Transient Fluorescence of the Off State in Blinking CdSe/CdS/ZnS Semiconductor Nanocrystals Is Not Governed by Auger Recombination

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The observed intermittent light emission from colloidal semiconductor nanocrystals has long been associated with Auger recombination assisted quenching. We test this view by observing transient emission dynamics of CdSe/CdS/ZnS semiconductor nanocrystals using time-resolved photon counting. The size and intensity dependence of the observed decay dynamics seem inconsistent with those expected from Auger processes. Rather, the data suggest that in the ''off'' state the quantum dot cycles in a three-step process: photoexcitation, rapid trapping, and subsequent slow nonradiative decay.

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The physical properties of chemically synthesized semiconductor nanocrystal quantum dots (QDs) have been the subject of extensive research in the last two decades. Utilized as fluorescent labels, they demonstrate good photostability, high absorption cross sections, wide excitation spectra and narrow emission lines, which makes them an attractive alternative to organic fluorophores in a wide range of life science applications [1]. In addition, QDs can serve as tunable light absorbers and emitters in optoelectronic devices such as light-emitting diodes and QD sensitized solar cells.

A general property of QDs is a fluorescence intermittency apparent in single dot emission, also known as blinking. It is observed as abrupt jumps from a strongly emitting state to episodes of darkness during which the emission intensity is heavily attenuated despite continuous laser excitation [2]. This is an intriguing phenomenon as it results in a clearly measurable manifestation of microscopic dynamical changes in a single nanocrystal. Blinking is of practical importance since it reduces the effective quantum yield of QDs. It also limits the utility of QDs in applications such as single particle tracking. The luminescence intensity fluctuations of blinking QDs occur on time scales which are immensely longer than the longest characteristic time normally associated with QD dynamics, a radiative lifetime of tens of nanoseconds [3]. Hence, they must be associated with ''slow'' variations of the microscopic state of the QD. Yet, despite the broad literature regarding the statistics of the blinking process, as well as its dependence on temperature, excitation wavelength and intensity, the detailed mechanism inducing this behavior is, surprisingly, still under debate.

The vast majority of the existing theoretical models [4], as well as much of the experimental literature (including recent realizations of nonblinking QDs [5–9]), associate the ''off'' periods with a long-lasting change in the charging state of the QD. This may be brought about by photoionization, as suggested originally by Efros and Rosen [10], or by trapping of an excited charge carrier in a long-lived surface trap. In either case, QDs in the ''off'' state are essentially ionized and can, upon further photoexcitation, nonradiatively decay via Auger recombination. This is an intra-QD energy transfer interaction by which the excess energy from a recombination event is transferred to the spectator charge carrier rather than emitted as a photon [11]. To account for the observed power-law statistics of ''off'' and ''on'' times [3], several modifications of the Efros and Rosen formulation have been recently suggested. These include multiple traps with an exponential distribution of trapping and escape rates [12] and a fluctuating energy difference between the trap state and the excited state [13].

One alternative model, which does not require the existence of long-lived charge traps, has been suggested by Frantsuzov and Marcus [14]. In the model, the off state arises from opening of a nonradiative decay channel of the singly excited dot. In the proposed mechanism the excess energy from the trapping of the hole is resonantly transferred to the electron in the lowest excited state ($1S$), ejecting it to the next excited state ($1P$). After quickly relaxing back to the $1S$ state the electron recombines nonradiatively with the trapped hole. Thus, Auger processes are not invoked to account for photodarkening, although these should be observed at an excitation rate exceeding the nonradiative decay rate. The only experimental support to this model obtained so far comes from relatively indirect statistical measurements [15].

