Quantification of photoinduced and spontaneous quantum-dot luminescence blinking

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(Received 16 December 2004; revised manuscript received 1 July 2005; published 6 September 2005)

Photoluminescence blinking of Zn_{0.42}Cd_{0.58}Se colloidal quantum dots was investigated experimentally as a function of the excitation intensity and modeled via a Monte Carlo method. In order to test the current blinking model of electron tunneling to states external to the quantum dot, experiments were performed with quantum dots on (insulating) glass and (conducting) indium-tin-oxide substrates. Comparison of simulated and experimental data allows one to extract characteristic parameters of the blinking free of artifacts and shows that the blinking can be understood in terms of two independent processes. First, a process is active for switching between the on and off states and has a power-law probability distribution for the length of both on and off periods. Second, a single-rate transition from the on to the off state is evoked. The power-law blinking process is found to be insensitive to excitation intensity and the electronic states of the substrate and presents identical statistics for the two switching directions, pointing to an intrinsic symmetry. The single-rate on→off transition can account for all experimentally observed photoinduced and environmental (substrate) effects. On glass, its behavior is well described by a one-photon process in agreement with earlier studies on insulators. In contrast, a different behavior is found on the conducting substrates.

DOI: 10.1103/PhysRevB.72.125304

PACS number(s): 78.67.Hc, 78.55.−m

I. INTRODUCTION

Colloidal semiconducting nanocrystals, also known as quantum dots (QDs) are attractive chromophores for a variety of applications, they can be used as markers for single biological molecules,1,2 and as single-photon light sources for quantum information processing.3 Their high photostability, narrow and tunable emission, and wide band-edge absorption provide an advantage compared to organic dyes. However, the emission of QDs presents a severe intermittence also known as on/off blinking; i.e., QDs emit detectable luminescence for limited time periods (t_{on}) interrupted by dark periods (t_{off}) in which only background intensity is detected. On/off blinking has been universally observed in QDs of different compositions and structures4–6 and represents an important limitation for their practical use. Especially in view of recently reported results that show that the intrinsic (on-state) quantum efficiency of QDs can reach values very close to unity,7 the blinking remains the ultimate obstacle to achieve chromophores with the highest performance. Since the discovery of the QD luminescence blinking,8 the responsible process has remained an intriguing question of fundamental importance for the physics of confined semiconductors. Understanding of the blinking mechanism should lead to new pathways to achieve the optimum performance of QDs.

The usual way to study the blinking is to compute a time-histogram of the emitted intensity which provides direct access to the emission fluctuations.9,10 [Fig. 1(a)]. By means of a suitable intensity threshold, the t_{on} and t_{off} can be identified [Fig. 1(b)]. Early studies on colloidal CdSe QDs showed that the experimental average t_{on} obtained from such a time-binning analysis decreases linearly with excitation intensity.8,11 This finding was interpreted in terms of a transition rate from the on to the off state in a one-photon process. Later, it was discovered that the probability of a certain off period P(t_{off}) follows a power law [P(t_{off})=n_{off}t^\nu] with an exponent \nu between 1 and 2,5,12 as shown in Fig. 1(c). This exponent was found to be independent of temperature and excitation intensity.5 At low temperature and/or low laser excitation intensity, the probability of a certain on-period P(t_{on}) shows the same power-law behavior as P(t_{off}).5 As the temperature and/or the excitation intensity increases, P(t_{on}) deviates from the power-law to lower values at long times. This deviation is observed either as an abrupt cutoff of the power-law distribution at a certain maximum t_{on} [e.g., in typical single QD traces; Fig. 1(c)] or, if the data is rich enough in long t_{on} events, as a gradual decay or roll off (e.g., in the common computation t_{on} events obtained from many QDs).5,13 Consequently, the maximum observed t_{on} decreases as the excitation intensity or the temperature increases.

Unlike the exponential distributions of t_{on} and t_{off} of single fluorescent molecules, this power-law behavior of QDs cannot be explained in terms of transition rates between a finite set of (on/off) states. Another consequence of the power-law behavior is that the averages of t_{on} and t_{off} are ill-defined quantities.12,14 Thus, previous results not interpreted in the context of the power law should be considered with caution.

