

Fluorescence Blinking Statistics from CdSe Core and Core/Shell Nanorods

Siying Wang,[†] Claudia Querner,[†] Thomas Emmons,[‡] Marija Drndic,^{*,†} and Catherine H. Crouch^{*,‡}

Department of Physics and Astronomy, University of Pennsylvania, 209 South 33rd Street, Philadelphia, Pennsylvania 19104, and Department of Physics and Astronomy, Swarthmore College, 500 College Avenue, Swarthmore, Pennsylvania 19081

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We report fluorescence blinking statistics measured from single CdSe nanorods (NRs) of seven different sizes with aspect ratios ranging from 3 to 11. This study also included core/shell CdSe/ZnSe NRs and core NRs with two different surface ligands producing different degrees of surface passivation. We compare the findings for NRs to our measurements of blinking statistics from spherical CdSe core and CdSe/ZnS core/shell nanocrystals (NCs). We find that, for both NRs and spherical NCs, the off-time probability distributions are well described by a power law, while the on-time probability distributions are best described by a truncated power law, $P(\tau_{\text{on}}) \sim \tau_{\text{on}}^{-\alpha} e^{-\tau_{\text{on}}/\tau_c}$. The measured crossover time, τ_c , is indistinguishable within experimental uncertainty for core and core/shell NRs, as well as for core NRs with different ligands, for the same core size, indicating that surface passivation does not affect the blinking statistics significantly. We find that, at fixed excitation intensity, $1/\tau_c$ increases approximately linearly with increasing NR aspect ratio; for a given sample, $1/\tau_c$ increases very gradually with increasing excitation intensity. Examining $1/\tau_c$ versus the single-particle photon absorption rate for all samples indicates that the change in NR absorption cross section with sample size can account for some but not all of the differences in crossover time. This suggests that the degree of quantum confinement may be partially responsible for the aspect ratio dependence of the crossover time.

Introduction

Fluorescence intermittency, also called blinking, is a widely observed property of single fluorophores, from colloiddally synthesized semiconductor nanocrystals (NCs) or quantum dots (QDs)¹ and polymer nanoparticles² to organic dye molecules³ and green fluorescent protein (GFP).⁴ Rather than steadily emitting light under continuous excitation, the fluorescence from individual NCs turns “on” and “off”, with individual “on” or “off” events lasting from microseconds to many minutes.¹ This behavior has been widely studied in spherical CdSe NCs, both experimentally and theoretically,^{5–32} as well as in some other materials such as PbS.³³ The random and uncontrollable nature of NC blinking is a major obstacle to single-NC optoelectronic applications such as lasers³⁴ and single-photon sources²¹ as well as to using single NCs as biological fluorescent markers.^{35,36} Consequently, understanding blinking may facilitate many single-NC applications.

Although the mechanism of blinking is not fully understood, it is thought that NCs become “dark”—cease emitting light—when one of the charge carriers in the photoexcited exciton becomes trapped at the surface of the NC, or tunnels entirely off the NC into the environment, leaving a net charge delocalized in the NC core. Fluorescence then resumes once the core regains electrical neutrality.^{1,5,9,10} The exact mechanism is still under theoretical and experimental investigation.

Blinking in semiconductor NCs differs significantly from blinking observed from many other single fluorophores in the probability distribution of “on” or “off” events of a particular duration. If a histogram of the duration τ_{off} of all “off” events observed from each NC is calculated, the resulting probability distribution of the off times, $P(\tau_{\text{off}})$, has been found for spherical core/shell CdSe/ZnS NCs to follow a power law, $P(\tau_{\text{off}}) = A\tau_{\text{off}}^{-\alpha}$ ($\alpha \sim 1.5$).^{7,10,14,17,19,20,24,28} The probability distribution of “on” times, $P(\tau_{\text{on}})$, likewise follows a power law for short τ_{on} but falls below the power law at longer “on” times at room temperature. Probability distributions observed from most other single fluorophores are exponential or near-exponential.²⁷

Recently, novel anisotropic NC shapes have been synthesized.³⁷ These are expected to offer a rich variety of electrical and optical properties; solar cells³⁸ and transistors³⁹ based on these shapes have been proposed. One example is the nanorod (NR), a NC that is elongated along the crystal *c*-axis so that charge carriers are most strongly quantum-confined along the NR cross section. Studying the optical and electrical properties of NRs offers the possibility of observing the transition from quantum states confined in all three dimensions (0D states), as in a spherical NC, to states confined in only two dimensions (1D states). The elongation of NRs also makes them better conductors than spherical NCs, and thus more suitable for certain device applications.^{38,40} While a variety of fluorescence measurements have been made on single NRs^{40–45} and other elongated nanocrystals,^{46,47} blinking statistics from NRs have not been reported to date.

In this paper, we report the first measurements of blinking statistics from single CdSe NRs. We study seven different types of NRs, with lengths ranging from 18 to 38 nm and diameters

* To whom correspondence should be addressed. Phone: (215) 898-5810 (M.D.); (610) 328-8386 (C.H.C.). Fax: (215) 898-2010 (M.D.); (610) 328-7895 (C.H.C.). E-mail: drndic@physics.upenn.edu (M.D.); ccrouch1@swarthmore.edu (C.H.C.).

[†] University of Pennsylvania.

[‡] Swarthmore College.

TABLE 1: Characteristics of the CdSe Core Spherical Nanocrystal (NC) and Nanorod (NR) Samples Used in This Study^a

sample	d^b (nm)	l^b (nm)	l/d^b	A^c (nm ²)	V^c (nm ³)	$N_{\text{TOPO}}/N_{\text{CdSe(surf)}}^d$ (%)	σ_λ^e (10 ⁻¹⁵ cm ²)	σ_{532}^e (10 ⁻¹⁵ cm ²)
NC	5.2		1	85	74	49	2.7	2.6
NR1	3.4	18	5.3	192	153	45	5.3	4.0
NR2	3.5	25	7.1	275	229	42	6.7	5.0
NR3	3.4	38	11.2	406	335	42	7.9	6.1
NR4	5.2	18	3.5	295	345	37	8.0	8.9
NR5	5.2	28	5.4	457	558	36	8.3	9.6
NR6	6.4	22	3.5	442	639	34	9.6	19
NR7	6.9	34	4.9	737	1185	32	14	30

^a Core/shell NC and NR samples are named according to the core sample on which the shell was grown followed by “cs”, e.g., NR1cs. ^b Diameter, d , length, l , and aspect ratio, l/d , determined from the absorption spectra and TEM analysis. ^c Surface area, A , and volume, V , estimated from the dimensions of the particles assuming perfect sphere or rod shape. ^d Surface coverage of available CdSe surface sites with TOPO molecules estimated from the ligand volume according to the procedure described by Bullen and Mulvaney.⁵⁵ ^e Absorption cross section at the excitonic peak, σ_λ , and at 532 nm, σ_{532} .

