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Short-time power-law blinking statistics of single quantum dots and a test of the diffusion-controlled electron transfer model

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In this work we analyzed the blinking statistics data of single CdSe/ZnS quantum dots at vey short times to test some predictions of the diffusion-controlled electron transfer (DCET) model. Using autocorrelation function (ACF) approach we could extract the exponent of the inverse power-law blinking statistics down to 1 μs. Such an approach also minimizes human subjectivity in choosing a bin time and an on-off threshold. We showed that the observed stretched exponential decay in the ACF and its relationship to the blinking statistics are consistent with the DCET model, and we set an upper bound for the characteristic time constant t_c. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3205406]

I. INTRODUCTION

Single-molecule or single-particle techniques allow researchers to investigate events of an individual nanosize structure[1–4] so that some problems in ensemble measurements due to heterogeneous distribution could be overcome. One of the commonly seen phenomena in these experiments is fluorescence intermittency in quantum dots (QDs),[5–15] nanorods,[16] and organic chromophores.[17–19] Each single nanoparticle or molecule under continuous light illumination displays a fluorescence intensity histogram showing randomly distributed light and dark periods. The waiting time distribution for either "on" or "off" events often follows an inverse power law. Several models[6,7,20–23] have been proposed to explain such a phenomenon, but some details of the mechanisms remain not fully understood and await further experimental tests. In most power-law blinking studies, the analysis requires a choice of a bin time (usually 10–100 ms) and an on-off threshold. Such a practice is often prone to artifacts. Due to low photon counts for a shorter bin time, the histogram (fluorescence time trajectory) appears to be nonbinary and noisy; also, the choice of an on-off threshold is very subjective. Therefore, short-time behavior of the blinking statistics well below 1 ms is seldom seen in reports. In this letter we report an alternative to circumvent these difficulties, that is, using fluorescence intensity autocorrelation function (ACF) measurements. Such an approach allows us to observe the inverse power law from 10 ms down to 1 μs and to extract its power-law exponent. In addition, the observed ACF could be fitted nicely by a stretched exponential decay, covering seven decades in time. The stretched exponential decay of the ACF and its relationship to the blinking statistics could be used as a test of the diffusion-controlled electron transfer (DCET) model proposed by Tang and Marcus.[22] Moreover, we report here an upper bound for the characteristic time constant t_c which is a crucial parameter in the DCET model. Our value appears to be much shorter than the estimate by others.[23]

II. MODEL PREDICTIONS BASED ON DCET

In the following, we describe the relationship between ACF $G(t)$ and the blinking statistics $P(t)$. We also show the relationship for the exponent extracted from $G(t)$ and the exponent m of the inverse power law for $P(t)$. According to the DCET model, blinking is caused by charge transfer between a photoexcited light state and a dark state due to diffusion-controlled reactions involving a potential $U_1(Q)$ and $U_2(Q)$ coupled with electronic coupling V_{12}. The blinking statistics $P(t)$ is given by[22]

$$P(t) \sim t^{-\beta/2} \quad \text{if } t < t_c$$
$$P(t) \sim t^{-2+\beta/2} \exp(-\Gamma t) \quad \text{if } t > t_c, \tag{1}$$

where t_c is a time constant depending on diffusion correlation time and the electronic coupling. This characteristic time constant separates the short- and long-time regimes, which have a different power-law exponent. For normal diffusion, $\beta=1$, and otherwise for anomalous diffusion. According to the work of Tang and Marcus,[24] the Laplace transform of the normalized ACF $G(t)$ is given by

$$\bar{G}(s) = \frac{1}{s}\left[1 - \frac{\gamma_1}{s(1+\bar{g}_1(s)+\bar{g}_2(s))}\right], \tag{2}$$

where γ_1 is the nonadiabatic ET rate and $\bar{g}_k(s) \approx ((s+\Gamma_k)t_c)^{\beta_k/2-1}$ which is related to the Green function in the light and dark states ($k=1$ and 2, respectively). A similar expression or ACF in terms of the blinking statistics $\bar{P}_k(s)$ was obtained independently by Margolin and Barkai.[21] The inverse Laplace transform of Eq. (2) cannot be obtained in a closed form, but we could use a stretched exponential as an empirical approximation,[24]

