Simple model for the power-law blinking of single semiconductor nanocrystals

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We assign the blinking of nanocrystals to electron tunneling towards a uniform spatial distribution of traps. This naturally explains the power-law distribution of off times, and the power-law correlation function we measured on uncapped CdS dots. Capped dots, on the other hand, present extended on times leading to a radically different correlation function. This is readily described in our model by involving two different, dark and bright, charged states. Coulomb blockade prevents further ionization of the charged dot, thus giving rise to long, power-law distributed off and on times.

Nanocrystals of II-VI semiconductors (e.g., CdS or CdSe), with a diameter of a few nm, present original optical properties due to quantum exciton confinement.[1,2] In addition to their use as model systems for quantum optics and solid-state physics,[3,4] single nanocrystals (NC's, often called quantum dots) are attracting much attention because of their potential use as luminescent probes in molecular biology.[5] To improve their emission properties, one often protects them with an organic layer (uncapped), or with another layer of a semiconductor with a higher band gap, for example ZnS (capped). Under steady laser illumination, the photoluminescence of single NC's displays strong fluctuations,[6] with long dark periods or off times. This phenomenon called blinking is a hallmark of single fluorescent nano-objects.[7] It limits the brightness and visibility of NC's, and thus their potential applications. The mechanism of blinking is still an open problem, whose understanding may open new paths to improve luminescent nanoprobes. The most direct way to evaluate blinking is to record luminescence intensity as a function of time, to distinguish between on times and off times by means of a pre-defined threshold, and to measure the distributions of these times as histograms. By using this technique, researchers have been able to obtain a wealth of experimental results on blinking of capped NC's.[8,9] A striking observation in these studies is that both on-time and off-time distributions follow an inverse power law. Whereas power-law behavior of the off times can easily be explained by a wide distribution of trapping potentials for a charge carrier that is ejected by an Auger process, the power-law behavior of the on-time distributions appears to be inconsistent with all proposed physical models. Interestingly, results on uncapped CdSe NC's (Ref. 9) show a power-law behavior for the off times, with similar exponents as for the capped dots, but suggest less dispersed kinetics for the on times.

An alternative method to probe the dynamics of fluorescence intermittency is the autocorrelation function, defined for a time-dependent intensity $I(t)$ by

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}.$$

This function keeps track of all intensity fluctuations over a long acquisition time.[10] Whereas the on-time and off-time distributions are sensitive to detection yield and to back-

ground, the normalized $g^{(2)}(\tau)$ is insensitive to detection yield, and only its overall contrast is reduced by background. Furthermore, measuring a correlation function does not require thresholding with an arbitrary parameter, and the time resolution is higher. Measured correlation functions are therefore reliable and particularly useful in comparing blinking data to theoretical models.

We investigated the blinking of single uncapped CdS nanocrystals, to compare it to that of capped NC's. A solution of demineralized water with 0.5% (w/w) polyvinylalcohol (MW 125 000) and 5×10^{-11}M CdS particles (5 nm in diameter, prepared in the group of Professor A. Meijerink at Utrecht University) was spin cast onto a fused silica substrate to obtain a film with an estimated thickness of less than 1 μm. The luminescence was measured with a home-built confocal microscope at 1.2 K, exciting with the 457.9-nm line of an argon-ion laser. The maximum count rate of a few thousands per second gave us a time resolution of 10 ms for the trace and about 2 μs for the correlation function. As Fig. 1(a) shows, the intensity traces display very strong blinking. Their appearance is self-similar on various time scales. The distribution of off times follows a power law with an exponent of -1.65 ± 0.2, whereas the distribution of on times decays much faster and can be fitted with a single exponential. The intensity correlation function of Fig. 1(b) is a power law of time, with an exponent of about -0.3.