The most commonly suggested mechanism relates the switching between off and on states to ionization and neutralization events in the QD. It is proposed that a neutral QD can absorb and emit photons normally, thus it is in the on state. A charged QD, on the other hand, can still absorb photons but the emission is quenched by rapid relaxation due to energy transfer to the free charge carrier in the ionized dot.
The first proposed ionization mechanism was a photoassisted Auger process. However, such a process predicts a two-photon dependence on excitation intensity never observed in the experiments and cannot explain the power-law statistics. Although charging and blinking could not be measured simultaneously on a single QD, the ionization mechanism received strong support from the observation that colloidal QDs ionize thermally and induced by light. Furthermore, the emission of QDs presents spectral shifts consistent with a Stark shift produced by one-electron charge in the vicinity of the QDs which follow the same power-law dynamics as the emission blinking. As an alternative to the photoassisted Auger ionization, Kuno et al. proposed a tunneling ionization model which has two important implications. First, fluctuating tunneling barriers have to be introduced to account for the power-law probabilities. Second, electron tunneling to/from external states at a distance of ~2 nm away from the QD is necessary to explain the observed blinking time scale. Thus this model predicts an influence of the environment. In particular for QDs on a surface, those external states should be in the substrate. Reported experimental results are not conclusive on this respect; e.g., for CdSe/ZnS core/shell QDs, Hohng and Ha found a strong suppression of the blinking in the presence of thiols, whereas Pelton et al. reported no measurable difference on the blinking behavior of QDs on glass and dissolved in chloroform.

Based on studies at different temperatures and excitation fluxes, Shimizu et al. postulated that two different processes are behind the blinking, one being responsible for the power-law distributed blinking and another for the limitation of on-times to a maximum value. Recently, Chung and Bawendi presented a model for these two processes very similar to the one used in our investigations. In this paper, we show that such a two-process model describes quantitatively the photoluminescence blinking of colloidal QDs by means of a minimal set of parameters. We obtain accurate values for those characteristic parameters by comparing experimental results and simulations, thus avoiding artifacts introduced by the time-binning analysis which otherwise provides misleading results. To find out which process is light induced, different excitation intensities are employed. In order to investigate the influence of the environment in the context of an ionization mechanism, the emission of QDs was studied on insulating (glass) and (conducting) ITO-coated glass substrates.

II. EXPERIMENTAL

Monocrystalline, Zn$_{0.32}$Cd$_{0.68}$Se QDs with an average diameter of 6.2 nm were prepared as described in Ref. 22, presenting an ensemble band-edge absorption peaking at 515 nm and an ensemble emission maximum at 545 nm. They were diluted in toluene (99.7%, Riedel-de Haën) and spin-casted onto glass (N1, Menzel-Glaser) or indium-tin-oxide- (ITO-)coated glass substrates (50 nm, Fraunhofer-Institut IST, Braunschweig). The concentration was adjusted to a surface density of approximately one QD per µm$^2$. The QDs were investigated through the glass slides on a homemade sample scanning confocal microscope, under continuous flow of nitrogen. A region of the samples was imaged, a single QD was moved in the focus and the photoluminescence emission was recorded as a function of time. Circularly polarized light (Ar-ion laser, CW, coherent, λ = 514.5 nm) was used to excite the QDs through a 1.4 NA oil-immersion objective. Photons emitted by the QDs were collected by the same objective, separated from the excitation light by suitable dichroic and notch filters and their arrival times were recorded by a single photon counting system (avalanche photo diode Perkin-Elmer SPCM-AQR-13 +TCSPC module Becker&Hickl SPC-630).

III. MODEL AND SIMULATIONS

Simulations were performed to generate photon-arrival times in the same fashion as the experiments so that the evaluation could be equally performed with both experimental and simulated data sets. This avoids artifacts which have been noticed to be introduced by the time-binning...
analysis and allows one to quantify the errors introduced by those artifacts.

The simulations are based on a phenomenological model inspired by the work of Shimizu et al. and the statistics behind is basically the same of a model developed independently by Chung and Bawendi. The model accounts for the experimental observations by means of two independent switching processes. One process gives rise to the power-law distributed blinking process and an additional single-rate (exponentially distributed) transition from the on-state to the off-state is responsible for the deviations of \( P(t_{\text{on}}) \) from the power law.