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$$G(t) \propto \exp[-(t/\tau)^{\beta/2}], \tag{3}$$

where $\beta/2$ is the exponent of the stretched exponential decay. The time constant τ is related to γ_1 and t_c, and its actual value needs to be determined empirically. Defining $F(t)$ as $G(t)/G(0)-1$ one obtains from Eq. (2)

$$\bar{F}(s) = \frac{\gamma_1}{s^2(1+\bar{g}_1(s)+\bar{g}_2(s))}, \tag{4}$$

from which one obtains two simple asymptotes,

$$\begin{aligned} F(t) &\sim t^2 \quad \text{if } t < t_c, \\ F(t) &\sim t^{\beta/2} \quad \text{if } t > t_c. \end{aligned} \tag{5}$$

III. EXPERIMENTS, DATA ANALYSIS, AND DISCUSSION

In the following we describe the experimental conditions for the measurements. We prepared a very dilute concentration of CdSe/ZnS QDs (emission at 600 nm, ~5 nm in size, purchased from Invitrogen). With supersonic agitation, the nanoparticles were dispersed very well in the solution and then directly spin casted onto a clean glass slide. Single QD fluorescence was measured using a time-resolved single molecule confocal microscope (MT200, PicoQuant). Time-correlated single photon counting unit (PicoHarp 300H) was used for the data acquisition. The software SYMPHOTIME of MT200 was used for the equipment operation and data analysis. Time-tagged time-resolved mode was also used for investigation of fast dynamics. The fluorescence from the sample was collected through the oil-immersion objective (Olympus). A picosecond diode laser was used as a light source with an excitation wavelength of 467 nm and a repetition rate of 10 MHz. All samples were measured at room temperature in air. A typical fluorescence intensity histogram is shown in Fig. 1(a) to illustrate blinking behavior. A threshold of about 1/3 of the highest peak was used. The photon count or intensity distribution per bin after averaging over 15 QDs is shown in Fig. 1(b) to illustrate two distinctive bumps representing the on events and the off events. The measured blinking statistics $P(t)$ of single QDs for on time and off time is illustrated in Fig. 2. An average over 20 QDs was done at a light intensity of about 190 W/cm^2 using a bin time of 1 ms. Averaging over many QDs is necessary to improve signal to noise (S/N) ratio due to low occurrence probability at longer times. The data were plotted in a log-log scale and were fitted using $t^{-m}\exp(-\Gamma t)$ from Eq. (1), where m represents the exponent and Γ the bending rate. For normal diffusion $m=3/2$ but could take other values for anomalous diffusion.[22] The error bar for m for the fit was determined by the nonlinear curve fitting routine from graphic software ORIGIN. As illustrated in Fig. 2, the exponent m of the inverse power law appears to vary with the threshold, yielding an m from 1.57 to 1.45. Moreover, if one changes the bin time, the exponent m also changes. As illustrated in Fig. 3, m changes from 1.41 to 1.54 if one reduces the bin time from 10 to 1 ms. Such variations in the exponent m illustrate the inconsistency often seen in literature reported by various groups due

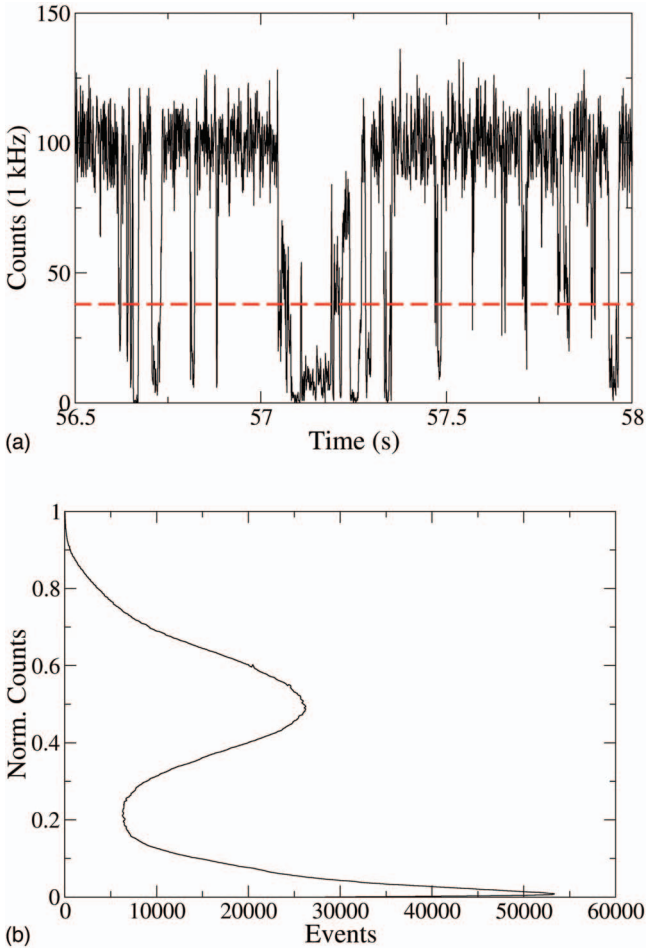

FIG. 1. (a) A typical fluorescence intensity histogram of a specific single QD with bin time of 1 ms. The red dashed line represents a threshold of about 120. (b) The distribution of fluorescence intensity (averaged over 15 QDs) per bin showing two bumps, corresponding to the on events and the off events, respectively.