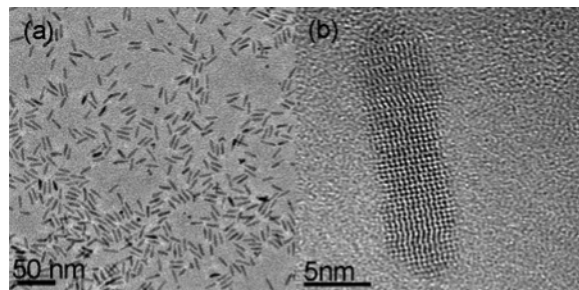


Figure 1. (a) Low-resolution and (b) high-resolution transmission electron microscopy (TEM) images of NR4 deposited on thin films of amorphous carbon supported by a copper grid.

ranging from 3.5 to 6.9 nm, giving aspect ratios from 3.5 to 11.2. For four sizes of NRs, we studied both core CdSe and core/shell CdSe/ZnSe NRs; for one size, we studied core NRs with two different surface ligands—trioctylphosphine oxide and hexadecylamine—which produce different degrees of surface passivation. We compare the measured probability distributions of off and on times to those measured from spherical NCs, both core and core/shell. This set of samples allows us to distinguish the effects of surface passivation and shape on the blinking statistics. We fit the on-time distributions to a truncated power law, $P(\tau_{\text{on}}) \sim \tau_{\text{on}}^{-\alpha} e^{-\tau_{\text{on}}/\tau_c}$. Finally, we investigate the effect of excitation intensity and absorption cross section on the on- and off-time statistics to gain further insight into NR blinking.

Experimental Methods

Synthesis of CdSe NRs. We synthesized CdSe NRs of different lengths and diameters (Table 1), capped with a 1.1 nm layer of trioctylphosphine oxide (TOPO), by adapting literature procedures.^{48–50} A ZnSe shell was grown on some of the core samples according to ref 51; hexadecylamine (HDA)-capped NRs (NR5-HDA) were prepared by heating TOPO-capped NRs in HDA for 1 h and precipitating/washing with methanol. Transmission electron microscopy (TEM, JEOL 2010F) confirmed the monodispersity (Figure 1a) and crystallinity (Figure 1b) of the NRs. Spherical CdSe and core/shell CdSe/ZnS NCs with core diameters of 5.2 nm were purchased from Evident Technologies. The samples studied are listed in Table 1.

Measurement of the Absorption Cross Section, σ_λ . We prepared a series of concentrations of dispersions of NCs and NRs in toluene, including at least seven different concentrations between $\sim 5 \times 10^{-8}$ and $\sim 5 \times 10^{-6}$ mol·L⁻¹ (maximum concentration of 6×10^{-7} mol·L⁻¹ for NR6 and NR7). Absorption spectra were measured using a USB2000-VIS-NIR spectrometer (Ocean Optics; integration time, 30 ms; resolution,

1 nm; path length, 1 cm). A Beer’s law plot of the absorbance intensities at the excitonic peak and at 532 nm (the laser wavelength used to excite fluorescence) was made to determine the molar extinction coefficients, ϵ_λ . The per particle absorption cross section, σ_λ , was then calculated according to ref 52 (Table 1).

Fluorescence Measurements. We performed wide-field fluorescence imaging⁵³ of a very sparse sample of NCs or NRs, using an epifluorescence microscope (Olympus) with a 100× 0.95 NA dry objective. Samples were prepared by drop- or spin-casting a very dilute toluene solution of CdSe NCs or NRs onto a freshly cleaved mica substrate. The concentration of the solution was chosen so that individual NCs or NRs were typically separated by a few micrometers. The sample was illuminated by 532 nm light from a continuous-wave (cw) frequency-doubled YAG laser (Coherent Compass). The excitation intensity used for most measurements was 210 W·cm⁻². To study intensity dependence, the intensity was varied from 90 to 1000 W·cm⁻². All samples were measured at room temperature in air immediately after preparation to minimize sample oxidation. Fluorescence movies were captured by a thermoelectrically cooled CCD camera (Princeton Instruments Cascade 512F) at 10 frames/s. All measurements presented in this paper lasted 2000 s unless otherwise specified. A background image measured from a clean mica substrate was subtracted from each frame of the movies. Individual emitters were identified in the image acquisition software, and the fluorescence intensity, $I(t)$, of each emitter was determined in each frame throughout the entire movie.

Results

Statistical Analysis of Fluorescence “On” and “Off” Times. Figure 2a shows an example of the time-dependent fluorescence intensity, $I(t)$, measured for 2000 s from a single 5×18 nm NR (NR4). To define the threshold above which the NR is considered “on”, we measured $I(t)$ in 10 dark regions of the sample (i.e., regions with no NRs) and found the greatest intensity range, ΔI_{dark} , and standard deviation, σ_{dark} , represented among those 10. As shown in Figure 2a, the “on” threshold (solid line) for each NR is set by adding $\Delta I_{\text{dark}} + \sigma_{\text{dark}}$ to the minimum intensity measured from that NR (dotted line).