In order to compare the autocorrelation function with on- and off-time distributions, we derived a mathematical relation between the two. We consider a Markovian random telegraph whose on and off periods deterministically succeed one another, but without any memory of former on and off times.[8] We have related[11] $g^{(2)}(\tau)$ to the distributions $P(\tau)$ of on times and $Q(\tau)$ of off times by expanding the probability of a photon pair as a series of probabilities of independent events occurring between $t=0$ and τ. The Laplace transform $\tilde{g}^{(2)}(s)$ of $g^{(2)}(\tau)$ is related to those, $\tilde{P}(s)$ and $\tilde{Q}(s)$, of these distributions by

$$\tilde{g}^{(2)}(s) = \left(1 + \frac{\langle t_{\text{off}}\rangle}{\langle t_{\text{on}}\rangle}\right)\frac{1}{s}\left(1 - \frac{(1-\tilde{P})(1-\tilde{Q})}{s\langle t_{\text{on}}\rangle(1-\tilde{P}\tilde{Q})}\right), \quad (1)$$

where $\langle t_{\text{on}}\rangle$ ($\langle t_{\text{off}}\rangle$) is the average on time (off time), supposed to be definable. For power-law distributions, this defi-
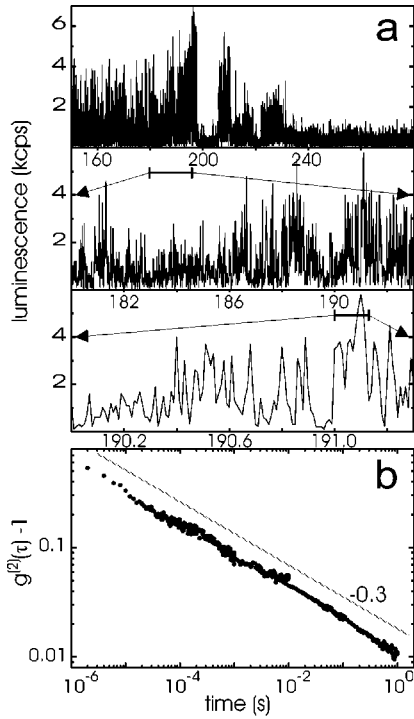
FIG. 1. (a) Experimental intensity trace of a single uncapped CdS nanocrystal, showing only short on times at all time scales. (b) The correlation function of this signal decays as a power-law over six decades of time, with an exponent about −0.3 (solid line).

nition requires cutoffs at short or long time scales. For the important special case of our uncapped NC's, when the on times follow a single-exponential distribution $P(\tau)=ae^{-a\tau}$ with an average on time $\langle t_{\text{on}}\rangle=a^{-1}$, Eq. (1) becomes

$$\widetilde{g}^{(2)}(s)=\frac{1+a\langle t_{\text{off}}\rangle}{s+a(1-\widetilde{Q})}. \tag{2}$$

For off times distributed according to a power law, $Q(\tau)\propto\tau^{-m}$, the Laplace transform varies as $\widetilde{Q}(s)\approx1-(\theta s)^{m-1}$, where θ is the shortest off time. Equation (2) then shows that the correlation function is itself a power law at long times, varying as τ^{m-2}.

This shows that the measured autocorrelation function from Fig. 1(b) is compatible with a power-law distribution of off times with $m=1.7$, in good agreement with the measurements and with earlier observations of capped dots.[8,9] In order to explain these observations, we propose a simple model, following the ideas of Efros and Rosen.[12] We too assume that an electron can tunnel from the excited NC to a trap. After transfer, the charged NC still absorbs, but is dark because of fast Auger recombination, i.e., charge-induced nonradiative relaxation of the exciton energy. The dark period ends, and the NC becomes bright again when the trapped electron hops back. Instead of a single trap, we postulate a uniform distribution of traps in the matrix around the NC. Assuming spherical symmetry, the exciton wave function outside the dot decreases like $e^{-\alpha r}/r$. Since the radial density of traps varies as r^2, the trapping probability de-
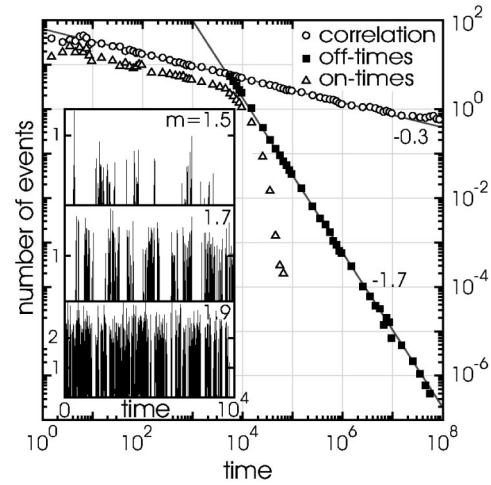

