Size Effects and Breakdown of the Power-Law Blinking Statistics of CdSe Nanorods†

Jau Tang*

Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan, and Physical Biology Center of Ultrafast Science and Technology, California Institute of Technology, Pasadena, California 91125

Received: May 3, 2007; In Final Form: July 27, 2007

In this study, the dependence of sample size and light intensity on the fluorescence intermittency of semiconductor nanorods is investigated. We present a model with diffusion-controlled electron-transfer reactions involving anomalous diffusion in energy configuration space. This model leads to a general formula t^{-m} $\exp[-(\Gamma t)^n]$ for the temporal behavior of blinking statistics, where m and n are related to the time dependence of the spectral diffusion. We reanalyze the experimental data of the long-time bending tail of CdSe nanorods and elucidate the size effects of the bending rates and activation energy.

Introduction

Developments in nanofabrication of low-dimension materials such as quantum dots (QDs), nanorods (NRs), and nanotubes have generated much interest in scientific research.[1,2] Intensive experimental studies have been made to explore the photophysical properties, such as band-edge exciton states[3−5] and fluorescence intermittency (or blinking) of single QDs[6−14] and NRs.[15] Blinking in single QDs or NRs under continual light illumination occurs due to transitions between a dark state and a light state, involving electron-transfer reactions. Unlike the conventional studies of the electron-transfer (ET) processes of an ensemble system where the fluorescence decay is often characterized by a single-exponential decay, the probability distribution of the waiting time for either "on" or "off" events, or so-called blinking statistics, in single-particle or single-molecule experiments often follows nonexponential decay. The dark state is believed to represent a hole residing in the core of a QD, whereas the electron is probably trapped in surface states. A QD in the charged separated state that appears dark is likely due to rapid Auger relaxation process; however, the light state represents exciton states that decay to the ground state by emitting a photon. If the transition rate between the dark and light states were a constant in time, then the blinking statistics would have followed a single-exponential decay. However, in most single-QD experiments, the blinking statistics is found to be nonexponential.[6−16]

Since the early work by Wang and Wolynes,[17] considerable theoretical understanding of blinking phenomena has been advanced. Supplementing other theoretical efforts to improve physical insight into the power-law blinking phenomena,[7,13,18−21] we present here an improved model to explain the cause of the breakdown of the poser law and the long bending tails observed in experiments recently.[16] In this study, we investigate the temporal behavior of blinking statistics for CdSe NRs and the size dependence of the bending rate. On the basis of this improved model involving diffusion-controlled reactions with anomalous diffusion, we derive a general formula that prescribes a short-time power law and a crossover to a stretched exponential decay at later times. We will use the blinking data of CdSe nanorods (NRs)[16] as an example to demonstrate interesting temporal behavior and show that the data are consistent with our model predictions. In addition, the blinking statistics of NRs of various sizes and light intensities will be analyzed to extract useful physical quantities not reported previously.

Diffusion-Controlled Electron Transfer Involving Anomalous Diffusion. Here we extend the diffusion-controlled electron-transfer (DCET) model[20,21] using a more-general anomalous diffusion. As suggested by experimental observation, there is a strong correlation between blinking and spectral diffusion as manifested by energy fluctuation for the light and dark states. We consider the following anomalous diffusion involving the reactions coordinate Q in an energy configuration space

$$\frac{\partial}{\partial t} G(Q, Q'; t) = \frac{\partial}{\partial Q}\left(D_2(t) \frac{\partial}{\partial Q} + D_1(t)\, Q\right) G(Q, Q'; t) \quad (1)$$

The Green function below can be shown to satisfy eq 1

$$G(Q, Q'; t) = \frac{1}{\sqrt{2\pi\Delta_2(t)}} \exp\left[-\frac{(Q - Q'\Delta_1(t))^2}{2\Delta_2(t)}\right] \quad (2)$$

with time-dependent drift and diffusion coefficients as

$$D_1(t) = -\frac{\mathrm{d}}{\mathrm{d}t} \ln\langle Q(t)\rangle$$

$$D_2(t) = D_1(t)\, \Delta_2(t) + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\Delta_2(t) \quad (3)$$

The above diffusion equation and the Green function are more general than the one used earlier in the DCET model,[20,21] but the Laplace transform of $P(t)$ is still related to the Green function at the sink Q_c

$$\bar{P}(s) = \frac{A\bar{G}(Q_c, Q_c; s)}{1 + A\bar{G}(Q_c, Q_c; s)} \quad (4)$$

where A is proportional to the electronic coupling for the charge transfer.

