Blinking statistics in single semiconductor nanocrystal quantum dots

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Statistical studies of fluorescence intermittency in single CdSe nanocrystal quantum dots (QD's) reveal a temperature-independent power-law distribution in the histogram of *on* and *off* times—the time periods before the QD turns from emitting to nonemitting (bright to dark) and vice versa. Every QD shows a similar power-law behavior for the *off*-time distribution regardless of temperature, excitation intensity, surface morphology or size. We propose a dynamic model of tunneling between core and trapped charged states to explain the universal power-law statistics of the blinking events observed. The *on*-time probability distributions show evidence of both a tunneling mechanism similar to the *off*-time statistics and a secondary, photoinduced process that leads to a truncation of the power law. The same blinking statistics are also observed for single CdTe nanocrystal QD's.

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Power-law statistics are indicative of complex, long-range order. Examples of this non-exponential behavior include measurements of dispersive transport in organic photorefractive glasses,[1] momentum fluctuations in single-atomic systems,[2] and conformation dynamics of protein folding.[3] Fluorescence intermittency or blinking, also observed in fluorescent polymers, green fluorescent proteins, porous Si nanoparticles, surface-enhanced raman spectroscopy and of single dye molecules,[4–7] refers to the fluorescence emission behavior switching from *on* to *off* and vice versa on time scales ranging from submillisecond to hours under continuous-wave (cw) laser excitation. Although this optical switching is observed in many different systems, the mechanisms for these dynamics vary for each system. Recently, room-temperature (RT) fluorescence intermittency of single CdSe nanocrystal quantum dots (QD's) was found to exhibit long-range statistical order.[8] In this paper, we report ''power law'' statistical results within a physical framework to begin the dissection of the complex mechanism for blinking in single, semiconductor nanocrystal QD's. Due to their small size (2–6 nm diameter) and ease of fabrication, nanocrystal QD electro-optic applications have been promoted. Understanding the mechanism for this blinking phenomenon may help develop an area of electro-optic applications on the single QD level.

The initial model for CdSe QD fluorescence intermittency[9,10] correlated a theoretical model for photodarkening observed in CdSe-doped glasses[11] with the blinking phenomenon under the high excitation intensity used for single QD spectroscopy. In the photodarkening experiments, Chepic *et al.*[12] described a QD with a single delocalized charge carrier (hole or electron) as a dark QD. When a charged QD absorbs a photon and creates an exciton, it becomes a quasi-three-particle system. The energy transfer from the exciton to the lone charge carrier and nonradiative relaxation of the charge carrier ($\sim$100 ps) (Ref. 13) is predicted to be faster than the radiative recombination rate of the exciton (100 ns–1 μs). Therefore, within this model, a charged QD is a dark QD. This describes the state of a dark QD, but proves to be incomplete to explain the transition mechanism between a dark and bright QD.

In the present work, we use a highly parallel imaging microscope setup to study fluorescence intermittency in single CdSe, CdSe/ZnS core-shell, and CdTe semiconductor nanocrystals, providing insight into the mechanism of single QD blinking dynamics. The statistics of both *on*- and *off*-time distributions are obtained under varying temperature, excitation intensity, size, and surface morphology conditions. Although similar experiments have been conducted earlier, the analysis of the data did not include the framework of power-law statistics, and the data sets were limited to small numbers of single QD's and relatively short observation times.[9,14] Here we show an unexpected temperature independence in the observed power-law probability distribution of *off* times. Furthermore, we report that the *on*-time behavior also shows a power-law component to the probability distribution. However, a secondary, thermally activated and photoinduced process causes the probability distribution of the *on*-time statistics to be truncated at the ''tail'' of the power-law distribution. The temperature-independent power-law statistics observed for all the CdSe QD's studied suggest a complex, yet universal, tunneling mechanism for the blinking *on* and *off* process.

We study over 200 individual QD's simultaneously using a home-built, epifluorescence microscope apparatus described previously.[15] Under cw laser excitation (Ar ion), the emission intensity fluctuations are measured with a time resolution of 100 ms for durations of an hour. Single-dot fluorescence was acquired through an oil immersion lens (numerical aperture 1.25) for room temperature studies while temperature-dependent studies were performed in a liquid-helium, cold-finger cryostat with a long-working-distance air objective (numerical aperture 0.7). A CCD detector was used to collect data from *all* of the dots that emit light during the observation period to ensure a complete statistical treatment of blinking. The CdSe QD's are prepared following the method of Murray, Norris, and Bawendi[16] and protected with ZnS overcoating[17,18] while the CdTe were prepared following Ref. 19.

