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Model of Fluorescence Intermittency of Single Colloidal Semiconductor Quantum Dots Using Multiple Recombination Centers

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We present a new physical model resolving a long-standing mystery of the power-law distributions of the blinking times in single colloidal quantum dot fluorescence. The model considers the nonradiative relaxation of the exciton through multiple recombination centers. Each center is allowed to switch between two quasistationary states. We point out that the conventional threshold analysis method used to extract the exponents of the distributions for the on times and off times has a serious flaw: the qualitative properties of the distributions strongly depend on the threshold value chosen for separating the on and off states. Our new model explains naturally this threshold dependence, as well as other key experimental features of the single quantum dot fluorescence trajectories, such as the power-law power spectrum ($1/f$ noise).

Substantial progress has been made recently in the study of long range correlations in the fluctuations of emission intensity (blinking) in single colloidal semiconductor nanocrystals (QD) [1–5], nanorods [6], nanowires [7] and some organic molecules [8]. By introducing an intensity threshold level to separate bright (on) and dark (off) states, Kuno *et al.* [2] found that the on- and off-time distributions in QDs exhibit a spectacular power-law dependence over 5–6 orders of magnitude in time.

$$p_{\mathrm{on/off}}(t) \sim t^{-m} \qquad (1)$$

As discovered later by Shimizu *et al.* [3], the power-law on-time distribution is cut off at times ranging from a few seconds to 100 s, depending on the dot and its environment. During the past eight years or so the truncated power-law form of the blinking on-time distributions was confirmed by many experimental groups (see [4,5,9,10] and references therein), but its microscopic origin remains a mystery. Remarkably, there are no "set" values for the on-time and off-time exponents. They are scattered in the region from 1.2 to 2.0. Similar on- and off-time distributions were found recently for the other blinking systems mentioned above: semiconductor nanorods (NRs) [6,11], nanowires (NWs) [7] and organic dyes [8]. The generality of the phenomenon is rather intriguing. We argued that there must be a common underlying mechanism responsible for the long time correlated fluorescence intermittency detected in all these systems [12]. Most theoretical explanations of the QD blinking [2,3,13–15] are based on the Efros-Rosen charging mechanism [16]. The mechanism attributes on and off states to a neutral and a charged QD, respectively. The light-induced electronic excitation in the charged QD is quenched by a fast Auger recombination process. A number of experimental results indicate, however, that there are no unique bright (on) and dark (off) states of the QD, but a continuous set of emission intensities [17–19]. One can therefore suggest an alternative

mechanism of the blinking, assuming slow fluctuations in the nonradiative recombination rate of the excited state [20–22].

In order to gain further insight into the possible blinking mechanism, we performed an extensive analysis of the on and off distributions of actual single QD fluorescence trajectories. Our procedure is different from the conventional ones, as we applied the maximum likelihood estimator (MLE) method to find the best gamma distribution $p(t) \sim t^{-m} \exp(-t/T)$ fit for the set of on and off durations. The MLE approach [23] gives an unbiased estimation for the parameters of the power-law distribution with minimal statistical error. These properties are crucial and allow for the investigation of a *single* trajectory. Our approach, in contrast with procedure used by Hoogenboom *et al.* [23], allows us to find optimal values for not only for m, but for the truncation time T as well. The fluorescence trajectories we investigated were obtained by Protasenko and Kuno and have already been analyzed by others [24,25].