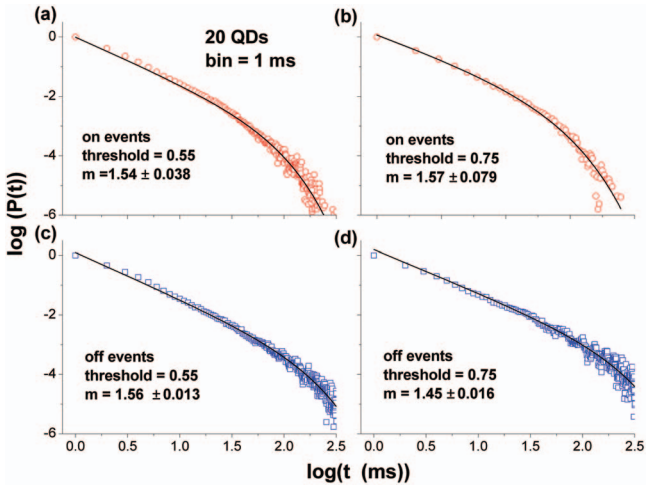

FIG. 2. [(a) and (b)] The on-time blinking statistics $P(t)$, showing an inverse power-law decay with exponents $m=1.54\pm0.04$ and 1.57 ± 0.08 at threshold levels of 0.55 and 0.75, respectively. [(c) and (d)] The off-time blinking statistics $P(t)$ showing $m=1.56\pm0.01$ and 1.45 ± 0.02 at threshold levels of 0.55 and 0.75, respectively. An average over 20 QDs at intensity about 190 W/cm^2 using a bin time of 1 ms was made. The fits were obtained using Eq. (1).

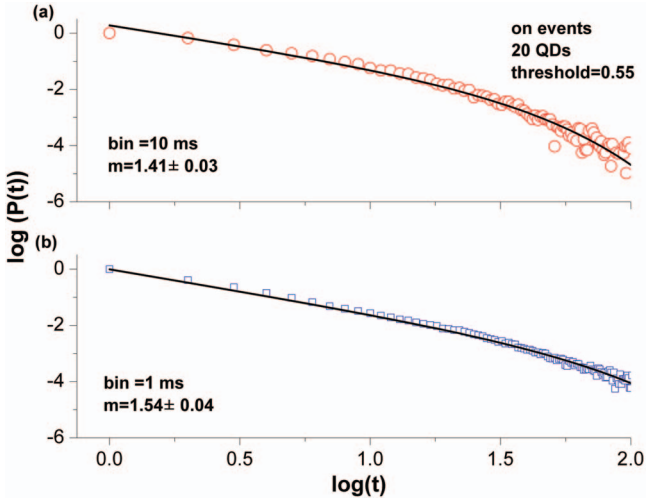

FIG. 3. [(a) and (b)] The on-time blinking statistics $P(t)$ using a different bin time but the same threshold level of 0.55. The curves show an inverse power-law decay with exponents $m=1.54\pm0.04$ and 1.41 ± 0.03 for bin times of 10 and 1 ms, respectively.

to sample variations as well as human subjectivity in choosing the threshold level and the bin time.

As an alternative less prone to subjectivity, we have measured ACF $G(t)$ and calculated $F(t)$, or $G(t)/G(0)-1$. As displayed in Fig. 4, $F(t)$ shows a simple power-law rise as predicted by Eq. (5), which allows us to determine that $\beta/2=0.37\pm0.01$. The ACF data were averaged over 15 QDs at 570 W/cm^2. Because $F(t)$, or $G(t)/G(0)-1$, is very small at short times, great care need to be taken to determine $G(0)$. To improve the S/N ratio at short times, averaging $F(t)$ over 15 QDs was taken instead of using only one specific QD. Such a practice of averaging over many QDs was often used by researchers in computing the blinking statistics $P(t)$ from the histograms. Using Eq. (3), a stretched exponential decay, to fit the experimental $G(t)$ in Fig. 5(a), we obtained $\beta/2=0.37\pm0.01$. The relationship of $m=2-\beta/2$ from Eq. (1)