An illustrative 3000-s time-trace of fluorescence intermittency is shown for a CdSe/ZnS QD at RT and at 10 K in

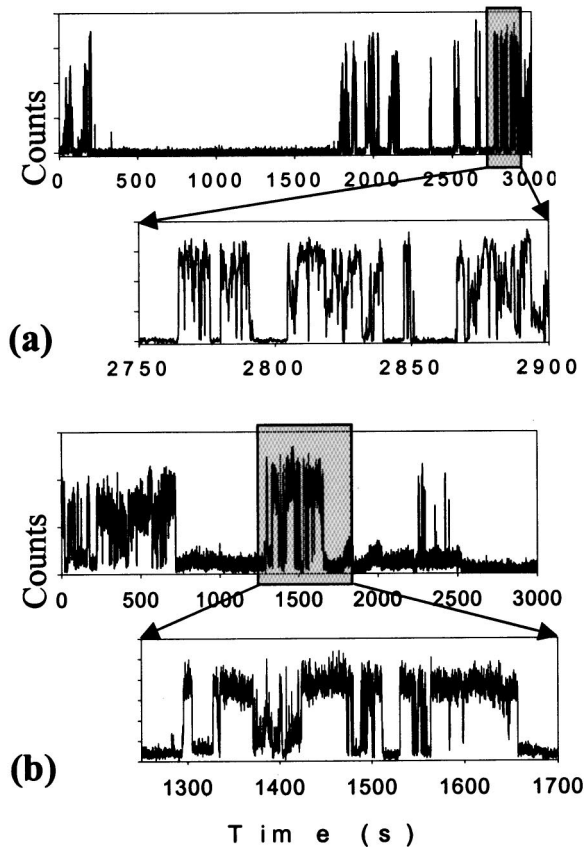

FIG. 1. Typical intensity time trace of CdSe(ZnS) QD fluorescence intermittency at (a) RT and (b) 10 K. Expanded view illustrates the similar nature of the blinking events at RT and 10 K but with different time scales.

Figs. 1(a) and 1(b), respectively. A small section of the time trace is expanded to show the self-similarity and complexity of the traces on different time scales. We define the *on* time (or *off* time) as the interval of time when no signal falls below (or surpasses) a chosen threshold intensity value. The probability distribution is given by the histogram of *on* or *off* events of length t:

$$P(t)=\sum_{t}[\text{events of length } t]. \tag{1}$$

The *off*-time probability distribution for a single CdSe/ZnS QD at room temperature is shown in Fig. 2(a). The distribution follows a pure power law for the time regime of our experiments ($\sim 10^3$ s):

$$P(t)=At^{-\alpha}. \tag{2}$$

Most individual dots also follow a power-law probability distribution with the same value in the power-law exponents ($\alpha \approx 1.5 \pm 0.1$). A histogram of α values for individual QD's is shown in the inset of Fig. 2(a). The universality of this