From $I(t)$ for a single NR, we determined the probability density of “off” or “on” events of duration $\tau_{\text{off(on)}}$. Probability density is commonly defined as

$$P(\tau_{\text{off(on)}}) = \frac{N(\tau_{\text{off(on)}})}{N_{\text{off(on)}^{\text{tot}}}} \times \frac{1}{\Delta t} \quad (1)$$

where $N(\tau_{\text{off(on)}})$ is the number of “off” (“on”) events of duration

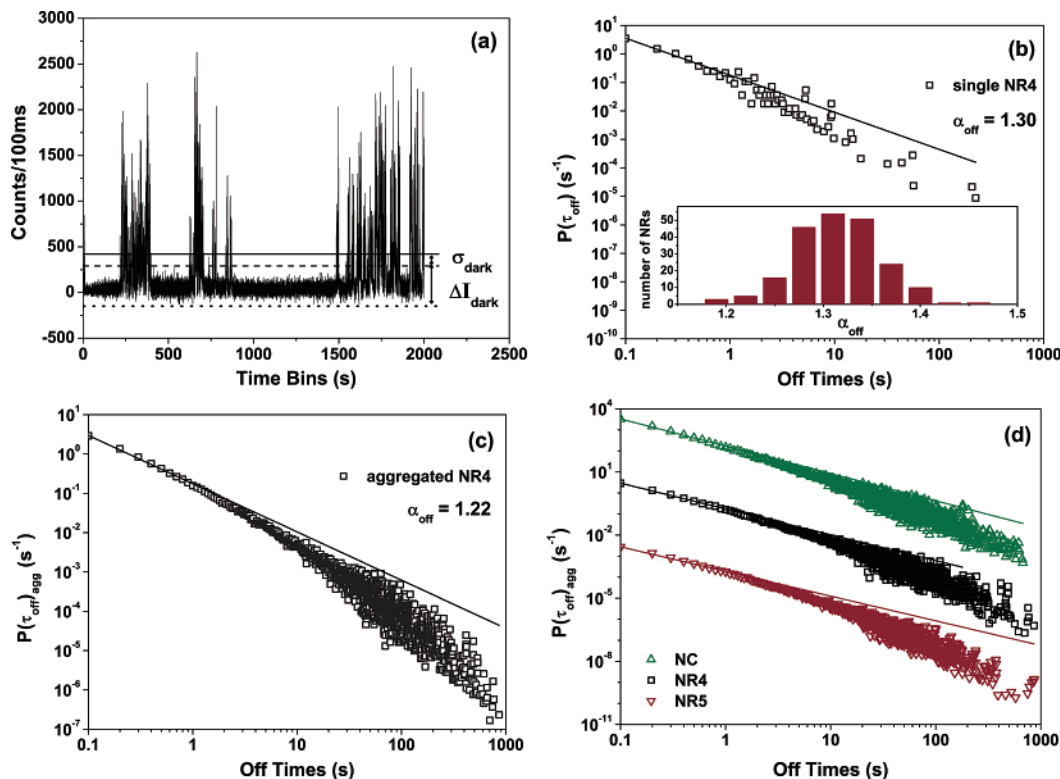


Figure 2. (a) Representative intensity vs time data, $I(t)$, obtained from a single NR (sample NR4) with the threshold above which it is considered to be “on” indicated by the solid line. (b) Off-time probability density, $P(\tau_{\text{off}})$, obtained from the data shown in part a. Inset in part b: histogram of exponents α_{off} for best-fit power law for each of the 210 individual NRs observed in this sample. (c) Aggregated probability density of off-times, $P(\tau_{\text{off}})_{\text{agg}}$, obtained by combining all off times from all individual NRs observed. (d) Comparison of $P(\tau_{\text{off}})_{\text{agg}}$ obtained from NC (green upright triangles), NR4 (black squares), and NR5 (red inverted triangles), offset vertically by multiples of three decades. The parameters of the best-fit power law (solid lines) are provided in Table 2.

$\tau_{\text{off}(\text{on})}$, $N_{\text{off}(\text{on})}^{\text{tot}}$ is the total number of “off” (“on”) events observed from that NR, and Δt is the 100 ms frame duration of the movies. However, calculating the probability density from eq 1 assigns the same probability density to any $\tau_{\text{off}(\text{on})}$ occurring only once during a particular experiment and assigns a probability of zero to any $\tau_{\text{off}(\text{on})}$ not observed in that experiment. A much longer experiment with more events would most likely give different probability densities for these rare events. We therefore calculated a weighted probability density according to the method of Kuno et al.:⁹

$$P(\tau_{\text{off}(\text{on})}) = \frac{N(\tau_{\text{off}(\text{on})})}{N_{\text{off}(\text{on})}^{\text{tot}}} \times \frac{1}{\Delta t_{\text{off}(\text{on})}^{\text{av}}} \quad (2)$$

defining $\Delta t_{\text{off}(\text{on})}^{\text{av}} = (a + b)/2$, where a and b are the time differences to the next longest and next shortest observed event. For common event durations, a and b both equal the 100 ms frame duration and thus $\Delta t_{\text{off}(\text{on})}^{\text{av}} = 100$ ms; $\Delta t_{\text{off}(\text{on})}^{\text{av}}$ increases for rare event durations if a or b exceeds 100 ms. This weighting scheme estimates the true probability of these rare events.

Previous studies^{7,9,10} have used different approaches to fit the off-time probability density to a power law. We fit our measured off-time probability distributions for core/shell NCs (NCs) with each approach (fits and discussion are provided in the Supporting Information). The same off-time data can give a power law exponent ranging from 1.34 to 1.87 depending on the fitting approach used. For all results in this paper, we binned our data by the 100 ms frame duration of the experiment and fit $P(\tau_{\text{off}})$ to the power law $A\tau_{\text{off}}^{-\alpha}$ (rather than fitting a line to $\log[P(\tau_{\text{off}})]$ versus $\log[\tau_{\text{off}}]$). This approach gives somewhat (20–30%) lower exponents than the other approaches. We chose

this approach because it minimizes manipulation of the data, and because the fits are dominated by the most reliable (short-duration) points in the probability distribution.