The residence times in each state are calculated as follows. First, the power-law (PL) distributed blinking process have probabilities \( P_{\text{PL}}(t_{\text{on}}) \) and \( P_{\text{PL}}(t_{\text{off}}) \) given by

\[
P_{\text{PL}}(t_{\text{on}}) = \frac{m - 1}{t_{\text{min, on}}} t_{j}^{m}, \quad t_{\text{min, on}} < t_{j} < \infty.
\]

with \( m \) between 1 and 2. The same \( m \) was used for \( P_{\text{PL}}(t_{\text{on}}) \) and \( P_{\text{PL}}(t_{\text{off}}) \) because both show identical power-law behavior at low excitation intensities. In order to make the power laws normalizable, it is necessary to restrict their domains by means of minimum times \( t_{\text{min, off}} \) and \( t_{\text{min, on}} \).

Second, the additional pathway from the on to the off state is included to account for the photoinduced (PI) deviations of \( P(t_{\text{on}}) \) from the power law. This transition is assumed to be exponentially distributed with a characteristic time \( \tau_{\text{PI}} \):

\[
P_{\text{PI}}(t_{\text{on}}) = \frac{1}{\tau_{\text{PI}}} e^{-t_{\text{on}}/\tau_{\text{PI}}}.
\]

From Eqs. (1) and (2), the times that the simulated QD spends in the off- and on-state are calculated as

\[
t_{\text{off}} = t_{\text{min, off}} R_{\text{dn}}^{1/(1-m)},
\]

\[
t_{\text{on}} = \min\left[t_{\text{min, on}} R_{\text{dn}}^{1/(1-m)} - \tau_{\text{PI}} \ln(R_{\text{dn}})\right],
\]

where \( \min[a, b] \) selects the earlier event by taking the minimum of \( a \) and \( b \) and \( R_{\text{dn}} \in (0,1) \) is a random number. It is important to note that although it is not possible to assign an average \( t_{\text{on}} \) because of the power-law distribution (which normalization depends on the arbitrary \( t_{\text{min, on}} \)), the exponentially distributed pathway has a well defined \( \tau_{\text{PI}} \). In contrast to Chung and Bawendi, we do not incorporate in the model a single-rate transition from the off to the on state. Nonetheless, practically, both models are equivalent for the analysis of single QD data because the lifetime of such a transition that fits the experimental results greatly exceeds the off-times observed in our experiments.

Photon arrival times are assigned to the off and on periods in the following way. First, background photon detection times are calculated throughout the total simulated time \( T \). They are separated by exponentially distributed times \( t_{\text{hr, off}} \) calculated from the average background intensity \( I_{\text{on}} \) as

\[
t_{\text{hr, off}} = \frac{1}{I_{\text{off}}} \ln(R_{\text{dn}}).
\]

Within the on periods, extra photons are added with detection times separated by \( t_{\text{hr, on}} \) calculated by replacing \( t_{\text{off}} \) by \( t_{\text{on}} \), the fluorescence intensity emitted by the dot, in Eq. (5).

IV. DETERMINATION OF THE BLINKING PARAMETERS

The simulations are based on seven parameters: the total observation time \( T \), the background and fluorescence intensities \( I_{\text{off}} \) and \( I_{\text{on}} \), the exponent of the power laws \( m \), the minimum times \( t_{\text{min, off}} \) and \( t_{\text{min, on}} \), and the characteristic time of the photoinduced on-off transition \( \tau_{\text{PI}} \). All seven parameters were determined by comparing simulated and experimental data sets as explained in detail below.

The first parameter to be fixed is the total simulation time \( T \) which is trivially done by considering equal observation times for experiments and simulations. This is of fundamental importance because the observed behavior may depend on the observation time due to statistical aging induced by the power-law distribution of \( t_{\text{on}} \) and \( t_{\text{off}} \).

The experimental and simulated time traces of fluorescence intermittence were analyzed by computing histograms of the photon-arrival times and placing a suitable threshold in order to classify the bins as on or off which in turn allows the determination of the apparent on- and off periods. Then, in order to obtain an experimental measure of the distribution of on and off times, histograms of the detected on and off times were computed [see Fig. 1(c)].