FIG. 2. Simulated on- and off-time distributions and correlation function in our model of uncapped NC's, for $m=1.7$. The inset shows the appearance of intensity traces for three different exponents, $m=1.5$, 1.7, and 1.9. The time unit is the luminescence lifetime.

creases exponentially with distance r, just as in a one-dimensional model with a constant linear density of traps. The probability density to tunnel at distance r from the NC surface is therefore $p(r)=\alpha e^{-\alpha r}$. The recovery rate, describing the back-tunneling rate of the trapped electron to the ionized NC also varies exponentially with distance r, like $e^{-\beta r}$,[13] but with a different decay length. Expressing the distance r as a function of the average recovery time $T=T_0e^{\beta r}$, we can write the probability density of T as

$$\Pi(T)=\frac{\alpha}{\beta}\frac{1}{T}\left(\frac{T_0}{T}\right)^{\alpha/\beta},$$

i.e., an inverse power law with exponent $m=1+\alpha/\beta$. Because this power-law distribution is much broader than the single-exponential Poisson distribution of off times for a given average recovery time T, we may approximate the overall distribution of off times to the same power law. Relating the decay coefficients α and β to the tunneling barriers, we obtain

$$\frac{\alpha}{\beta}=\sqrt{\frac{V_{\text{matrix}}-V_{\text{e}}}{V_{\text{matrix}}-V_{\text{trap}}}}, \tag{3}$$

where V_{matrix}, V_{e}, and V_{trap} are the electron's potentials in the matrix, in the excited state of the dot, and in the traps, respectively. Because the trap must be deeper than the excited state, we have $\alpha<\beta$. Therefore Eq. (3) naturally explains why the exponent m lies between 1 and 2.[8,9] Since the process is electron tunneling, m does not depend on temperature, as observed in Ref. 9. Note that this model predicts a single-exponential distribution of on times. The inset of Fig. 2 shows a set of simulated traces obtained with our model, for three values of the exponent m (which could correspond to various matrices or trap depths). The intensity traces were simulated in a personal computer by picking an exponentially distributed random time for each elementary process

having a well-defined single rate (photon emission, electron trapping to a given distance, back tunneling). We thus generated a series of detected counts similar to an experimental trace, which was further used as input for correlation and on/off-time counting. The simulated traces are self-similar on a wide range of time scales (as soon as these are much longer than the minimal hopping time to the closest trap). Figure 2 also shows the off-time and on-time distributions obtained from a trace for $m = 1.7$, and the correlation function, a power-law with exponent -0.3, in good agreement with our experimental findings, as shown in Fig. 1(b).

We now consider the blinking of capped NC's,[8,9,14] for which both the on- and off-time distributions have been found to obey a power law.[8,9] The intensity traces of capped NC's show much longer on times on average, yielding a completely different correlation function. The long on times are heavily weighted in the average, giving rise to a nearly flat correlation for short times, and to a steep decrease at the end of the integration time.[14] For power-law distributions of off and on times, if m is the larger exponent, Eq. (1) gives

$$g^{(2)}(\tau) = A(1 - B\tau^{2-m}), \tag{4}$$

where A and B are two constants. In accordance with experiments, this dependence indeed appears flat on a logarithmic time scale. In the present version of our model, the ionization rate of the NC (and therefore its probability to go to an off state after each excitation) is always finite, leading to a single-exponential distribution of on times. Background and quantum yield cannot bias the distribution towards long on times. The model must therefore be extended to describe the long on times observed in the blinking of capped dots.