If $Q(t)$ represents an Ornstein−Ulenbeck process[21] that occurs in a Debye medium, then one has the second moment $\Delta(t) \equiv$ $<(Q(t) - <Q(t)>)^2>$ or $D\tau_c\lfloor 1 - \exp(-2t/\tau_c)\rfloor \propto t$ and the

† Part of the "Sheng Hsien Lin Festschrift".

* E-mail: jautang@gate.sinica.edu.tw.

10.1021/jp073384p CCC: $37.00
Published on Web 08/24/2007

first moment $<Q(t)> - <Q(0)> = <Q(0)> [\exp(-t/\tau_c) - 1] \propto t$. The blinking statistics $P_{on}(t)$ for the on events or $P_{off}(t)$ for the off events is shown to follow an inverse power-law statistics with an exponent $^3/_2$ and a long-time exponential tail as[20]

$$P_k(t) \propto t^{-3/2} \exp[-\Gamma_k t]$$

$$\Gamma_k \tau_k = E_{A,k}/2k_B T \qquad (5)$$

Γ_k is the bending rate for the tail, τ_k *is* the diffusion correlation time, $E_{A,on} = (\lambda + \Delta G^0)^2/4\lambda$ is the activation energy for forward ET and $E_{A,off} = (\lambda - \Delta G^0)^2/4\lambda$ for reverse ET, ΔG^0 is the free-energy gap, and λ is the reorganization energy.

We consider here a non-Debye response for the energy fluctuations with Kohlrausch−Williams−Watts (KWW) function,[23] we have

$$\Delta_2(t) = \Delta_2(\infty)[1 - \exp(-(t/\tau_c)^{\mu})] \approx \Delta_2(\infty)(t/\tau_c)^{\mu} \qquad (6a)$$

and

$$1 - \Delta_1(t) = 1 - \exp(-(t/\tau_c)^{\nu}) \approx (t/\tau_c)^{\nu} \qquad (6b)$$

It leads to a time-dependent diffusion constant with $\Delta_2(t) \propto t^{\mu}$ and $<Q(t)> - <Q(0)> \propto t^{\nu}$ at short times. For such anomalous diffusion, we obtained the following temporal behavior for the blinking statistics $P(t)$ as

$$P(t) \propto (t/\tau_c)^{-2+\mu/2} \exp(-(\Gamma t)^{2\nu-\mu})$$

$$\propto t^{-m} \exp(-(\Gamma t)^n) \qquad (7)$$

showing an inverse power law with an exponent $m = 2 - \mu/2$ and an exponent n for the stretched exponential with $n = 2\nu - \mu$. Equation 7 is the central result of this work that describes the crossover for a power law with an exponent m to a stretched exponential decay with an exponent n. The exponent values m and n are shown to be related to the temporal behavior for the first and second moments in eq 6. Although a power law with an m different from $^3/_2$ was obtained in our previous report,[20] the crossover to a stretched exponential with an exponent n was not treated. The above general formula, derived in eq 7, is the core result of the present work and has not been addressed previously. For normal diffusion, $m = {}^3/_2$, $n = 1$, and eq 7 reduces to eq 5.

Although we used KWW function, which was used commonly to describe the dielectric relaxation of polymers, we did not necessarily mean that anomalous diffusion in NRs for energy fluctuations is caused by the same dielectric relaxation mechanism as that in polymers. The KWW-type behavior simply means a wide distribution in the spectral density of energy fluctuations. In eq 1, we considered a decoupled 1D reaction. Such a description for light-state blinking represents a reduced equation from a more-general treatment involving the ground state and the photoexcited state.[21] As shown by us previously,[21] due to fast population recycling between these two states of a light QD, the effective diffusion correlation time has light-intensity dependence. In contrast, for the dark state with an electron trapped in surface states, the waiting time distribution is insensitive to change of light intensity.

