Photodarkening of blinking quantum dots is not governed by Auger recombination

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Abstract

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 are inconsistent with the those expected from Auger processes. Moreover, the data suggests that in the ‘off’ state the quantum dot cycles in a three-step process: photoexcitation, rapid trapping and subsequent slow nonradiative decay.
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 existing 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]. In order 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. Thus, multiple traps with an exponential distribution of trapping and escape rates [12] or a fluctuating energy difference between the trap state and the excited
state [13] have been postulated.

One alternative model, which does not require the existence of long-lived charge traps, has been suggested by Frantsuzov and Marcus [14]. In this model, the ‘off’ state arises from the 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) thereby 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. In particular, 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 and find that it exhibits size-independent dynamics. 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 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 non-blinking QDs, and discuss possible experimental pathways to further elucidate the detailed dynamics of this fundamental system.

CdSe/CdS/ZnS QDs were synthesized in three sizes following standard procedures [19]. Briefly, QDs were grown in a non-coordinating solvent and overcoated using successive ion layering [20]. We used nanocrystals with diameters of 3.8nm, 5nm and 8nm (corresponding to emission peaks at 590nm, 618nm and 665nm, respectively). All QDs were slightly rodlike, with an aspect ratio of \( \approx 2 \). The quantum yield of the respective samples was determined in solution to be 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/\( \mu \)m\(^2\). The QDs were excited by frequency-doubled pulses from a Ti-Sapphire oscillator at 400nm, with a duration of 100fs and a repetition rate of 80MHz. Light was focused on the sample by an oil immersion objective with a numerical aperture of 1.4. Epi-fluorescence 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 65ps.

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 \( \sim 100\text{ps}\) and relatively long ones of \( \sim 1\text{ns}\). Multiexponential decays were previously observed on CdSe/ZnS QDs [17], and recently in CdSe/CdS QDs [8], implying that such behavior is is not unique to our system.

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
FIG. 1: (a) Intensity time trace of a single CdSe/CdS/ZnS QD showing fluorescence intermittency (bin width = 60ms). The ‘on’ and ‘off’ intensity thresholds are also shown. The excitation power is adjusted to an excitation rate of about 0.2, taking into account the radiative lifetime and absorption cross section [21]. (b) ‘On’ (red) and ‘off’ (blue) PL decay curves. The dotted line represents the dark count level of the detector.

$1/e$ decay time to each data set. Histograms of these decay times are presented in Fig. 2 for all three sizes of QDs. The observed distributions demonstrate a broad peak at about 250ps and are evidently size-independent. This is in stark contrast with the significant variance in the biexciton Auger decay lifetimes, which are approximately 30ps, 65ps and 350ps respectively for the three sizes [11, 22]. Since both the slow and the fast components of the ‘off’ state decay curve contribute to the $1/e$ decay time, the lifetimes of the slower components are significantly longer than biexciton Auger recombination lifetimes, particularly for the smaller QDs (for these, they are even longer than the expected trion Auger lifetime [23]). This fact, in combination with the lack of size dependence in the observed rates, leads us to the conclusion that the nonradiative recombination process causing the intermittent darkening of QDs is not Auger recombination.

Further information on the ‘off’ state decay can be extracted from intensity dependent measurements, performed here on the 3.8 nm QDs. For each QD the excitation rate (i.e. 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 multie exciton 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 \( \sim 0.2 \) to \( \sim 1 \). The two QDs have a low intensity 1/e decay time of \( \sim 2\text{ns} \) (Fig. 3i(a)) and \( \sim 400\text{ps} \) (Fig. 3ii(a)). As can be seen, at an elevated excitation level a fast transient component emerges in the ‘off’ state decay traces. The multiexponential fit (Fig. 3c) gives the fast components lifetimes of (i) \( 82 \pm 31\text{ps} \) and (ii) \( 68 \pm 7\text{ps} \), which, when taking into account the 65 ps instrument response, correspond to even shorter lifetimes. These values are in good agreement with the biexciton Auger decay rate of \( \sim 30\text{ps} \) for 3.8nm CdSe QDs [11]. The emergence of such 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.

These observations can be summarized as follows: while the decay rates at low intensities are inconsistent with the assumption of Auger recombination driven decay, at elevated intensities the Auger process seems to become the dominant recombination channel.

One 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 order \( \sim 0.2 \), in contrast to the ‘on’ state, in which the Auger feature emerges when the excitation rate approaches unity. Based on this key observation, we wish to offer the following interpretation. The Auger 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 Auger recombination feature. Therefore, the additional charge taking part in
FIG. 3: ‘On’ (red) and ‘off’ (blue) decay curves taken from two QDs ((i) and (ii)) of 3.8nm 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) $1960 \pm 570$ps (ib) $660 \pm 260$ps (ic) $200 \pm 30$ps and (iia) $400 \pm 20$ps (iib) $144 \pm 6$ps (iic) $139 \pm 4$ps

the Auger process must have a lifetime longer than the radiative recombination time. On the other hand, the absence of Auger-like 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 $\approx 10\tau_{rad}$ ($\approx 200$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’ 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.
FIG. 4: 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 non-radiative recombination from the trap ($k_{nr}$).

At very low intensities, $k_tr$ determines the observed ‘off’ state decay rate and 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 a relatively long nonradiative recombination process (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 the trapped charge recombination rate $k_{nr}$ 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 the origin of this process, it is clear that the above scheme of QD operation is inconsistent with physical models of QD blinking assuming that a charge must be 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 the spectral diffusion of the
energy levels in QDs.

Several types of nanocrystals have recently shown nonblinking or nearly nonblinking behavior [5–7]. Significantly reduced blinking has also been observed by modification of the surrounding matrix of the QDs [24]. 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 demonstrates that Auger recombination alone cannot account for QD blinking. The comparison of the decay curve intensity dependence for the ‘on’ and ‘off’ states suggests that the darkening of QDs involves fast trapping of a charge carrier in a relatively short lived trap state, as opposed to the conventional idea of the a charge trapped throughout the entire ‘off’ time. The operation of QDs during the ‘off’ times can therefore be described as a three-step cyclic process of excitation, trapping and slow non-radiative relaxation. This phenomenological model can serve as a basis for the future research on the microscopic mechanisms of QD blinking.

Financial support by the Minerva foundation and by the Israeli Science Foundation (Grant No. 1621/07) is gratefully acknowledged.

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