smaller than $\Gamma_{mf}$.

IV. CONCLUSIONS

In summary, stable CdSe/ZnS QDs with alloyed core/shell interface regions were synthesized, and time resolved PL experiments were conducted at both the ensemble and single dot level. In the PL trajectories of the individual QDs, the apparent blinking behavior was observed with discernible bright (on) and dark (off) states. After applying a threshold to exclude off periods, the exciton decay of an individual QD followed a single-exponential function. A decay rate extracted with this method is often regarded as a good estimate of the purely radiative decay rate for QDs with high quantum yield. In the QDs investigated, the average single dot decay rate was determined to be about $0.035$ ns$^{-1}$.\[103509-5 Ratchford et al.

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Because the threshold removes the dominant nonradiative contributions from the apparent decay rate, the value quoted in the preceding text is smaller than total decay rates revealed in the ensemble measurements. The exciton decays collected in ensemble measurements followed a multi-exponential dependence with the distribution given by a log-normal function. Both the total decay rate and the width of distribution of decay rates decrease with wavelength.

From these results, we suggest that the core/shell interface persists as a significant factor in exciton nonradiative recombination in compositionally graded CdSe/ZnS QDs. The structural modification fails to suppress PL blinking because the large difference of the energy band gaps between CdSe and ZnS promotes nonradiative Auger processes. Further systematic studies are necessary to pinpoint synthesis conditions that would result in nonblinking CdSe/ZnS QDs. Speculatively, a chemical gradient spreading over a larger distance or precise tailoring of diameters to fit “magic” sizes may lead to CdSe/ZnS QDs with diminished blinking.

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