In order to allow for long on-times, ionization of the NC's core to far-away traps must be prevented. We propose Coulomb blockade as the ionization-stopping mechanism. For a small enough NC, once one electron has been transferred to a far-away trap, another ionization would cost more electrostatic energy than the exciting photon can provide. Indeed, elegant experiments[15] have recently shown that blinking is related to charge rearrangements via electron transfer, and that individual NC's accommodate at most one or two positive charges (or holes). We now have the apparent difficulty that, as blinking models postulate, a charged NC should not emit. This assumption, however, holds only as far as the residual hole is located in the core. If the hole is trapped further away, for example in the capping shell, or on the shell surface, the radiative recombination yield may still be significant because the exciton wave function decreases exponentially in the shell. Yet, because the trapped hole's Coulomb potential varies slowly with distance, it still effectively prevents ionization. Depending on the distance of the trapped hole to the core, we may expect a broad range of luminescence levels. Neuhauser et al.[16] presented a similar argument in their discussion of the correlation between spectral diffusion and blinking of NC's. In order to keep this extended model simple, we consider only two possibilities to trap the residual hole: either on the shell with probability ε, giving an extended on time, or in the core with probability $(1 - \varepsilon)$, giving an extended off time. These extended on/off times will last until the far-away electron comes back. We
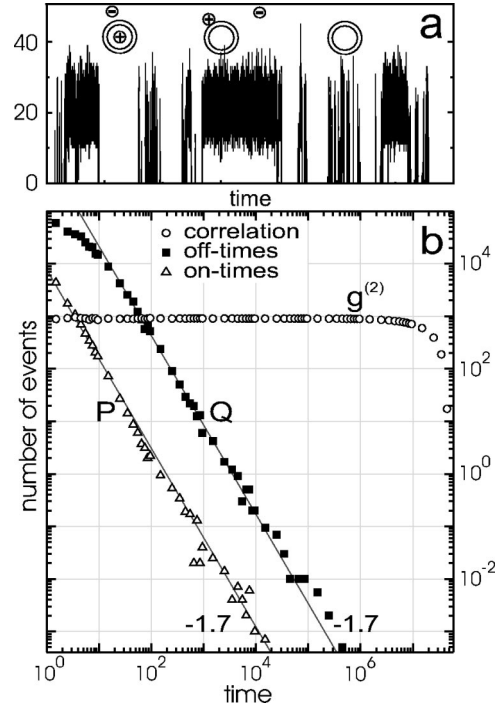
FIG. 3. (a) Simulated intensity trace in our extended model of capped NC's. One may distinguish three different states in the trace: on, off, and blinking. (b) The on-time and off-time distributions are both power laws of time with exponent -1.7. The distribution of off times has been shifted upward by a factor of 50 for clarity's sake. Note that the correlation function is now much flatter than that of the uncapped dot (see Fig. 2 and compare with Ref. 14).

have performed simulations of intensity traces for this new model with $\varepsilon = 0.2$, shown in Fig. 3. The trace of Fig. 3(a) consists of a random juxtaposition of three modes of luminescence pertaining to the three possible states of the NC: with a charged core, corresponding to an off-time; with a charged shell, leading to steady emission, i.e., an "extended" on-time; and neutral, corresponding to "true" on times, too short to be resolved on the long time scale of Fig. 3. In practice, because of low experimental time resolution, the neutral state is likely to appear as a "gray," blinking trace, similar to those shown by the simulations of Fig. 2. Some experimental evidence for three states can be seen in the trace published in Ref. 14. Using our capped-dot model, we have simulated the distributions of on times and off times, as well as the correlation function. As Fig. 3(b) shows, the simulations agree very well with the published power-law distributions of on and off times.[8,9] Although the expression (4) of the correlation function does not rigorously apply here (because it pertains to a deterministic instead of random succession of on and off times), its form agrees qualitatively with experiments[14] and with the simulation of Fig. 3(b).

Our model naturally accounts for most current observations of blinking in both uncapped ($\varepsilon = 0$) and capped NC's, and provides a general frame for blinking kinetics. Further model predictions can be tested experimentally: First, hole tunneling must be very unlikely or short range, because the dot could not keep its positive charge very long under heavy laser illumination. Further, Eq. (3) indicates that blinking sta-

tistics and power-law exponents should depend on substrate material, and on the doping with electron traps. Capping thickness and quality must be critical. Depending on the location of the hole, states with various luminescence yields could exist, i.e., with various brightnesses, lower than that of the true on states of the neutral dot. Recent observations[17] of lifetime fluctuations correlated to brightness changes in a single NC support this hypothesis. Finally, our model suggests that the role of capping is not so much to prevent ionization (ionization to far-away traps and very long off times occur for both capped and uncapped NC's), as to keep the residual hole away from the emitting core, making long on-periods possible for capped dots. Even though it probably oversimplifies the complex photophysics of real NC's, where charge rearrangements upon blinking cause spectral diffusion,[16] we hope that our model will lead to a better understanding of blinking, and thereby to more efficient luminescent nanoprobes.

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