Analysis of the Blinking Statistics for CdSe Nanorods. We now proceed to analyze the experimental data of CdSe nanorods using eq 8. As an example of the application of this model, we used the data from the recent work by Wang et al.[16] In their report, the blinking statistics data were fitted directly assuming $P(t) \propto t^{-m} \exp(-\Gamma t)$ with a single-exponential tail. Such an approach yields poor fits to the tail especially if the tail is far from a single exponential. Here we reanalyze their data based on our model and formulas presented in this work. In our analysis using eq 7 with $P(t) \propto t^{-m} \exp[-(\Gamma t)^n]$, we first determined m of the power-law dependence for all samples by extracting from some data points at very-short times. Once m and the proportional constant of eq 7 were obtained, the full-range data of $\log_{10}[P(t)]$ versus $\log(t)$ were analyzed. We first chose a fixed n but let Γ float to determine the χ^2 deviation for

TABLE 1: Fitted Decay Time Constant Γ^{-1} for Both On and Off Events at $I = 210$ W/cm^2 for Seven NR Samples of Various Sizes[a]

	R (nm)	L (nm)	Γ_{on}^{-1} (s) $m_{on} = 1.35$, $n_{on} = 0.85$	Γ_{off}^{-1} (s) $m_{off} = 1.10$, $n_{off} = 0.30$
NR1	1.70	18	0.83	2.29
NR2	1.75	25	0.52	1.75
NR3	1.70	28	0.65	1.59
MR4	2.60	18	1.59	1.53
NR5	2.60	28	0.86	0.89
NR6	3.20	22	1.75	0.79
NR7	3.45	34	0.92	0.47

[a] The error is about 10% for Γ_{on}^{-1} and about 25% for Γ_{off}^{-1}.