Off-Time Statistics. The off-time probability density, $P(\tau_{\text{off}})$, obtained from the $I(t)$ data in Figure 2a is shown on a log-log scale in Figure 2b. We obtained similar distributions from each of the 210 individual NRs of this sample (NR4). The probability density obtained by combining all events from all individual NRs observed (the “aggregated” probability density, $P(\tau_{\text{off}})_{\text{agg}}$) is shown in Figure 2c. The probability densities obtained from individual NRs and from the aggregated data are well described by a power law. For the single NR shown in Figure 2b, the best-fit power law gives $\alpha_{\text{off}} = 1.30$; the distribution of exponents obtained from 210 individual NRs (inset to Figure 2b) has an average value of 1.3 and a standard deviation of 0.1. The power law fit to the aggregated results (Figure 2c) gives $\alpha_{\text{off}} = 1.22$, which is within one standard deviation of the average α_{off} obtained from individual NRs. We therefore estimate the uncertainty in α_{off} from the aggregated data to be 0.1, the standard deviation of the distribution, and conclude that the aggregated probability distribution is consistent with the range of individual probability distributions observed.

To investigate the effect of NR shape and surface passivation on blinking, we determined blinking statistics for all 14 samples (Tables 1 and 2). All aggregated off-time probability distributions show power law behavior, with the longest “off” times falling slightly below the power law. The distributions for the 5.2-nm-diameter core NC and NRs, that is, NC, NR4, and NR5, are shown in Figure 2d.

The best-fit exponents of the power law fit to the aggregated data for all samples (Table 2) show no significant dependence

TABLE 2: Off-Time (On-Time) Exponents, $\alpha_{\text{off(on)}}$, and On-Time Crossover Times, τ_c , Obtained for CdSe Core and Core/Shell NCs and NRs^a

sample	α_{off}^b	α_{on}^c	τ_c^c (s)
NC	1.30	1.32	4.6
NR1	1.17	1.18	0.60 ^d
NR2	1.08	0.96	0.36 ^e
NR3	1.16	0.98	0.44 ^d
NR4	1.22	1.10	1.1
NR5	1.17	1.17	0.88
NR6	1.23	1.05	1.0
NR7	1.20	0.93	0.62
NCcs	1.34	1.35	7.1
NR1cs	1.18	1.12	0.66
NR2cs	1.17	1.14	0.50
NR3cs	1.17	1.2	0.59
NR5cs	1.22	1.10	0.95 ^f
NR5-HDA	1.22	1.02	0.66

^a The fits were performed on data aggregated from 100 nanoparticles. Except when otherwise specified, data were obtained from movies 2000 s long. ^b Off-time exponent obtained from power law fit (eq 2). ^c On-time fitting parameters obtained from truncated power law fit (eq 3). The average uncertainty in the values of τ_c was 20%. ^d 1200 s long movie (uncertainty +30%/−20%). ^e 600 s long movie (uncertainty +40%/−30%). ^f Mean value of two independent measurements. Determination of uncertainties is discussed in the Supporting Information.

of α_{off} on NR dimension, the presence of a ZnSe shell, or surface ligand; all values for NRs ($\alpha_{\text{off}} = 1.08\text{--}1.22$) fall within the ± 0.1 uncertainty range. The values obtained for the spherical NCs (core and core/shell) are slightly higher ($\alpha_{\text{off}} = 1.30$ and 1.34).

On-Time Statistics. Although the off-time distributions for NRs and NCs are essentially indistinguishable and independent of shape and surface passivation, the on-time distributions show a distinct dependence on aspect ratio. Figure 3a shows the on-time probability density for the single NR4 data from Figure 2a; the aggregated probability density from all NR4 appears in Figure 3b. The shape of the on-time distributions obtained from each type of sample is similar to those shown in Figure 3b; the distributions follow a power law for on times up to roughly 1 s for NRs and up to about 5 s for NCs, while longer “on” times fall below the power law, consistent with previous findings for NCs.^{7–10}

To better match the shape of the on-time distributions, we fit them to a truncated power law

$$P(\tau_{\text{on}}) = A\tau_{\text{on}}^{-\alpha_{\text{on}}}\text{e}^{-\tau_{\text{on}}/\tau_c} \quad (3)$$

shown by the curves in Figure 3. This function can be used to describe a physical process which is governed by a power law at short times and an exponential at long times, as has been proposed for NC blinking;^{23,29–31} the time τ_c then represents the crossover time between the two regimes. This function matches the shape of the on-time distributions well for both individual and aggregated data, and fits to this function consistently give χ^2 values 100 times smaller than fits to a pure power law.

We also examined whether a stretched exponential probability distribution, $P(\tau_{\text{on}}) = A \exp(-\tau_{\text{on}}/\tau_c)^{-\beta}$, fits the on-time distributions (fits not shown), as these distributions are predicted by some models of disordered systems.⁵⁴ However, the χ^2 for the fits was much poorer than that obtained with the truncated power law (comparable to that obtained with the pure power law). More significantly, the parameter τ_c varied by 2 orders of magnitude between individual NRs or NCs within the same sample, rather than displaying consistent values as with the truncated power law fit.