Most of the experimental work on blinking has focused on characterization of the statistics of on and off times [3]. The study of the transient decay dynamics of QDs during the on and off periods is a complementary approach, which has greatly benefited from recent advances in time-resolved photon counting instrumentation. In particular, monitoring the decay dynamics of the remaining fluorescence during off periods provides detail on the nonradiative decay mechanism responsible for photodarkening. Such measurements revealed that the emission transient following pulsed excitation is generally nonexponential, and that the emission intensity is correlated with its lifetime [16]. By creating decay curves from only the photons

arriving at periods with the highest emission rates, it was shown that the on state emission is well fit by a single exponent [17]. Later work demonstrated that there exists, in fact, a continuous distribution of emitting states [18] and found a strong correlation between fluorescence intensity and decay times. Very recently, studies on CdSe/CdS QDs with reduced blinking [8,9] have shown relatively strong emission in the off state. In both, this was attributed to slower Auger dynamics due to the large QD size.

Here we attempt to elucidate the microscopic mechanism of QD darkening by a systematic study of the off state dynamics in the most studied system of CdSe/CdS/ZnS QDs. Our aim is to clarify the role of the Auger processes, which are known to be strongly dependent on both the nanocrystal size and the excitation intensity. We first study the off state fluorescence at low illumination intensities for several QD sizes, and find that off lifetimes exhibit a broad distribution with no clear size dependence. This is in clear disagreement with the strong size dependence expected from Auger-assisted photodarkening. We then proceed to characterize the excitation intensity dependence of the off state lifetimes, and discover that the off state decay dynamics becomes shorter under relatively strong excitation. This seems to indicate that under strong excitation Auger processes do dominate the nonradiative decay. Finally, we present a phenomenological model accounting for the results, provide guidelines for the design of nonblinking QDs, and discuss possible experimental pathways to further elucidate the dynamics of this system.

CdSe/CdS/ZnS were grown in a noncoordinating solvent and overcoated using successive ion layering [19]. We used QDs with diameters of 3.8 nm, 5 nm and 8 nm (corresponding to emission peaks at 590 nm, 618 nm and 665 nm, respectively). All QDs were slightly rodlike, with an aspect ratio of ≈ 2. The quantum yield of the respective samples in solution was 80%, 70% and 15%. Nanomolar concentrations of QDs in a 3% mass/volume PMMA solution were spin cast onto glass cover slips creating samples with typical densities of 0.02 QDs/μm^2. QDs were excited by 400 nm, 100 fs pulses from a frequency-doubled Ti-Sapphire oscillator operated at 80 MHz. Light was focused on the sample by an oil immersion objective with a numerical aperture of 1.4. Epifluorescence was spectrally filtered and detected by a single-photon avalanche photodiode (id Quantique). Emission time traces from isolated QDs were recorded by a time-correlated single-photon counting system (Picoharp300, Picoquant), operated in the time-tagged mode such that each photon is assigned an absolute arrival time and an arrival time relative to the excitation pulse. The system temporal resolution was measured to be 65 ps.

A representative intensity histogram of a blinking QD is shown in Fig. 1(a). For each such data set we define the on and off count rate thresholds. On and off photoluminescence (PL) decay curves were produced by binning all photons which arrived during the respective periods according to their time of arrival relative to the excitation pulse. Both are presented in Fig. 1(b). For most observed QDs the on state exhibits single exponential decay, in agreement with previous observations [17]. The off state, however, demonstrates a more complicated decay curve with a wide range of lifetimes. Typical off time decay curves contain both rapid components of $\sim$100 ps and relatively long ones of $\sim$1 ns. Multiexponential decays were previously observed on CdSe/ZnS QDs [17], and recently in CdSe/CdS QDs [8], implying that such behavior is not unique to our system.