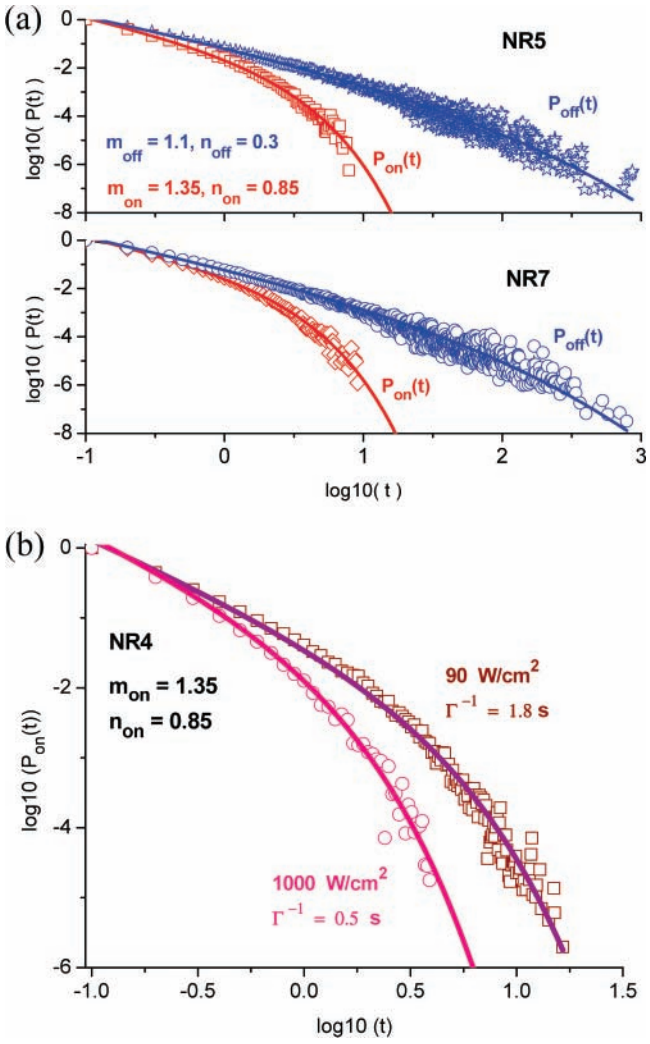

Figure 1. (a) Blinking statistics $P(t)$ of the on and off events for samples NR5 (top) and NR7 (bottom) in a log−log plot with fitted solid curves. The fitted parameters are listed in Table 1. The bending tail for $P_{off}(t)$ is far from single-exponential and can be best fitted using $t^{-m} \exp[-(\Gamma t)^n]$. (b) Log−log plot of $P_{on}(t)$ and the fitted curve for sample NR4 at two light intensities, showing more-pronounced bending at a higher intensity. The time scale is in seconds.

TABLE 2: Fitted Decay Time Γ^{-1} for NR4 (R = 2.6 nm, L = 18 nm) at Various Intensities with Fixed m_{on} = 1.35 and n_{on} = 0.85

I (W/cm^2)	90	210	300	400	500	600	690	870	1000
Γ^{-1} (s)	1.76	1.60	1.49	1.05	1.07	0.97	0.64	0.61	0.51

all NRs, then changed n and repeated the procedure to find the optimal n with a minimal χ^2. With such an optimal n, we could then determine the long-time bending rate Γ for each NR more accurately. The fitted Γ values of $P_{on}(t)$ and $P_{off}(t)$ at I = 210 W/cm^2 for seven NR samples are listed in Table 1. The experimental and fitted curves of $P_{on}(t)$ and $P_{off}(t)$ for samples NR5 and NR7 are illustrated in Figure 1a. The exponents for the power law of $P_{on}(t)$ and $P_{off}(t)$ appear to be slightly different with m_{on} = 1.35 (±0.05) and m_{off} = 1.10 (±0.05). The long-time tail for $P_{on}(t)$ yields n_{on} = 0.85 ± 0.05. The long-time tail of $P_{off}(t)$ for the off events, however, is highly nonexponential and can only be best described by a stretched exponential with n_{off} = 0.30 ± 0.05.

Because of the light-induced diffusion in light QDs,[8] the inverse of the diffusion correlation time τ_{on} increases with photoexcitation rate, that is, $1/\tau_{on} = 1/\tau_0 + cI\sigma_{abs}$, where I is the light intensity, σ_{abs} *is* the optical absorption cross section, and τ_0 is the intrinsic time constant that is not light-induced. As a consequence, the bending in the tail becomes more-pronounced at higher intensities as illustrated in Figure 1b. For the normal diffusion case, one obtains from eq 5

$$\frac{E_{A,on}}{2k_BT} = \Gamma_{on}\tau_{on} = \frac{\Gamma_{on}}{\tau_0^{-1} + cI\sigma_{abs}} \tag{9}$$

and from eq 8 for the anomalous diffusions

$$\frac{E_{A,on}}{2k_BT} = (\Gamma_{on}\tau_{on})^{n_{on}} = [\Gamma_{on}/(\tau_0^{-1} + cI\sigma_{abs})]^{n_{on}} \tag{10}$$

To analyze the size dependence of Γ_{on}, eq 10 was used. The cross section σ_{abs} is proportional to NR's physical volume. If $\Delta G^0 \propto \exp(-\beta R)$ and the reorganization energy λ is much smaller than the free-energy gap ΔG^0, then one has $E_{A,on} \sim (\Delta G^0)^2/4\lambda \propto \exp(-2\beta R)$. Using the values of Γ_{on} for NRs of different sizes from Table 1 and for NR4 at various light intensities in Table 2, we fitted Γ_{on} by $(a + bIV/V_4)[\exp(-2\beta(R - R_4))]^{1/n_{on}}$ according to eq 10, where the volume V_4 = 345 nm^3 and the radius R_4 = 2.6 nm for NR4. Because of light-induced spectral diffusion, the bending rate for $P_{on}(t)$ increases with light intensity as shown in Figure 2a with a fit of $a + bI$, where a = 0.32 (±0.10) and b = 0.0015 (±0.0002). In Figure 2b, the ratio $E_{A,on}$ (R)/$E_{A,on}$ (R$_4$) for NRs of various sizes is fitted by $C\exp(-2\beta R)$ with β = 0.35 ± 0.08 (nm^{-1}) and C = 7.9 ± 2.6. According to the work by Le Thomas et al.,[3] the exciton ground-state energy of NRs (in the inset of their Figure 5) appears to behave approximately as $\exp(-\beta R)$ with $\beta \sim$ 0.27 nm^{-1} within the range of 1−5 nm. This value is close to our estimated β for ΔG^0 between the light and dark states, which might have similar R dependence as the exciton ground state.