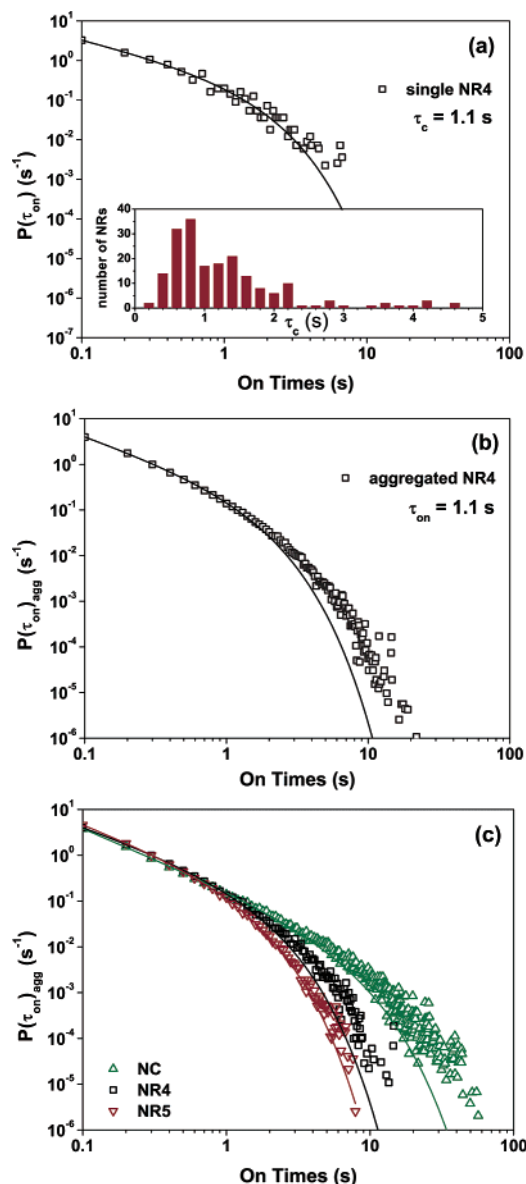


Figure 3. (a) On-time probability density, $P(\tau_{\text{on}})$, obtained from the data shown in Figure 2a. Inset: histogram of crossover times, τ_c , for best-fit truncated power law for each of the 210 individual NRs observed (sample NR4). (b) Aggregated on-time probability density, $P(\tau_{\text{on,agg}})$, obtained by combining on times from all individual NRs observed. (c) Comparison of $P(\tau_{\text{on,agg}})$ obtained from NC (green upright triangles), NR4 (black squares), and NR5 (red inverted triangles). The parameters of the best-fit truncated power law (solid lines) are listed in Table 2.

Comparing on-time distributions from different experiment durations (shown in the Supporting Information) indicates that increasing the experiment duration, so that more long-duration events are observed, produces an on-time distribution that increasingly resembles the distribution obtained by aggregating many shorter measurements. In addition, the histogram of individual crossover times calculated for the individual rods narrows, with the peak value staying the same within experimental uncertainty and with the number of long-crossover-time outliers greatly reduced. We therefore conclude that aggregated distributions, if enough rods are included, serve as a reasonably good representation of the distribution that would be obtained from an extremely long experiment. As collecting very long measurements from single NRs or NCs is difficult, we therefore focus our analysis on aggregated data from many individual

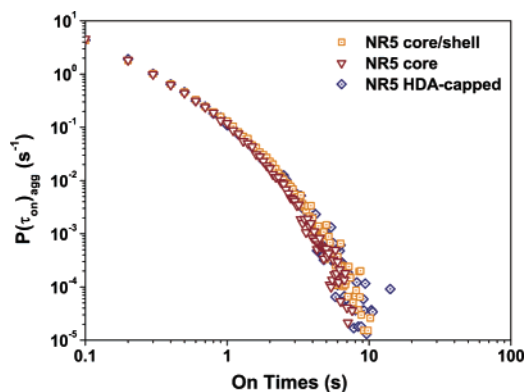


Figure 4. Aggregated on-time probability distributions for NR5 (red inverted triangles), NR5cs (orange squares), and NR5-HDA (blue diamonds), obtained from 100 NRs for each sample at $210 \text{ W}\cdot\text{cm}^{-2}$. Best-fit exponents and crossover times are provided in Table 2.

NRs, and use the distributions of crossover times for individual rods to determine the uncertainty in the value obtained from the aggregated data, as described in the Supporting Information. The histogram of crossover times for the ensemble of NR4 is provided as an inset to Figure 3a.

Aggregated results for the 5.2 nm diameter core samples (NC, NR4, and NR5) are shown in Figure 3c; equivalent data were obtained for all 14 samples in our study (Table 2). For all samples, the exponents α_{on} are slightly smaller for NRs ($\alpha_{\text{on}} \sim 1.2$) than for NCs ($\alpha_{\text{on}} \sim 1.3$), but show no significant dependence on NR length or surface passivation. Among the samples shown in Figure 3c, we obtain the shortest crossover time (0.89 s) for the longest NR (NR5); τ_c increases to 1.1 s for the shorter NR (NR4) and finally to 4.6 s for the NC.

Surprisingly, we found the same on-time distribution and crossover time within experimental uncertainty for the core and core/shell $5 \times 28 \text{ nm}$ NRs (NR5 and NR5cs), as shown in Figure 4 and Table 2, despite the significant improvement in fluorescence quantum yield and resistance to photobleaching displayed by core/shell NRs. We also found very little difference between the core NRs capped with TOPO and with HDA, NR5, and NR5-HDA (Figure 4), despite an expected 3-fold difference in surface coverage. HDA is expected to attach to nearly all surface CdSe units while TOPO to only $\sim 36\%$. This is because HDA has a linear geometry while TOPO has a cone-shaped geometry.⁵⁵

Examining the data from all NC/NR samples studied, we find a single clear trend in crossover time: τ_c decreases fairly steadily with increasing NR aspect ratio. Quantitatively, it appears that $1/\tau_c$ increases approximately linearly with NR aspect ratio, as shown in Figure 5. The uncertainties in τ_c are determined from repeated measurements and from the distributions of τ_c values from the individual NRs, as described in the Supporting Information. We find that α_{on} varies somewhat more (~ 0.9 – 1.1) than α_{off} , but with no clear trend.

Comparing the crossover times (Table 2) measured for 5.2-nm-diameter NRs to those for the 6.4- and 6.9-nm-diameter NRs, that is, NR6 and NR7, we observe that, for comparable length, a larger diameter reduces the crossover time. This is consistent with previous results from spherical NCs.¹⁰ Unexpectedly, the 3.5-nm-diameter NRs (NR1–3) show smaller rather than larger crossover times, compared to the 5.2-nm-diameter NRs. The 3.5-nm-diameter NRs also bleached more rapidly than the larger NRs, requiring shorter data acquisition times which resulted in larger uncertainties in the values of τ_c , as indicated in Table 2.

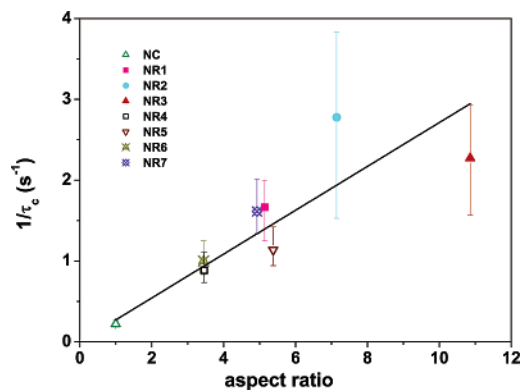


Figure 5. Inverse crossover time vs aspect ratio for all TOPO-capped core NC and NR samples studied.