Our fitting procedure is performed repeatedly for a number of threshold values for each trajectory. In all the cases the off-time distribution truncation time is found too long to be detected. Also, the threshold dependence of the distributions was all but ignored until now. The only exception is the recent observation made on nanorods (not QDs) by Drndic and her co-workers [11]. In any case, the fundamental nature of this dependence was not revealed until now. An example of the threshold dependency of the power-law exponent (slope on log scale) and on-truncation time for a singe QD trajectory is presented in Fig. 1. While we investigated a large number of trajectories, we have deliberately chosen for this Letter one with clearly visible telegraph noise–like features and well-defined on and off maxima in the intensity histogram [see inset in Fig. 1(b)]. As it is evident from Fig. 1, even for this apparently ideal case, the distribution parameters are strongly threshold
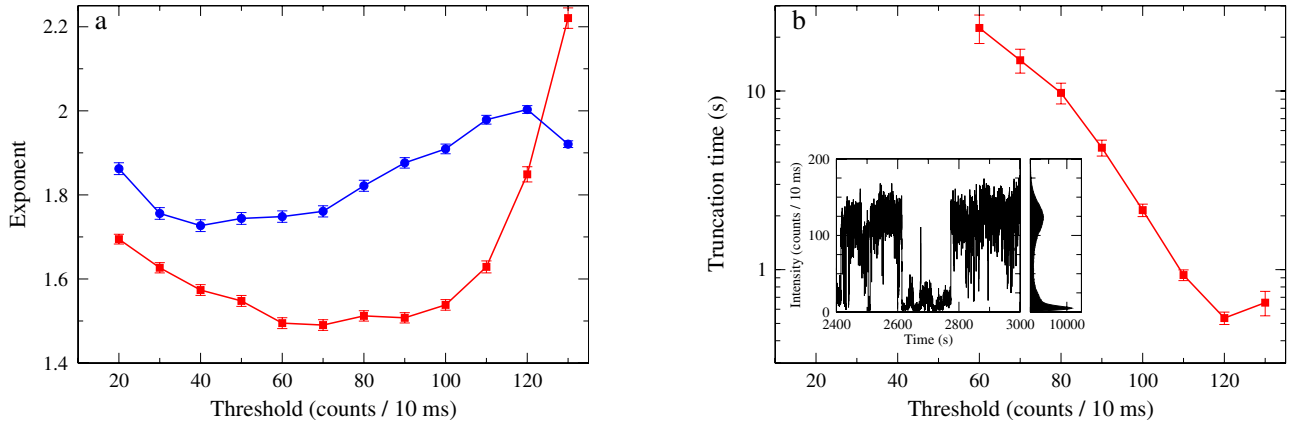
FIG. 1 (color online).   The threshold dependence of the on-time (red squares) and off-time (blue circles) distribution exponents (a) and on-time distribution truncation time (b) obtained from the experimentally measured single QD fluorescence trajectory. Error bars show the standard deviation values. Inset (b): a part of the trajectory and an intensity histogram.

dependent. While the majority of the analyzed trajectories are not like telegraph noise, we mention that *all* show similar threshold dependence. The on-time truncation time decreases monotonically with increasing of the threshold. This trend is the same for most single QD fluorescence trajectories we analyzed. The scaling of the slope as a function of the threshold is more complicated. The exponent of the off-time distribution shows several extrema, whereas the on-time exponent has a minimum as the threshold value is varied. We wish to emphasize that dependence of on- and off-time exponents on threshold can qualitatively change from one trajectory to another.

We interpret this strong dependence on threshold as a clear indication that the standard trajectory analysis—based on the separation between on and off events with a somewhat arbitrary threshold—is not quite adequate, and the trajectories should be analyzed over the full range of threshold parameter. It also explains wide distribution of the exponents found by different groups. As shown below, one of the key results of this Letter is to exploit the threshold dependence of the trajectory parameters to retrieve important information about the physical mechanism of the fluctuations.

The power spectrum of the fluorescence trajectory of a single QD has a power-law form [26,27] $S_I(\omega) \sim \omega^{-l}$ where l is close to 1. Therefore, we can consider the QD blinking process as an example of single particle $1/f$ (flicker) noise. The generally accepted phenomenological model for the electrical $1/f$ noise generation in solids is that of electrical transport in the presence of an environment consisting of multiple stochastic two-level systems (TLS) [28,29]. In the case of QD blinking we suggest a similar physical model based on a TLS environment [30].

In our model the nonradiative relaxation of the QD excitation occurs via trapping of holes to one of the N quenching centers, followed by a nonradiative recombination with the remaining electron. Each of these quenching centers could be dynamically switched between inactive and active conformations. The two conformational states differ in their ability to trap holes: the hole trapping rate is much larger in the active conformation than it is in the inactive state. Recent studies of trapping rates in the single QDs [32] showed that the number of hole traps on the surface and on the core-shell interface is in order of 10. Interestingly, we find that we only need a similar number of recombination centers in order to reproduce the basic features of the fluorescence trajectories. A possible microscopic origin of the conformation change in the recombination center could be due to the light-induced jumps of the surface or interface atom between two quasistable positions. The surface atoms in such a small object as colloidal QD can be found in a variety of local crystal configurations. Consequently, we can expect a wide distribution of switching rates. The nonradiative trapping rate in our model can therefore be expressed as

$$k_t(t) = \sum_{i=1}^{N} k_i \sigma_i(t) + k_0. \qquad (2)$$

For each TLS the stochastic variable $\sigma_i(t)$ randomly jumps between two values 0 and 1, corresponding to inactive and active conformations, respectively. Furthermore, k_i is the trapping rate in the active configuration, and k_0 is the background nonradiative relaxation rate. The time distribution functions for the $\sigma_i = 0 \rightarrow 1$ transitions and $\sigma_i = 1 \rightarrow 0$ transitions for the ith TLS are exponential and can be characterized by the transition rates γ_i^+ and γ_i^-, respectively. While in the simplest model the transition rates for the individual TLS are constants (noninteracting TLSs), we will show that a more general case of the interacting TLS systems must also be considered. The power spectral density of the process (2) within the noninteracting TLS model is a sum of Lorentzians

$$S_k(\omega) = \frac{1}{\pi} \sum_{i=1}^{N} \frac{\gamma_i^+ \gamma_i^-}{\gamma_i^+ + \gamma_i^-} \frac{k_i^2}{\omega^2 + (\gamma_i^+ + \gamma_i^-)^2}. \qquad (3)$$