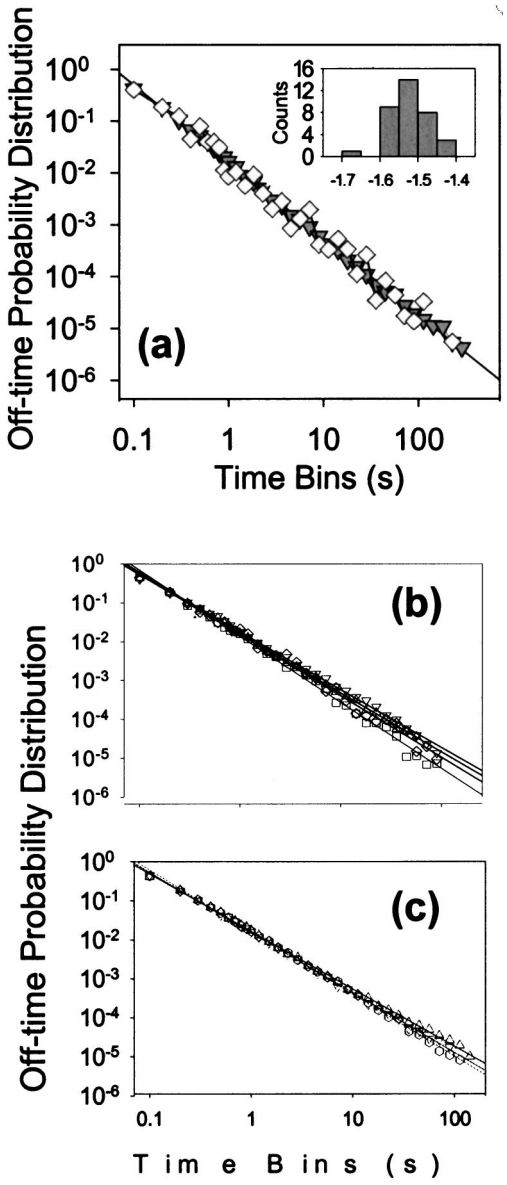

FIG. 2. (a) Normalized *off*-time probability distribution for one CdSe QD (◇) and average of 39 CdSe QD's (▼). Inset shows the distribution of fitting values for the power-law exponent in the 39 CdSe QD's. The straight line is a best fit to the average distribution with exponent ~ -1.5 (b) Average *off*-time probability distribution for 25-Å radius CdSe(ZnS) QD at 300 K (▽), 10 K (△), 30 K (◇), and 70 K (□). The α values are 1.41, 1.51, 1.37, and 1.45, respectively. (c) Average *off*-time probability distributions for 39 CdSe(ZnS) QD of radius 15 Å, (▽) and 25-Å radius CdSe(ZnS) QD (◇) and 25-Å radius CdSe QD (△) at RT. The α values are 1.54, 1.59, and 1.47, respectively.

statistical behavior indicates that the blinking statistics for the *off* times are insensitive to the different environments of each dot. Kuno *et al.*[8] first observed this behavior at room temperature using conventional confocal microscopy. Due to higher signal-to-noise ratio, confocal microscopy provides a time resolution as high as 200 μs; however, the same probability distribution is also observed with 100-ms integration times. Initial experiments at RT show that the same blinking

statistics are observed in CdTe QD's demonstrating that this power-law phenomenon is not restricted to only CdSe QD's.

To develop a physical model from this phenomenological power-law behavior, we probe the temperature dependence of the blinking statistics; this dependence should provide insight into the type of mechanism (tunneling vs hopping) and the energy scales of the blinking phenomena. Qualitatively, the data in Figs. 1(a) and 1(b) suggest that at low temperature the QD's blink less and stay in the *on* state for a larger portion of the time observed. However, when we quantify these observations by plotting the *off*-time probability distributions at temperatures ranging from 10 K to 300 K, as shown in Fig. 2(b), the statistics still show power-law behavior regardless of temperature. Moreover, the average exponents in the power-law distributions are statistically identical for different temperatures (10 K, -1.51 ± 0.1; 30 K, -1.37 ± 0.1; 70 K, -1.45 ± 0.1; RT, -1.41 ± 0.1). Such a seemingly contradictory conclusion is, however, resolved by plotting the *on*-time probability distribution at 10 K and RT as shown in Fig. 3(c). It is seen there that unlike the *off*-time distribution, the *on* times have a temperature dependence that is then reflected in the raw data of Fig. 1.

The *on*-time statistics yield a power-law distribution with the same exponent[20] as for the *off* times, but with a temperature-dependent ''saturation effect'' that alters the long time tail of the distribution. This saturation reflects a secondary mechanism that limits the maximum *on* time of the QD. The saturation effect can be seen in the *on*-time distribution of a single QD in Figs. 3(a) and 3(b) as a ''truncation,'' and in the average distribution of many single QD's as a downward deviation from the pure power law.[21] At low temperatures, the saturation effect sets in at longer times and the resulting time trace shows ''long'' *on* times. The extension of the power-law behavior for low temperatures on this logarithmic time scale drastically changes the time trace as seen in Fig. 1; i.e., fewer *on-off* events are observed and the *on* times are longer.

Given that the exponent for the *on*-time power law distribution is nearly the same for all of our samples, then a measure of the average truncation point (or maximum on-time) is possible by comparing the ''average *on* times'' for different samples keeping the same overall experimental time. We calculate an average *on* time: 312, 283, and 256 ms for the same CdSe/ZnS sample under 10 K and 175 W/cm^2, 10 K and 700 W/cm^2, and RT and 175 W/cm^2 excitation intensity, respectively. The effective truncation time can be extrapolated by determining the end point within the power-law distribution that corresponds to the measured average *on* time. In Figs. 3(c) and 3(d), the vertical lines correspond to this calculated average truncation point indicating the crossover in time domain from the first blinking mechanism to the other.

The saturation effect is not observed in the *off*-time statistics on the time scale of our experiments. It is important to note that the truncation/deviation is not an artifact of the experimental time since the power law of the *off*-time statistics extends well beyond the truncation point of the power-law distribution of the *on*-time statistics.