TABLE 3: Intensity Dependence of Off- and On-Time Parameters for Sample NR4^a

I^b ($\text{W}\cdot\text{cm}^{-2}$)	α_{off}^c	α_{on}^d	τ_c^d (s)
90	1.27	1.09	1.3
210	1.23	1.10	1.1
300	1.29	1.01	1.1
400	1.24	0.92	0.79
500	1.22	0.79	0.73
600	1.21	0.79	0.69
690	1.14	1.16	0.69
870	1.12	1.20	0.65
1000	1.08	1.04	0.40

^a The fits were performed on aggregated data from 50 individual NRs. ^b Excitation intensity. ^c Off-time exponent obtained from power law fit (eq 2). ^d On-time fitting parameters obtained from truncated power law fit (eq 3).

Effect of Excitation Intensity. Finally, we examined the effect of changing the intensity of the exciting light on the NR off- and on-time statistics, by measuring blinking from 5×18 NRs (NR4) at nine different intensities from 90 to $1000 \text{ W}\cdot\text{cm}^{-2}$. The off-time distribution is largely unaffected, as was found previously for spherical NCs.¹⁰ Minor variations in the distribution tail produce a slight though fairly steady decrease with increasing intensity in α_{off} from 1.3 to 1.1 (Table 3). As this variation is within experimental uncertainty, it is not clear that this trend is significant.

The on-time distribution shows a clearer trend with intensity. Over the entire intensity range studied, the on-time distribution is well fit by a truncated power law. As intensity increases, τ_c decreases. The theory of Tang and Marcus predicts that $1/\tau_c$ should be proportional to the photon absorption rate,²⁹ and hence for a particular sample, proportional to the excitation intensity. As shown in Figure 6a, $1/\tau_c$ shows a small, steady increase with intensity. The exponent from the truncated power law, α_{on} , also varies, but not in a consistent fashion and only within uncertainty (Table 3).

The variation of τ_c with excitation intensity leads to the following question: can the variation in τ_c with NR shape at fixed intensity be attributed entirely to the change in photon absorption rate due to changes in the single-particle absorption cross section? Indeed, our measurements of the single-particle cross section at the exciting wavelength, σ_{532} , for each sample (Table 1) indicate that the cross section increases with increasing NR volume, as has been found for spherical NCs.⁵⁶ We therefore examined whether τ_c remains constant if the single-NR photon absorption rate is also held constant.

Figure 6b shows $1/\tau_c$ versus the product of excitation intensity and single-particle cross section (proportional to photon absorption rate) with points from all core samples measured.

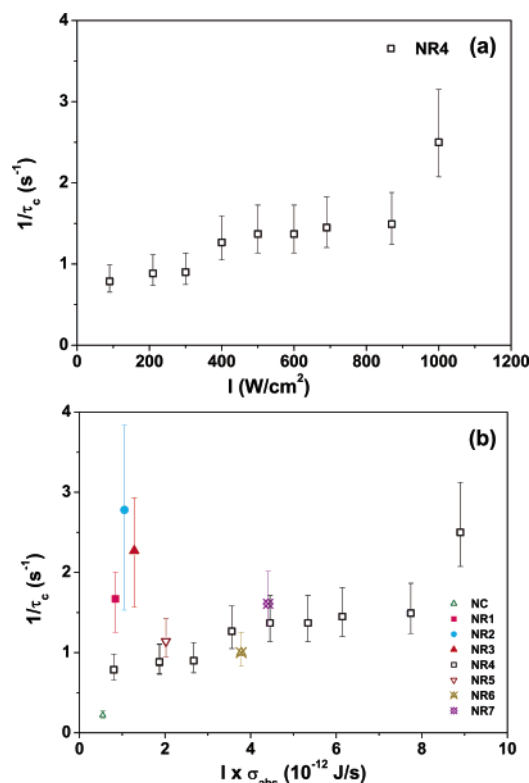


Figure 6. (a) Excitation intensity dependence of the inverse crossover time of NR4. Best-fit exponents and crossover times are provided in Table 3. (b) Inverse crossover times of measured core NRs and NC as a function of excitation intensity \times single-particle absorption cross section (this quantity is proportional to the single-particle photon absorption rate).

(Core/shell samples have essentially the same $1/\tau_c$ as the core sample of the same size and thus would be redundant on this plot.) The $1/\tau_c$ values obtained from the larger-diameter NRs (NR5, NR6, and NR7) are fairly consistent with the measured intensity dependence of NR4, when intensity is converted to single-particle absorption rate. However, values obtained from the 3.5-nm-diameter NRs (NR1–3) and the spherical NCs do not map onto the measured NR4 intensity dependence.

Discussion

Nanorod blinking displays many of the same features as blinking of spherical NCs: the off-time distributions follow a power law that is unaffected by excitation intensity or sample shape, and the on-time distributions follow a truncated power law with an intensity-dependent crossover time, τ_c . There are also significant differences between NR and NC blinking. In particular, τ_c is substantially shorter for NRs than for NCs; that is, NRs display far fewer long “on” events, and among a variety of NRs, τ_c decreases significantly with increasing NR aspect ratio.

Several important structural differences between NRs and NCs might be expected to contribute to these differences. First, because the NR surface is less sharply curved along its long dimension than the surface of spherical NCs (or the ends of NRs), and because the TOPO molecules typically used to cap both NRs and NCs are conical,⁵⁵ a lower percentage of surface CdSe units are attached to TOPO molecules on NRs than on NCs (Table 1), leading to less complete surface passivation. There should therefore be a larger number of nonpassivated surface traps on NRs, which might be expected to reduce the lifetime of the “on” state. Second, the quantum confinement of

the exciton in one-dimensional NRs is weaker than that in zero-dimensional spherical NCs. Consequently, there is less of a barrier than in spherical NCs for an excited charge carrier to tunnel to the surface or into the environment.^{42,43} The greater likelihood of such tunneling events would likewise be expected to reduce the probability of long “on” times. Finally, the shorter crossover time in NRs might also be a consequence of the greater surface charge density on NRs.^{57,58} Further experiments, such as comparing electrical force microscopy (EFM) measurements of surface charge and blinking statistics of individual NRs, could investigate this last point.