The number of parameters in the above expression can be drastically reduced if the experimental constraint of $1/f$ noise spectrum is imposed. Indeed, after choosing $k_i = k$

and $\gamma_i^+ = \gamma_i^- = \gamma_i \equiv \gamma_0 a^i$, where $a \ll 1$, one can effectively fit the spectrum in Eq. (3) with $1/\omega$ in the frequency region $\gamma_N \ll \omega \ll \gamma_1$ [28]. Assuming low excitation intensities and steady-state conditions for the fermionic degrees of freedom, the quantum yield $Y(t)$ is given by [20]

$$Y(t) = \frac{k_r}{k_r + k_t(t)}, \qquad (4)$$

where k_r is the radiative relaxation rate.

Let us now show that our suggested model of fluorescence fluctuations exhibits strong threshold dependence of the on- and off-time distribution parameters. The problem of finding these distributions for the stochastic process $Y(t)$ with known properties and threshold value y is equivalent to the well-known crossing problem [33]. There are only few cases when this problem can be solved exactly [34]. Fortunately, our present model can be reduced to such an exactly solvable case. The system at any moment t could be completely described by the configuration $\Sigma = \{\sigma_1, \ldots, \sigma_N\}$. Clearly, there are 2^N different configurations. A random walk in the given configuration space is a Markovian stochastic process. The vector $\vec{P}$ containing probabilities of all configurations P_Σ satisfies the Master equation

$$\frac{d}{dt}\vec{P}(t) = \hat{W}\vec{P}(t), \qquad (5)$$

where the transition matrix $\hat{W}$ contains the following non-zero elements:

$$W_{\Sigma_i^+ \Sigma_i^-} = \gamma_i^+, \qquad W_{\Sigma_i^- \Sigma_i^+} = \gamma_i^-, \qquad W_{\Sigma\Sigma} = -\sum_{\Sigma' \neq \Sigma} W_{\Sigma'\Sigma},$$

where $\Sigma_i^- = \{\sigma_1, \ldots, \sigma_i = 0, \ldots, \sigma_N\}$ and $\Sigma_i^+ = \{\sigma_1, \ldots, \sigma_i = 1, \ldots, \sigma_N\}$ for each given Σ. The nonradiative relaxation rate for given configuration Σ can be expressed by Eq. (2), which allows us to find the corresponding emission intensity level Y_Σ from Eq. (4). Let us introduce a threshold value for the quantum yield y.

By definition, the QD is in the bright (on) state if $Y(t) \geq y$ and dark (off) state otherwise. For each threshold level y all configurations can be separated to a bright group, satisfying a condition $Y_\Sigma \geq y$ and a dark group. The vector of probabilities can be presented in the form

$$\vec{P} = \begin{pmatrix} \vec{P}_b \\ \vec{P}_d \end{pmatrix},$$

where vectors $\vec{P}_b$ and $\vec{P}_d$ contain probabilities of bright and dark configurations, respectively. The transition matrix can be recast in block form

$$\hat{W} = \begin{pmatrix} \hat{W}_{bb} & \hat{W}_{bd} \\ \hat{W}_{db} & \hat{W}_{dd} \end{pmatrix}.$$

The expressions for the normalized on-time and off-time distribution functions in this notations are well known [35]

$$p_{\text{on}}(t) = \langle \vec{1}, \hat{W}_{db} \exp(\hat{W}_{bb}t)\hat{W}_{bd}\vec{P}_e \rangle \langle \vec{1}, \hat{W}_{bd}\vec{P}_e \rangle^{-1},$$
$$p_{\text{off}}(t) = \langle \vec{1}, \hat{W}_{bd} \exp(\hat{W}_{dd}t)\hat{W}_{db}\vec{P}_e \rangle \langle \vec{1}, \hat{W}_{db}\vec{P}_e \rangle^{-1}, \qquad (6)$$

where $\langle \vec{a}, \vec{b} \rangle$ denotes the scalar product, $\vec{1}$ is the unity vector, and $\vec{P}_e$ is the equilibrium probabilities vector, satisfying a stationary condition $\hat{W}\vec{P}_e = 0$. We found that the on-time and off-time distributions generated by Eqs. (6) can be fitted by a power-law function (1) [see the inset in Fig. 2(a)]. Beyond a certain off- and on-time value the power-law behavior sharply changes to exponential asymptotic behavior $\exp(-t/T)$. In our analysis, this value of T is defined as a truncation time. We performed simulations of on-time and off-time distributions for the model system of noninteracting TLS. This relatively simple model reproduces the general trend seen experimentally in the truncation times: the on-time truncation decreases and the off-time truncation increases when the threshold value goes up.