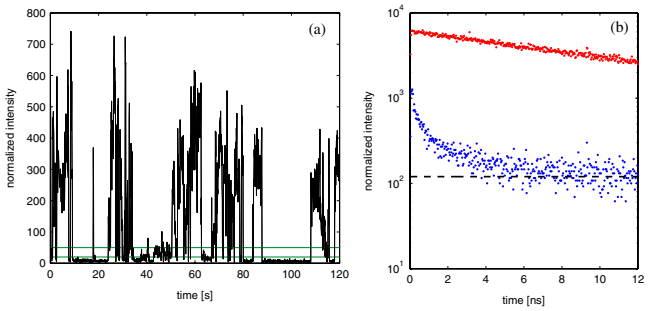

FIG. 1 (color online). (a) Intensity time trace of a single CdSe/CdS/ZnS QD showing fluorescence intermittency (bin width = 60 ms). The on and off intensity thresholds are also shown. The excitation power is adjusted to an excitation rate of about 0.2. (b) On (red [medium gray]) and off (blue [dark gray]) PL decay curves. The dotted line represents the detector dark counts.

Such measurements were performed on several tens of nanocrystals at each of the three sizes. As we cannot directly assign a lifetime to the off state decay, we resort to assigning a $1/e$ decay time to each data set. Histograms of these decay times are presented in Fig. 2 for all three sizes. The observed distributions exhibit a broad peak centered at about 250 ps and are evidently size independent. The lack of a systematic size dependence is in stark contrast with the significant variance in the biexciton Auger decay lifetimes of spherical QDs emitting at these wavelengths, which are approximately 30 ps, 65 ps and 350 ps, respectively, for the three sizes [11]. Although Auger rates depend on particle shape (so these rates cannot be directly associated with our QDs) as well as on the charging state of the QDs (charged colloidal QDs have been shown to exhibit slower Auger dynamics than the neutral biexciton by a factor of up to 7 [20]), the slowest $1/e$ times of $\approx$ 1 ns seem to be too long to be due to Auger processes, at least for the smallest QDs. This is particularly so since the multiexponential off state decay contains a component slower than the $1/e$ decay time. Combined with the lack of size dependence in the observed rates, this leads us to the conclusion that the nonradiative recombination process causing blinking is not Auger recombination.

A further test of this hypothesis can be performed by considering the excitation intensity dependence of the off state decay dynamics. If the microscopic cause of off

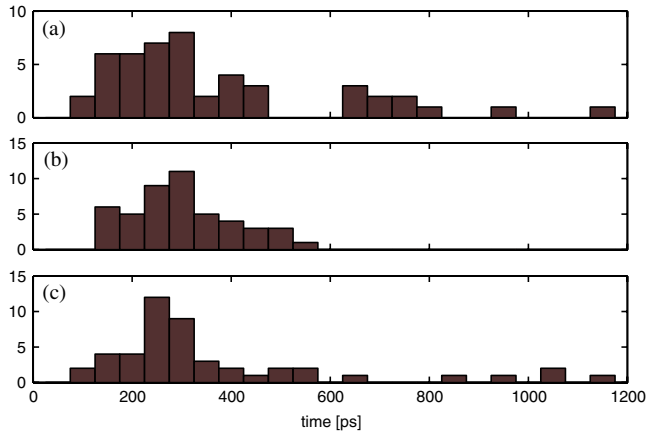

FIG. 2 (color online). Histograms of the off state $1/e$ decay times of (a) 3.8 nm QDs, (b) 5 nm QDs and (c) 8 nm QDs.