For the off events, the long-time bending tail is characterized by a highly stretched exponential and the values of Γ_{off} are listed in Table 1. As illustrated in Figure 3, Γ_{off} appears to increase with volume of an NR. The bending tail for the off events of QDs has not been noticed in previous reports because of the much-smaller physical volume for QDs than NRs. For the on events in Figure 2a, there is volume dependence in $1/\tau_{on} = 1/\tau_0 + cI\sigma_{abs}$ because σ_{abs} increases with volume. However, the bending for the off events is insensitive to the changes in light

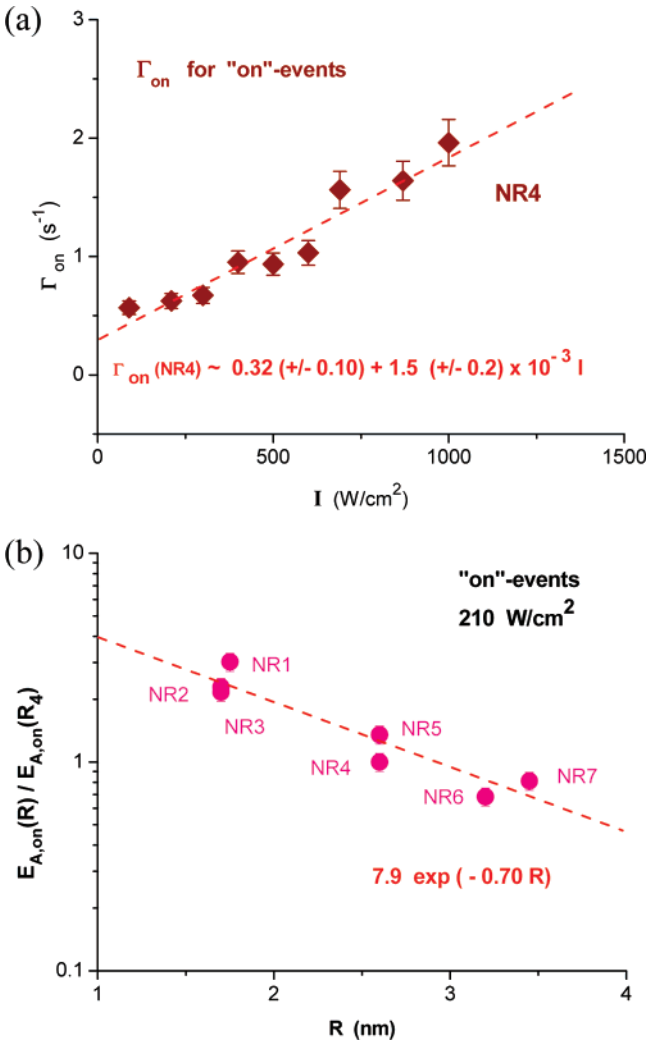

Figure 2. (a) Dependence of the on event bending rate Γ_{on} for sample NR4 on light intensity I in W/cm^2. (b) Semilog plot of the ratio of the activation energy $E_{A,on}(R)/E_{A,on}(R_4)$ vs the radius R for several NRs at 210 W/cm^2 with a fit by 7.9 $\exp(-2\beta R)$ where β = 0.35.