Previous studies have shown intensity-independent off-time behavior.[9,14] Intensity independent *off*-time statistics are also observed here. Varying the cw average excitation power in the range of 100 W/cm^2 to 3 kW/cm^2 at 300 and 10 K showed power-law *off*-time probability distributions with minimal changes in the exponent value. We also compared the *off*-time statistics for QD's differing in size (15 vs 25 Å core radius) and QD's with and without a 6-ML shell of ZnS overcoating shown in Fig. 2(c). Again, the results showed no difference to the statistical nature of the blinking-*on* process. However, modification of the surface morphology or excitation intensity does make drastic changes to the *on*-time distribution as shown in Figs. 3(c) and 3(d). With reduced excitation intensity, lower temperature, or greater surface overcoating, the deviation from the power-law distribution or ''saturation'' sets in at longer wait times and the power-law

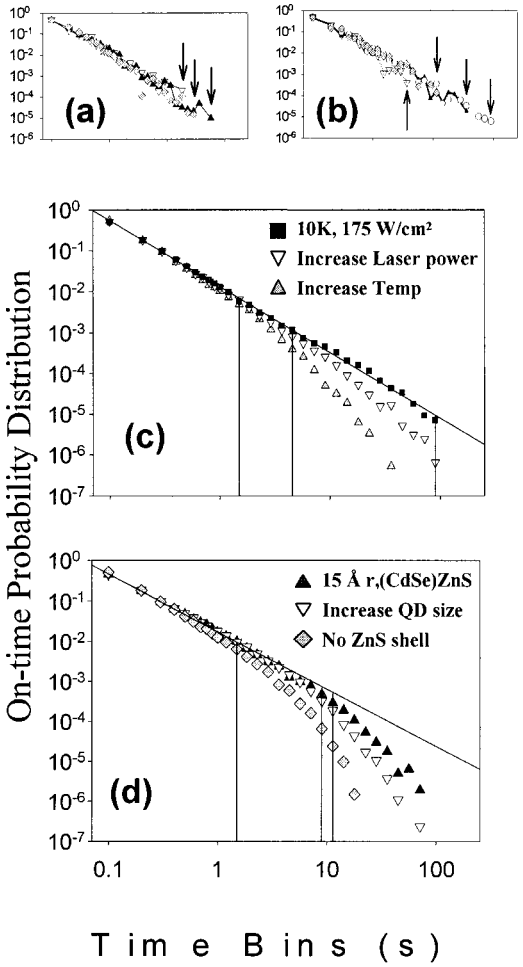

FIG. 3. (a) Three single QD on time probability distributions at 10 K, 700 W/cm^2. The arrows indicate the truncation point for the probability distribution for each QD. (b) Four single-QD *on*-time probability distributions for CdSe(ZnS) QD's at RT, 100 W/cm^2. (c) Average *on*-time probability distribution for 25-Å radius CdSe(ZnS) QD at 300 K and 175 W/cm^2 (▲), 10 K and 700 W/cm^2 (▽), and 10 K and 175 W/cm^2 (■). The straight line is a best-fit line with exponent ~-1.6. (d) Average *on*-time probability distribution for 15-Å radius CdSe(ZnS) QD (▲) and 25-Å radius CdSe(ZnS) QD (▽) and 25-Å radius CdSe QD (◆) at RT, 100 W/cm^2. The straight line here is a guide for the eye. The vertical lines correspond to truncation points where the power-law behavior is estimated to end.

distribution for the *on*-time becomes more evident. The statistical behavior observed is consistent with previous work;[9,14] however, the separation of the power-law statistics from saturation effects clearly demonstrates that two separate mechanisms govern the blinking of CdSe QD's.

The universality of the *off*-time statistics for all the QD's indicates inherent, fundamental physics. Furthermore, since the power-law statistics are temperature and excitation intensity independent, the process that couples a dark state to a bright state is a tunneling process and not photoassisted. Spectral information can also aid in modeling this blinking phenomena. At cryogenic temperatures, spectrally-resolved emission measurements showed a correlation between blinking and spectral shifting.[22] When spectral shifts occur, the transition energy of the QD system changes as a function of time; therefore, the tunneling mechanism would occur with changing bright-state energies. Due to large variations in the transition energy [as large as 60 meV (Ref. 23)] of the bright state, we propose a theoretical framework for this system using a random-walk–first-passage-time model[24] of a dark trap state that shifts into resonance with the excited state.