Our finding that the crossover time is the same within experimental uncertainty for core and core/shell NRs, and also for TOPO- and HDA-capped core NRs (Table 2 and Figure 4), indicates that surface passivation is not the primary determinant of NR blinking statistics. In core/shell NRs, the optically active core is almost perfectly passivated by the higher band gap semiconductor shell. Any defects arise from lattice mismatches between the two crystal structures; however, ZnSe and CdSe are very well lattice-matched.⁵⁹ In core NRs, the core surface is passivated only by the organic capping ligands, and the degree of passivation depends strongly on the type of ligand; the linear shape of the HDA molecule allows it to attach to nearly all CdSe surface units, while TOPO attaches to less than half of the surface units. The samples compared thus represent a wide range of surface passivation.

We did find, however, that core/shell spherical NCs had a somewhat greater crossover time than the corresponding core NCs (Table 2). One possible explanation for why the crossover time for NRs but not NCs is insensitive to surface passivation is that internal trap states, such as those induced by stacking faults in the crystal structure during growth, may affect carrier dynamics more than surface trap states in NRs. If so, improved surface passivation in NRs would not affect the crossover time substantially. Ultrafast measurements of carrier relaxation rates have likewise suggested that surface state trapping may be less significant in NRs than in NCs.⁴⁵

Our observation of a very gradual increase of $1/\tau_c$ with excitation intensity (Figure 6a) is consistent with, though far less pronounced than, the intensity dependence of the on-time distribution observed for spherical NCs, which has previously been attributed to a reduced hopping rate at lower excitation intensities.¹⁰ The intensity dependence we observe for the 5 nm \times 18 nm NRs (NR4) is far weaker than that predicted by Tang and Marcus,²⁹ though it could be a linear relationship with a constant offset.

Examining measurements of $1/\tau_c$ from different samples as a function of photon absorption rate (Figure 6b), we find that changes in absorption cross section can account for the changes of $1/\tau_c$ with length for the larger-diameter NRs (NR4–7), all of which have fairly similar aspect ratios (3.5–5.5). However, $1/\tau_c$ for the spherical NCs and the 3.5-nm-diameter NRs do not match that measured from the larger NRs with the same photon absorption rate. Our results therefore indicate that absorption cross section changes cannot account for all of the observed variation in $1/\tau_c$.

The roughly linear increase of $1/\tau_c$ with aspect ratio (Figure 5) could therefore be a manifestation of the reduced strength of quantum confinement with the increase in aspect ratio. If so, it also reveals that the transition from 0D to 1D confinement has a much greater effect on the crossover time than does decreasing confinement by increasing the diameter in spherical NCs. It could also reflect an increased number of internal trap states with increasing aspect ratio, or both effects could contribute. We postulate that changes in quantum confinement with NR

aspect ratio may play a significant role and should be considered in future models.

Conclusions

In conclusion, we find that blinking statistics from CdSe NRs of a wide range of aspect ratios (3–11) display power law off-time statistics and truncated power law on-time statistics, with the crossover time for the on-time statistics decreasing with increasing aspect ratio or with increasing excitation intensity. We observe no significant difference in on-time statistics between TOPO-capped core, core/shell, and HDA-capped core NRs, indicating that surface passivation is largely unimportant in NR blinking, while we see a greater crossover time for core/shell than for core spherical NCs. We find that the variation in crossover time with aspect ratio for NRs can be partly but not completely explained in terms of changes in the absorption cross section and hence the photon absorption rate.

We therefore attribute the shorter crossover time in higher aspect ratio rods to a combination of larger absorption cross section, weaker quantum confinement, and possibly a higher incidence of internal trap states. In contrast to these differences in the on-time statistics, the off-time power law exponents do not depend on NR shape or surface coverage, and are very similar for NRs and NCs. Consequently, the mechanism determining the off times is most likely the same for NRs and NCs, while the light-induced mechanism affecting the longer on-times sets in at shorter times in NRs than in NCs and is less sensitive to surface passivation. These findings indicate that blinking poses significant challenges for the use of single NRs in optoelectronic devices, and that the behavior of NR-based devices may be particularly sensitive to excitation intensity.