While this simple, noninteracting TLS model is useful in illustrating our procedure, it cannot reproduce the thresh-
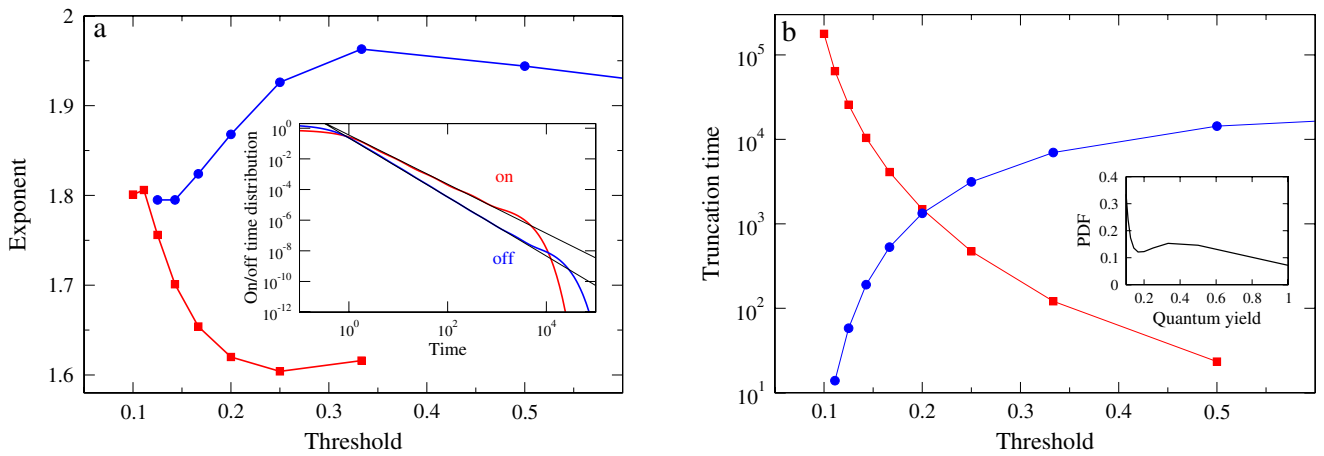

FIG. 2 (color online).　The theoretical threshold dependence of the on-time (red squares) and off-time (blue circles) distribution exponents (a) and truncation times (b) for the interacting TLS model (7). Inset (a): the on- and off-time distribution functions at the threshold value $y = 0.25$. Insert (b): probability distribution function (PDF) of the quantum yield.

old dependence of the exponents. The slope of the on-time distribution monotonically increases with the threshold value, when the off-time exponent has an opposite trend. In order to make our model more realistic, we introduce interaction between TLS in the simplest mean-field form (similar to Ref. [31]). The interaction is characterized by the parameter α, whereas the bias for an individual TLS is parametrized by β:

$$\gamma_i^{\pm} = \gamma_i \exp\left(\pm\alpha\sum_{i=1}^{N}(\sigma_i - 1/2) \pm \beta\right). \qquad (7)$$

Figure 2 provides the numerical calculation results for the interacting model with the following parameters: $N = 10$, $\gamma_1 = 1$, $a = 10^{-1/2}$, $k_r/k = 1$, $k_0 = 0$, $\alpha = 0.27$, and $\beta = -0.13$. As seen from this figure, the threshold dependence of the truncation times keep the same trend as for the noninteracting case. In contrast, the slopes now show a nonmonotonic threshold dependence reproducing qualitatively the experimental behavior shown in Fig. 1(a). The inset in Fig. 2(b) shows that the interacting TLS model is capable of generating the two-maximum intensity distribution seen in Fig. 1(b). The relative ease with which our simple phenomenological model captured the experimental trend gives us hope that the model can be used to extract interaction parameters for the TLS environment. These parameters could provide useful experimental constraints on future *microscopic* models for the TLS environment of a variety of systems showing fluorescence intermittency. The model proposed here also explains recent observations of the nonblinking dots. Furthermore, a similar model can be constructed for the fluorescence intermittency seen in quantum wires. The details for these results will be published elsewhere.

In conclusion, the phenomenological model we proposed in this Letter succeeds in qualitatively explaining the key experimental facts characterizing long-correlated fluorescence intensity fluctuations of the single colloidal quantum dots: (1) the truncated power-law distributions for on and off times obtained by the commonly used threshold procedure; (2) the strong threshold dependence of the distribution parameters m and T and wide range of the extracted exponents; (3) the $1/f$ noise form of the power spectrum of the intensity fluctuations; (4) the continuous distribution of emission intensities and excitation lifetimes; (5) the weak temperature dependence of the fluorescence intermittency due to the light-driven character of the TLS switching process.

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