In this random-walk model, we construct a dynamic phase space consisting of the bright and dark states. The *on-off* blinking takes place according to a random walk through this phase space as the states shift into resonance. The observed power-law time dependence can be understood as follows: If the system has been *off* for a long time, the system is deep within the charged state (*off* region) of the dynamic phase space and is unlikely to enter the neutral state (*on* region) of the phase space. On the other hand, close to the transition point, the system would interchange between the charged and neutral states rapidly. As the simplest random-walk model, we propose an illustrative example of a one-dimensional phase space with a single trap state that is wandering up and down in energy. At each crossing of the trap and intrinsic excited state energies, the QD changes from dark to bright or bright to dark. Since the transition from *on* to *off* is a temperature-independent tunneling process, it can only occur when the trap state and excited state of the QD are in resonance. More precisely, we can apply a semidiscrete model in which a temperature-dependent hopping process is used to model the discrete-time random walk where this semidiscrete hopping process is related to the movement and creation/annihilation of trapped charges surrounding the QD core.[22,23,25] The minimum hopping time of the surrounding charge environment gives the minimum time-scale for each step of the random walk to occur. This simple discrete-time random-walk model for blinking immediately gives the characteristic power-law probability distribution of *off* times with a power-law exponent of -1.5.[26] It is important to note that the intrinsic hopping time is likely to be orders of magnitude faster than our experimental binning resolution (100 ms). The intrinsic hopping time probably depends on temperature. This temperature dependence, however, would only be reflected in experiments that could probe time scales on the order of the hopping times, before power-law statistics set in and beyond the reach of our experimental time resolution.

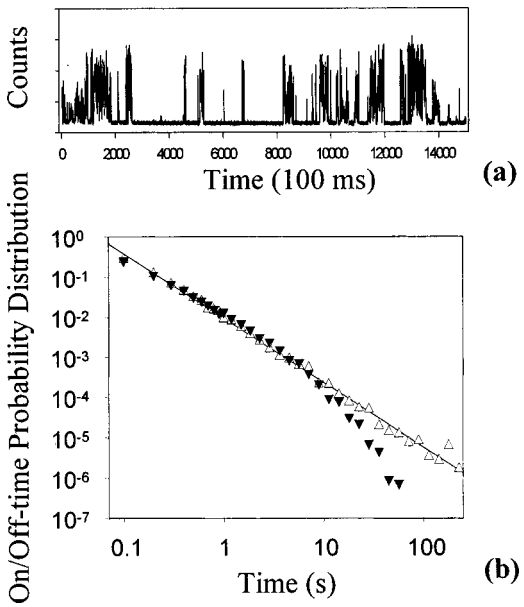

FIG. 4. (a) Time trace of a single CdTe QD at room temperature, 125 W/cm^2. (b) The probability distribution of the *on* time (▼) and *off* time (△) for CdTe QD's at room temperature. The best-fit line shows a power-law behavior with exponent ~ -1.6.

Although we suggest this simple random-walk model only as a guide to explore this physical system, it nevertheless explains the general properties observed. The *off*-time statistics are temperature and intensity independent because although the hopping rate of the random walker changes, the statistics of returning to resonance between the trap and excited state does not. In addition, size and surface morphology do not play a significant role in this model as long as a trap state is energetically accessible to the intrinsic excited state. Further experimental and theoretical work is needed to complete this model. Temperature- and state-dependent hopping rates as well as a higher-dimension random-walk phase space and multiple transition states may need to be included.

The magnitude of saturation of the *on*-time power-law distribution is dependent on the QD observed as shown in Figs. 3(a) and 3(b). In Fig. 3(b), the arrows indicate the *on*-time truncation point for four different QD's under the same excitation intensity at RT. Qualitatively, we can describe and understand the changes as a result of the interaction between the dynamic dark and bright states modeled earlier. As the excitation intensity or thermal energy is reduced, the hopping rate of the random walker slows down and the critical number of hopping cycles for the saturation to occur takes longer within our experimental time. Surface modification in the form of ZnS overcoating also extends the power-law distribution for the *on* times. This modification should not change the hopping rate of the random walker but rather decrease the number of trap states on the surface. A mechanism such as photoassisted ejection of a charge due to Auger ionization may be responsible for this saturation effect. Recent results on CdTe QD's (Fig. 4) show that the power-law behavior, its exponent, and the *on*-time phenomenology is reproduced, indicating that the effects observed are not unique to the particulars of CdSe QD's, but rather reflect more universal underlying physics of nanocrystal QD's.

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