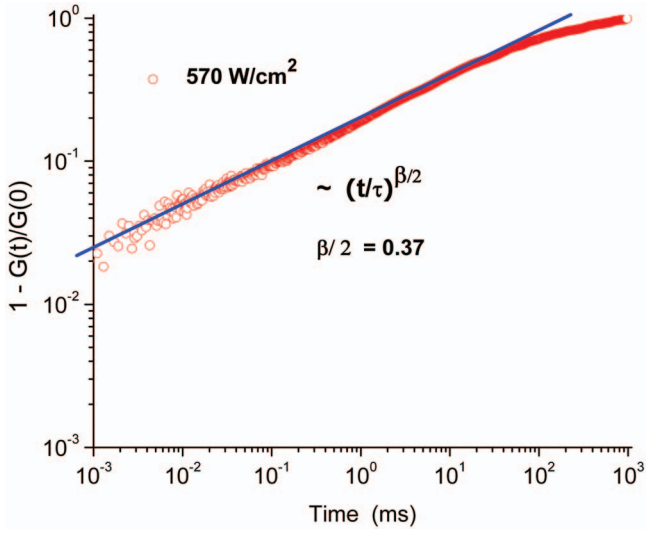

FIG. 4. Experimental curve of $F(t)$, or $G(t)/G(0)-1$, vs time showing strikingly simple power-law dependence, with a fitted $\beta/2=0.37\pm0.01$, covering five decades of time from 1 μs to 100 ms. An average over 15 QDs at intensity about 570 W/cm^2 was made and $G(0)=1.02$ was estimated.

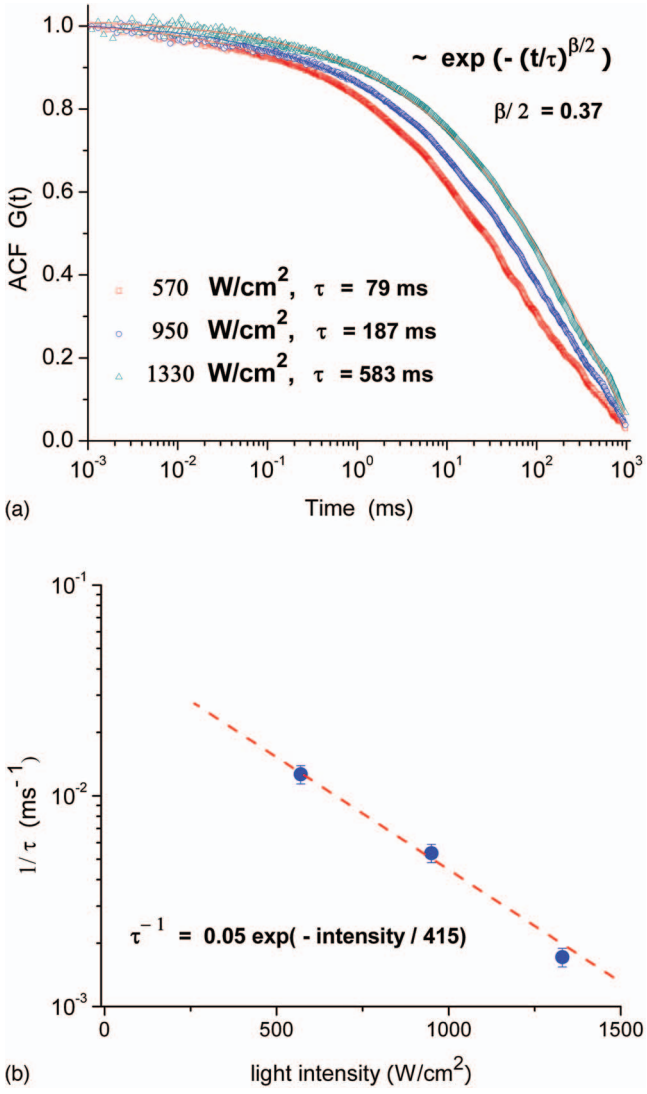

FIG. 5. (a) Semilog plots of the experimental ACF $G(t)$ and their fits at three light intensities. (b) Dependence of the fitted $1/\tau$ on light intensity showing the empirical fit of an exponential decrease as $1/\tau=0.05(\pm0.01)\times\exp(-\text{intensity}/415(\pm31))$. The exponent $\beta/2=0.37$ obtained in our earlier fit was held constant and the decay time constant τ in the stretched exponential function was allowed to vary during the fits.