From the time-binning analysis, one can obtain measures of \( I_{\text{on}}, I_{\text{off}} \) and \( m \) whose values may differ from the real ones due to the limited time resolution of the analysis. This is directly observed by analyzing simulated data for which the real values of the parameters are known. In the following, values of the parameters obtained from the histogram analysis are denoted with the subindex \( h \). In order to obtain accurate values of \( (I_{\text{on}}, I_{\text{off}}, m) \), we applied the strategy of searching for a set of \( (I_{\text{on}}, I_{\text{off}}, m) \) that yielded in the simulations values of \( (I_{\text{on}, h}, I_{\text{off}, h}, m_{h}) \) identical to the ones obtained in the experiments. Apparent background and fluorescence intensities \( I_{\text{on}, h} \) and \( I_{\text{off}, h} \) are obtained from the histogram of the photon arrival times as

\[
I_{\text{off}, h} = \frac{N_{\text{off}, h}}{T_{\text{off, h}}}, \quad I_{\text{on}, h} = \frac{N_{\text{on}, h}}{T_{\text{on, h}}} - I_{\text{off}, h},
\]

where \( T_{\text{off, h}}(T_{\text{on, h}}) \) and \( N_{\text{off, h}}(N_{\text{on, h}}) \) are the total time and number of photons, respectively, corresponding to the off state (on state) as extracted from the histogram. From the analysis of simulated data, it is found that due to bins containing a fraction of a \( t_{\text{on}} \) or several \( t_{\text{on}} \) shorter than the bin width, \( I_{\text{on}, h} \) is systematically slightly smaller than the true \( I_{\text{on}} \) used in the simulation; a similar mechanism leads to an \( I_{\text{off}, h} \) slightly higher than \( I_{\text{off}} \). Values of \( I_{\text{off}} \) and \( I_{\text{on}} \) for the experimental data were obtained as follows. The \( I_{\text{off}, h} \) and \( I_{\text{on}, h} \) as obtained from the experimental data were used as starting values of \( I_{\text{off}} \) and \( I_{\text{on}} \) for an iteration where simulations were...
run until the simulated data reproduced the experimental 
$I_{\text{off}}$ and $I_{\text{on}}$.

In order to determine $m$, histograms of the $t_{\text{on}}$ and $t_{\text{off}}$ were computed. Figure 2 shows histograms computed from the $t_{\text{on}}$ and $t_{\text{off}}$ detected in $T$ seconds of the emission of several (~15) experimental and simulated QDs on glass and ITO substrates under three excitation intensities $I$. Investigations were carried out on both substrates at six different excitation intensities; Fig. 2 shows only the results at three intensities as an example. The probability of a $t_{\text{off}}$ shows in all cases a clear power-law spanning more than 4 decades in time and 6 decades in probability density. In agreement with reported results, the probability of a $t_{\text{on}}$ is observed to deviate gradually from a pure power law at longer times. This effect is interpreted in terms of the photoinduced switching as is discussed in detail below. On a qualitative level, direct inspection of the raw data in Fig. 2 shows that the maximum observed $t_{\text{on}}$ decreases as the higher excitation power increases. This deviation of the on-times distribution from the power-law leaves the off-time distribution as the most suitable for the analysis of the power-law exponent $m$. A power law was fitted to the experimental $t_{\text{off}}$ histogram in order to obtain the exponent $m_{t_{\text{off}}}$, which is shown in the legends of the corresponding graphs. Again, the fit as straightforward evaluation routine of the simulated data does not recover values of $m_{t_{\text{off}}}$ matching perfectly the input parameter $m$ for the simulation. Instead, the values of $m_{t_{\text{off}}}$ that are found suggest a tendency to larger values as $I$ decreases which is an artifact of the data analysis. The best agreement between simulated and measured $m_{t_{\text{off}}}$ is found by keeping $m$ practically constant in the simulations. The experimental results for the QDs on glass and ITO and for all excitation intensities were reproduced with $1.72 \leq m \leq 1.74$, both for the on- and off-time distributions. This value is in excellent agreement with recently reported measurements of $m$ based on a careful analysis of the blinking of QDs on glass and chloroform by means of its power spectrum.