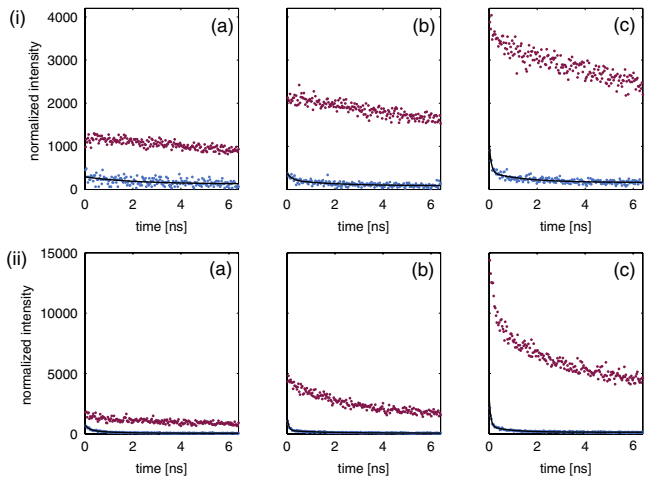

FIG. 3 (color online). On (red [medium gray]) and off (blue [dark gray]) decay curves taken from two QDs [(i) and (ii)] of 3.8 nm diameter at excitation rates of (a) 0.2, (b) 0.4 and (c) 1 photons per QD per pulse. The off state decay curves correspond to $1/e$ decay times of (ia) 1960 ± 570 ps (ib) 660 ± 260 ps (ic) 200 ± 30 ps and (iia) 400 ± 20 ps (iib) 144 ± 6 ps (iic) 139 ± 4 ps.

blinking is Auger recombination by a trapped charge, no intensity dependence should be observed in the off decay dynamics at excitation levels below saturation (absorption rate of ≈ 1 photon/pulse). To test this, we performed intensity-dependent dynamics measurements on the 3.8 nm QDs. For each QD the excitation rate (defined here as the average number of absorption events per exciton lifetime) was assessed by saturation of the on state emission. In addition, a clear indication of the average excitation rate approaching unity is the emergence of a fast multiexciton transient feature in the on decay curve. The measurements of the off and on decay transients on the same QD at varying excitation rates reveal a strong correlation between the excitation intensity and the off decay rate. While the effect is general, it is most dramatically observed in QDs with slow $1/e$ decay times in the off state. In Fig. 3 we present two such examples of off and on decay transients for single QDs excited at several intensities, ranging from an average excitation rate of ~ 0.2 to ~ 1. The two QDs have a low intensity $1/e$ decay time of ~ 2 ns [Fig. 3i(a)] and ~ 400 ps [Fig. 3ii(a)]. As can be seen, at an elevated excitation level a fast transient component emerges in the off state decay traces. Since it appears at intensities approaching saturation, it is reasonable to associate this with an Auger-related decay process. This is further supported by the fact that the fast component of the multiexponential fit at higher intensities is shorter than 100 ps (which implies an even shorter time scale considering the instrument response), in reasonable correspondence with the biexciton Auger decay rate of ~ 30 ps for spherical QDs emitting at 590 nm [11]. The emergence of a fast transient at high intensities is observed in all QDs of this size. In contrast varying the excitation rate at lower excitation intensities, below 0.1, revealed no significant change in the $1/e$ lifetime.

A cardinal feature of the data, as can be seen in Fig. 3, is that in the off state, the onset of the fast decay occurs at excitation rates of ~ 0.2, in contrast to the on state, in which the Auger-related transient emerges when the excitation rate approaches unity. The earlier saturation indicates existence of an off state time scale longer than the exciton radiative lifetime. Based on this key observation, we wish to offer the following interpretation: The fast component in the decay curve indicates the simultaneous presence of more than one pair of charge carriers. In the on state, the extra charge carriers are provided by multiple excitation of QDs. In the off time, however, the probability of multiple excitation is still low at the onset of the fast recombination feature. Therefore, the additional charge taking part in the Auger process must have a lifetime longer than the radiative recombination time. On the other hand, absence of the fast transient at low intensities shows that the extra charge cannot be present during the entire off period. This implies that either the electron or the hole are confined to a trap state with a lifetime longer than (but of the order of) the radiative recombination time, yet orders of magnitude shorter than the duration of the off state. Since no changes are observed in decay dynamics at excitation rates below 0.1, we can estimate the nonradiative recombination time of the trapped charge in the off state as $\approx 10\tau_{\mathrm{rad}}$ (≈ 200 ns for our QDs).

The above description assumes that some stochastic process randomly switches the dot between the on state and a range of off states. The physics of this process is responsible for the observed power law distribution of the on and off times.