with m determined from $P(t)$ and $\beta/2$ from $G(t)$, as predicted in the DCET model, is confirmed, given some inaccuracies in m due to subjective choices of a threshold value and a bin time. According to the DCET model for normal diffusion, at short times the exponent should be 2 for $F(t)$ [or $-\frac{1}{2}$ for the exponent in $P(t)$] but becomes $\frac{1}{2}$ for $F(t)$ [or $-\frac{3}{2}$ for the exponent in $P(t)$] at long times and then breaks off to a non-power-law tail for $F(t)$ [or $P(t)$]. Our experiments led us to set 1 μs as an upper bound for the cutoff characteristic time t_c in the DCET model. This value is much shorter than 10 ms estimated by others.[23] In Fig. 5(a), we have shown ACF curves for three light intensities. At smaller intensities the S/N ratio would be too low and at larger intensities photobleaching would occur. Using a stretched exponential decay fit of Eq. (3) we could extract the dependence of $1/\tau$ on light intensity. At higher light intensities, the spectral diffusion becomes faster and the effective diffusion correlation time becomes shorter. We expect from the DCET model $1/\tau$ to decrease as observed in Fig. 5(b).

Three new major findings were presented in this work: (1) Our approach using ACF measurements of single CdSe/ZnS QDs allows us to determine the exponent for the inverse power-law blinking statistics down to 1 μs, which has not been reported by others. This approach, less subject to artifacts, allows us to determine the shorter time behavior and complements the usual blinking statistics approach which provides longer time information. Although the ACF method was used previously by others,[10] we presented here a new analysis using the ACF data at very short time (1 μs) to extract the exponent of the inverse power-law blinking statistics. (2) Using the experimental data we established the relationship between the normalized ACF $G(t)$ and the blinking statistics $P(t)$ and confirmed the model predictions of the DCET model. This ACF approach to extract the power-law statistics avoids the need to choose a threshold and a long bin time, which are very subjective. Our measured $F(t)$, or $G(t)/G(0)-1$, displays a strikingly simple power-law growth with an exponent, $\beta/2$, close to 0.37 over five decades in time from 1 μs to 10 ms. According to the DCET model, the corresponding exponent m for the inverse power law $P(t)$ is related to β by $m=2-\beta/2=1.63$. This value is close to the exponent from the fits to $P(t)$ in Figs. 2 and 3, lying within the error bar and given the inaccuracies due to choice of the on-off threshold and bin time. The value $m=1.63$ indicates that a mild anomalous diffusion process in energy fluctuation is involved. For an ideal normal diffusion, $\beta/2=0.5$ and $m=1.5$. Moreover, the experimental ACF appears to follow a stretched exponential function of Eq. (3) nicely. According to Eq. (4), if the power-law behavior for the on times and off times are different, i.e., $\bar{g}_k(s)\approx((s+\Gamma_k)t_c)^{\beta_k/2-1}$ where $\beta_1 \neq \beta_2$, then the exponent for the growth in $F(t)$ could take an effective value between β_1 and β_2. (3) Another important finding of this work is that we did not observe a change in the exponent in the power-law growth in $F(t)$ down to 1 μs. Therefore, the characteristic time constant t_c has to be very small (<1 μs). If t_c were greater than 1 μs, we should have seen in Fig. 4 a bending with an initial slope of about 2 and then a slope of about 0.37. However, we did not observe such kind of changes. Moreover, we have not seen a sudden slope change in $P(t)$ in Fig. 2 or Fig. 3 for t from 1 ms up to 300 ms. Therefore, further independent studies could resolve such an issue about the previous estimate of t_c of 10 ms by others.

IV. CONCLUSIONS

In conclusion, we investigated blinking statistics of single CdSe/ZnS QDs down to 1 μs to test some predictions by the DCET model. We demonstrated the use of ACF for the fluorescence intensity to extract the exponent of the inverse power-law blinking statistics. Such an approach allowed us to investigate the short-time behavior and to minimize human subjectivity in choosing a bin time and an on-off threshold. Although in a previous study by others the characteristic time constant t_c of about 10 ms was reported, our results indicated a much smaller value likely to be shorter than 1 μs. Not seeing the regime of $t^{-1/2}$ is not a disproof of the DCET model. Actually, the observed dependence of the nanoparticle size and light intensity on the bending rate Γ reported previously[25] is in agreement with the DCET model. Here we also showed that the observed stretched exponential decay in the ACF and its relationship to the blinking statistics are consistent with the DCET model.

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