Two additional quantities which can be extracted from the histogram analysis were used to further characterize the blinking and fix parameters of the model. First, the apparent frequency with which a QD jumps between on and off (cycles per second) and secondly, the apparent fraction of time that the QDs spend in the on-state (on-time fraction). Figure 3(a) shows the on-time fraction and Fig. 3(b) the number of cycles per second for the QDs on glass and ITO as a function of the excitation intensity.
The influence of an arbitrary $t_{\text{min},j}$ was tested by varying it from $10^{-6}$ to 1 ms. In general, a smaller $t_{\text{min},j}$ produces shorter on- and off-times with higher probability and a consequently higher number of on/off cycles per second. Several kinetic traces were simulated with different values of $t_{\text{min},j}$ (and all the other input parameters fixed) and then analyzed. No changes in the detected number of cycles per second were noticed for $t_{\text{min},j}$ below $10^{-4}$ ms. The reason is that as $t_{\text{min},j}$ becomes smaller, the generated shorter on and off times become undetectable and their influence vanishes. In this regime, only the ratio of the two minimum times, which determines the relative strength of the on and off switching, is of relevance. Chung and Bawendi\textsuperscript{13} assumed $t_{\text{min,on}}/t_{\text{min,off}}=1$ in their simulations and found good agreement with the experiments. We found two experimental facts at the lowest excitation intensities, where the photoinduced effects are small and almost pure power-law blinking is observed, that strongly support this assumption. First, the power-law distributions of on and off times are practically identical (Fig. 2). Second, the QDs spend approximately 50\% of the time in the on state (Fig. 3). Thus, Both $t_{\text{min,off}}$ and $t_{\text{min,on}}$ were set to $10^{-2}$ ms in all simulations.

$I_{\text{on}}$ and $I_{\text{off}}$ were determined for each data set obtained at a different excitation intensity and substrate. $m$, $t_{\text{min,on}}$, and $t_{\text{min,off}}$ were held constant in all simulations. Therefore, $\tau_{\text{pt}}$ was the only parameter left free that could introduce a difference between the on- and off-time distributions. $\tau_{\text{pt}}$ was varied systematically in order to reproduce the experimental results by searching the optimum agreement between the simulated and experimental maximum observed $I_{\text{on}}$.

As can be seen in Fig. 2, the simulations reproduce with high accuracy not only the maximum detected $I_{\text{on}}$ but also the experimental $P(I_{\text{on}})$ and $P(I_{\text{off}})$ for the QDs on glass and ITO. The probability of a certain $I_{\text{on}}$ shows for short times the same power-law behavior as $I_{\text{off}}$, but for long times, it deviates gradually to lower values to reach some maximum $I_{\text{on}}$. As the excitation intensity increases, the deviation from the power law is larger and the maximum $I_{\text{on}}$ shorter. The simulations reproduce well this gradual deviation from the power law which arises from the common computation of several individual traces. Instead, in agreement with reported results,\textsuperscript{5,13} the individual traces appear simply truncated at a maximum $I_{\text{on}}$, both in experiment and in our simulation.

The presence of the photoinduced off switching has additional consequences in the blinking statistics. Since a shorter $\tau_{\text{pt}}$ makes long on-times less probable, the QDs cycle more frequently between the on and off state (i.e., higher number of on/off cycles per second) and spend less time in the on state (i.e., smaller on-time fraction). Figure 3 shows the excellent agreement between experimental and simulated cycles per second and on-time fraction of the QDs on glass and ITO for the 6 excitation intensities studied.

Then, for each substrate and excitation intensity, a single value of $\tau_{\text{pt}}$ accounts simultaneously for three effects: the maximum detected on-time, the on-time fraction and the number of cycles per second. The shape of the gradual deviation of $P(I_{\text{on}})$ from the power law could be considered as a fourth experimental measure that is also accounted for by $\tau_{\text{pt}}$.

FIG. 4. Photoinduced lifetime of the on-state ($\tau_{\text{pt}}$) used to reproduce the glass and ITO experimental data as a function of excitation power $I$ in log-linear and log-log scales.