The proposed scheme of QDs charge kinetics is illustrated in Fig. 4. In the on state the dynamics is conventional [see Fig. 4(a)]; at low intensities the transient dynamics shows the decay rate of the single exciton k_r, while at higher intensities the Auger recombination with the decay rate k_{Aug} takes over. The above random process "turns off"

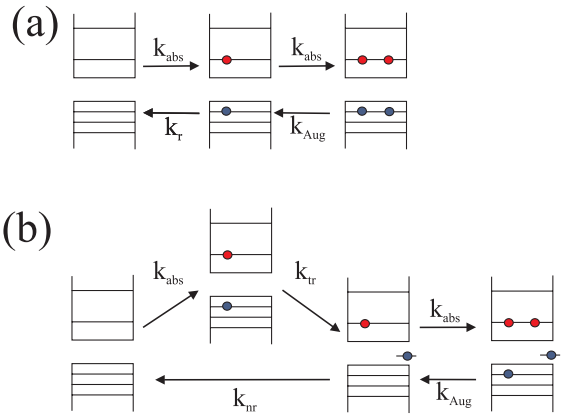

FIG. 4 (color online). Schematic description of the physical processes involved in (a) on and (b) off state dynamics. In the on state, predominance of the absorption rate (k_{abs}) over the radiative decay rate (k_r) results in doubly excited QDs while in the off state the competition is between the absorption rate (k_{abs}) and the rate of nonradiative recombination from the trap (k_{nr}).

the QD fluorescence by opening a transition channel into a trap state either for electrons or for holes. Thus, rapid trapping at a rate k_{tr}, corresponding to hundreds of picoseconds, inhibits QD luminescence. At very low intensities, k_{tr} determines the observed off state luminescence decay rate (and correspondingly the quantum yield). At higher intensities another exciton can be generated before the trapped charge recombines (with the rate k_{nr}), and Auger recombination becomes visible in the decay curve [see Fig. 4(b)]. At a low illumination intensity the off QD cycles in a three step loop process including excitation, rapid trapping of a charge carrier and nonradiative recombination [left part of the picture in Fig. 4(b)]. When k_{abs} is increased and becomes comparable to k_{nr}, the QD shifts to the right part of the scheme in Fig. 4(b) and the observed decay rate changes to k_{Aug}. The relations between the decay rates mentioned above determine whether the off state emission is dominated by trapping dynamics or by Auger dynamics at a given excitation rate. In particular, it is plausible that for some species of QDs k_{nr} is much smaller than for the CdSe/CdS/ZnS dots. This corresponds to an effectively long-lived trap state, meaning that in the off state under typical experimental conditions such QDs would only exhibit the Auger decay dynamics.

The nature of the physical process responsible for the time dependence of k_{tr} has yet to be investigated. Regardless of its origin, the above scheme of QD operation is inconsistent with models of QD blinking assuming that a charge is trapped during the entire off period. The experimental results seem to be consistent, however, with the model proposed by Frantsuzov and Marcus [14], wherein the random process responsible for the time variation of the trapping rate is spectral diffusion.

Several types of nanocrystals have recently shown nonblinking or nearly nonblinking behavior [5–7]. Reduced blinking has also been observed by modification of the surrounding matrix of the QDs [21]. Based on the above understanding, efficient elimination of surface trapping and rapid nonradiative recombination upon trapping are sufficient to eliminate blinking. Long Auger recombination lifetimes are not required for this to occur, but help in supporting a high quantum yield despite the existence of traps with relatively slow nonradiative recombination lifetimes.

In summary, the data presented above, particularly the lack of a clear size dependence of the off state luminescence decay time and its intensity dependence at excitation rates below saturation, indicate that Auger recombination alone cannot account for QD blinking. The intensity-dependent data suggest that the darkening of QDs involves carrier trapping in a relatively short lived trap state, as opposed to the conventional idea of a charge trapped throughout the entire off time. QD operation during off times can thus be described as a three-step cyclic process of excitation, trapping and nonradiative relaxation. This phenomenological model can serve as a basis for the future research on the microscopic mechanisms of QD blinking.

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