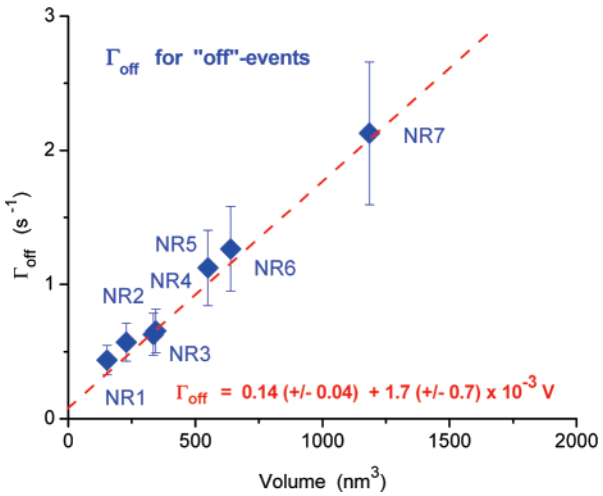

Figure 3. Bending rate Γ_{off} of the off events vs the physical volume of seven CdSe NR samples, showing simple linear volume dependence.

intensity. Therefore, the linear volume dependence of Γ_{off} might involve different mechanisms. The Auger constant is found to increase with the physical volume of a QD or NR.[24,25] Because both the Auger relaxation process and the bending rate for the dark NRs have similar volume dependencies, we suspect that such a relaxation process in a dark NR due to the excessive hole might play a key role in causing the volume dependence in Γ_{off}. More studies will be needed to verify our intuitive arguments and clarify the origin for such a size effect.

Conclusions

In conclusion, we derived in eq 7 a general formula $t^{-m}\exp[-(\Gamma t)^n]$ for better description of blinking statistics, and reported for the first time the characterization of the blinking statistics of single NRs by an initial power law with a crossover to a stretched exponential decay. These exponents *m* and *n* are shown to be related to the first and second moments of the spectral diffusion process. For the normal diffusion case, $m = {}^3/_2$ and $n = 1$, but for anomalous diffusion, *m* and *n* can be different from their ideal values. Our estimates of $m_{on} \sim 1.35$ (close to ${}^3/_2$) for the on events and $n_{on} \sim 0.85$ (close to 1) indicate nearly normal diffusion for the light NRs. For the off events, however, our finding of $m_{off} \sim 1.10$ and a very small $n_{off} \sim 0.30$ indicates that the bending tail follows a highly stretched exponential decay due to anomalous diffusive processes for dark NRs. Anomalous diffusion is often observed in disordered systems with dispersive diffusion correlation times.[26] Because the dark state involves an electron in many possible surface traps, these traps could result in a distribution of the diffusion correlation times due to different energy barriers for these trap states. Therefore, it is reasonable to expect that the spectral diffusion for dark NRs could be highly anomalous. The bending rate Γ_{on} for the on events was shown to increase with light intensity. From Γ_{on} of various sizes, we deduced the radius dependence for the energy gap. The diffusion equation and the temporal behavior for the first and the second moments we used in eqs 1−3 describe energy fluctuations and could be derived from a Hamiltonian of very-general multimode harmonic oscillators including linear displacement and Duschinsky mode mixings.[27,28] Such a subject will be treated elsewhere.

This work improves the understanding of anomalous diffusion and its influence on the temporal behavior of the blinking statistics, and the size dependence for the activation energy. In addition, we found simple volume dependence for Γ_{off}, indicating that the dark-state diffusion might be related to an Auger-assisted process, which has a similar volume dependence. The details about how Auger relaxation affects diffusion correlation times remain to be explored. The exponent *m* of the power-law blinking statistics in QDs appears to be affected by choices of dielectric media.[12] It deserves future systematic investigation to understand how dielectric media affect *m* and *n* for the blinking statistics of NRs.

Acknowledgment. I am thankful for the support by National Science Foundation, Ahmed H. Zewail and Academia Sinica. I benefited from helpful discussion with C. H. Crouch, and thank her, M. Drndic, and S. Wang for kindly providing the data in their paper (ref 16) to be reanalyzed in this work.

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