V. DISCUSSION

Contrary to the proposed light-induced mechanisms,\textsuperscript{8,19} our results show that the power-law distributed blinking can be described in terms of a process completely independent of excitation intensity. Furthermore, this power-law blinking is found to be independent of substrate material. This leads to the conclusion that the distribution of electronic states in the surroundings of the QD does not play an important role, therefore an electron tunneling mechanism involving states external to the QD necessarily $\sim 2$ nm away,\textsuperscript{4,19} seems highly improbable. Although we were not able to test other reported results, visual inspection of published data indicates that the same power-law blinking is observed in colloidal QDs of all kinds (i.e., capped, uncapped and of different compositions) and in different environments.\textsuperscript{4–6,21} All of this points toward an underlying process occurring spontaneously (not photoinduced) and inside the dot or immediately at its surface.

Another remarkable characteristic of the spontaneous power-law blinking is the symmetry, reflected in the facts that both $P(I_{\text{on}})$ and $P(I_{\text{off}})$ have the same exponent $m$ and that the on- and off-switching processes are equally probable ($t_{\text{min,on}}/t_{\text{min,off}}=1$) as is directly evident from the observation that at very low intensities the QDs spend half the time on and half off. We find this hard to understand in terms of a simple ionization model that involves a neutral on and a charged off state which lacks such a physical symmetry. We
believe that further experimental and theoretical efforts are necessary to obtain a physical model consistent with all experimental observations, including the reported results implying that charges are involved in the blinking\textsuperscript{18,24,25} and the ones that show that photo-ionization of QDs is strongly dependent on substrate properties.\textsuperscript{26} It may be worth considering alternative processes which provide the required symmetry such as statistics of two independent spins.

The additional transition from the on to the off state is found to be not only photoinduced but also substrate dependent. The existence of the assumed transition is strongly supported by the fact that it can account simultaneously and quantitatively for three different photoinduced effects. Figure 4 shows the $I$ dependence of its characteristic time $\tau_{PI}$ for the two substrates investigated. The behavior of $\tau_{PI,\text{glass}}(I)$ can be described by a power law with exponent $-1$, suggesting the presence of a (pseudo)one-photon photoinduced process responsible for the shortening of the on times. This confirms, on a sound data treatment, a trend suggested by previous studies on other QDs in insulating environments\textsuperscript{8,11} This further supports both the validity of our results and of our model. A for a given $I$, $\tau_{PI,\text{ITO}}$ takes larger values than $\tau_{PI,\text{glass}}$ and its behavior as a function of $I$ can be well represented by a single exponential. This indicates that a different mechanism is ruling the photoinduced shortening of the on-times on the conducting substrate.

VI. SUMMARY

In summary, a phenomenological model was applied to quantitatively characterize the photoluminescence blinking of colloidal QDs on (insulating) glass and (conducting) ITO substrates. Data analysis artifacts were avoided by equally analyzing simulated and experimental data sets, thus allowing for an accurate determination of characteristic parameters of the blinking. The photoluminescence blinking can be well described by two processes: one power-law distributed on/off switching and a single-rate transition from the on to the off state. The power-law component of the blinking is found to have equally strong on- and off-switching pathways, and seems independent of the excitation intensity and the surrounding medium (electronic states of the substrate). This suggests the presence of a symmetric spontaneous process happening inside the QD or immediately at its surface. The single-rate on-off transition, which is fully described by its lifetime $\tau_{PI}$ can account for all the observed substrate and photoinduced effects. For a given excitation intensity and substrate, a single value of $\tau_{PI}$ can simultaneously account for the observed on-time fraction, cycles per second and the maximum $t_{on}$. Completely different behaviors of $\tau_{PI}$ as a function of the excitation intensity are found for QDs on glass and on ITO substrates. The behavior of $\tau_{PI}$ on glass, in agreement with previous studies on insulating matrices,\textsuperscript{8,11} can be understood in terms of a one-photon process. On ITO, an exponential dependence on the excitation intensity indicates the presence of a different process. We believe it would be very interesting to further apply this two-processes evaluation to data obtained under different experimental conditions (such as temperature and surrounding medium) and/or to existing data indicating environmental effects,\textsuperscript{20,27–29} because it might provide important insight into the intriguing problem of the photoluminescence blinking of colloidal QDs.

ACKNOWLEDGMENTS

This work was supported by the Bundesministerium für Bildung und Forschung (Grant No. 03N8702).