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Supporting Information Available: Details about different methods used to analyze the blinking data, the effect of experiment length on the blinking statistics, and the procedures used to determine the uncertainties in the fitting parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802.
- Vanden Bout, D. A.; Yip, W. T.; Hu, D. H.; Fu, D. K.; Swager, T. M.; Barbara, P. F. *Science* **1997**, *277*, 1074.
- Yip, W. T.; Hu, D. H.; Yu, J.; Vanden Bout, D. A.; Barbara, P. F. *J. Phys. Chem. A* **1998**, *102*, 7564.
- Dickson, R. M.; Cubitt, A. B.; Tsien, R. Y.; Moerner, W. E. *Nature* **1997**, *388*, 355.
- Efros, A. L.; Rosen, M. *Phys. Rev. Lett.* **1997**, *78*, 1110.
- Banin, U.; Bruchez, M.; Alivisatos, A. P.; Ha, T.; Weiss, S.; Chemla, D. S. *J. Chem. Phys.* **1999**, *110*, 1195.
- Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. *J. Chem. Phys.* **2000**, *112*, 3117.
- Kuno, M.; Fromm, D. P.; Gallagher, A.; Nesbitt, D. J.; Micic, O. I.; Nozik, A. J. *Nano Lett.* **2001**, *1*, 557.
- Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. *J. Chem. Phys.* **2001**, *115*, 1028.
- Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G. *Phys. Rev. B* **2001**, *63*, 205316.
- Jung, Y.; Barkai, E.; Silbey, R. J. *Chem. Phys.* **2002**, *284*, 181.
- Verberk, R.; van Oijen, A. M.; Orrit, M. *Phys. Rev. B* **2002**, *66*, 233202.
- Ebenstein, Y.; Mokari, T.; Banin, U. *Appl. Phys. Lett.* **2002**, *80*, 4033.
- van Sark, W. G. J. H. M.; Frederix, P. L. T. M.; Bol, A. A.; Gerritsen, H. C.; Meijerink, A. *ChemPhysChem* **2002**, *3*, 871.
- Kuno, M.; Fromm, D. P.; Johnson, S. T.; Gallagher, A.; Nesbitt, D. J. *Phys. Rev. B* **2003**, *67*, 125304.
- Verberk, R.; Orrit, M. *J. Chem. Phys.* **2003**, *119*, 2214.
- Brokmann, X.; Hermier, J. P.; Messin, G.; Desbiolles, P.; Bouchaud, J. P.; Dahan, M. *Phys. Rev. Lett.* **2003**, *90*, 120601.
- Margolin, G.; Barkai, E. *J. Chem. Phys.* **2004**, *121*, 1566.
- Kobitski, A. Y.; Heyes, C. D.; Nienhaus, G. U. *Appl. Surf. Sci.* **2004**, *234*, 86.
- Hohng, S.; Ha, T. *J. Am. Chem. Soc.* **2004**, *126*, 1324.
- Brokmann, X.; Giacobino, E.; Dahan, M.; Hermier, J. P. *Appl. Phys. Lett.* **2004**, *85*, 712.
- Pelton, M.; Grier, D. G.; Guyot-Sionnest, P. *Appl. Phys. Lett.* **2004**, *85*, 819.
- Chung, I. H.; Bawendi, M. G. *Phys. Rev. B* **2004**, *70*, 165304.
- Muller, J.; Lupton, J. M.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. *Appl. Phys. Lett.* **2004**, *85*, 381.
- Issac, A.; von Borczyskowski, C.; Cichos, F. *Phys. Rev. B* **2005**, *71*, 161302.
- Margolin, G.; Protasenko, V.; Kuno, M.; Barkai, E. *arXiv:cond-mat* **2005** *v1*, 0506512.
- Frantsuzov, P. A.; Marcus, R. A. *Phys. Rev. B* **2005**, *72*, 155321.
- Yao, J.; Larson, D. R.; Vishwasrao, H. D.; Zipfel, W. R.; Webb, W. W. *Proc. Natl. Acad. Sci.* **2005**, *102*, 14284.
- Tang, J.; Marcus, R. A. *J. Chem. Phys.* **2005**, *123*, 054704.
- Tang, J.; Marcus, R. A. *Phys. Rev. Lett.* **2005**, *95*, 107401.
- Tang, J.; Marcus, R. A. *J. Chem. Phys.* **2005**, *123*, 204511.
- Chung, I.; Witkoskie, J. B.; Cao, J. S.; Bawendi, M. G. *Phys. Rev. E* **2006**, *73*, 011106.
- Peterson, J. J.; Krauss, T. D. *Nano Lett.* **2006**, *6*, 510.
- Chan, Y.; Caruge, J. M.; Snee, P. T.; Bawendi, M. G. *Appl. Phys. Lett.* **2004**, *85*, 2460.
- Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.
- Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759.
- Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700.
- Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.
- Cui, Y.; Banin, U.; Bjork, M. T.; Alivisatos, A. P. *Nano Lett.* **2005**, *5*, 1519.
- Millio, O.; Katz, D.; Steiner, D.; Rothenberg, E.; Mokari, T.; Kazes, M.; Banin, U. *Nanotechnology* **2004**, *15*, R1.
- Chen, X.; Nazzari, A.; Goorskey, D.; Xiao, M.; Peng, Z. A.; Peng, X. *Phys. Rev. B* **2001**, *64*, 245304.
- Rothenberg, E.; Ebenstein, Y.; Kazes, M.; Banin, U. *J. Phys. Chem. B* **2004**, *108*, 2797.
- Rothenberg, E.; Kazes, M.; Shaviv, E.; Banin, U. *Nano Lett.* **2005**, *5*, 1581.
- Le Thomas, N.; Herz, E.; Schops, O.; Woggon, U.; Artemyev, M. V. *Phys. Rev. Lett.* **2005**, *94*, 016803.
- Mohamed, M. B.; Burda, C.; El-Sayed, M. A. *Nano Lett.* **2001**, *1*, 589.
- Müller, J.; Lupton, J. M.; Lagoudakis, P. G.; Schindler, F.; Koeppel, R.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. *Nano Lett.* **2005**, *5*, 2044.
- Müller, J.; Lupton, J. M.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. *Phys. Rev. B* **2005**, *72*, 205339.
- Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 1389.
- Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2002**, *124*, 3343.
- Shieh, F.; Saunders, A. E.; Korgel, B. A. *J. Phys. Chem. B* **2005**, *109*, 8538.
- Reiss, P.; Bleuse, J.; Pron, A. *Nano Lett.* **2002**, *2*, 781.
- Leatherdale, C. A.; Woo, W. K.; Mikulec, F. V.; Bawendi, M. G. *J. Phys. Chem. B* **2002**, *106*, 7619.
- Moerner, W. E.; Fromm, D. P. *Rev. Sci. Instrum.* **2003**, *74*, 3597.
- Beadie, G.; Sauvain, E.; Gomes, A. S. L.; Lawandy, N. M. *Phys. Rev. B* **1995**, *51*, 2180.
- Bullen, C.; Mulvaney, P. *Langmuir* **2006**, *22*, 3007.
- Klimov, V. J. *J. Phys. Chem. B* **2000**, *104*, 6112.
- Krauss, T. D.; Brus, L. E. *Phys. Rev. Lett.* **1999**, *83*, 4840.
- Krishnan, R.; Hahn, M. A.; Yu, Z.; Silcox, J.; Fauchet, P. M.; Krauss, T. D. *Phys. Rev. Lett.* **2004**, *92*, 216803.
- Reiss, P.; Carayon, S.; Bleuse, J.; Pron, A. *Synth. Met.* **2003**, *139*, 649.