

Exciton–Trion Transitions in Single CdSe–CdS Core–Shell Nanocrystals

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At the single molecule level, most semiconductor nanocrystals (NCs) are affected by photoluminescence (PL) blinking displaying interruptions in the PL that have a significant variability in duration and which can last up to several seconds at a time.¹ These random interruptions in the PL pose a limitation on potential applications of NCs as efficient and reliable nanoscale emitters. Currently, charge accumulation at the NC surface or photoinduced ionization have been proposed as the most likely mechanisms responsible for PL blinking, since it is assumed that while in one of these charge-separated states, the NC is unable to radiate due to efficient nonradiative Auger recombination.^{1,2} However, the observation of broadly distributed blinking dynamics is still the subject of intense debate,^{3,4} since the large time scales involved are many orders of magnitude larger than those predicted by standard quantum-mechanical models.

This photoionization hypothesis has been supported by a number of experimental observations, most remarkably by the fact that illumination can lead to ionization of single NCs.⁵ To account for the large dynamic range observed in the blinking statistics, several models, based on the Auger mechanism, have been put forward;^{3,4,6} these models often invoke distributions of charge traps that could be either external to the NC^{6–11} or surface-localized.^{12–14} In most of these attempts the effort is devoted to accounting for binary-like “on-off” transitions in the PL; however, as we demonstrate in this letter, blinking in CdSe/CdS core–shell NCs involves an additional transition state that acts as an intermediary between the “on” and “off” states. Here we demonstrate that single CdSe/CdS

ABSTRACT We report on the observation of an intermediate state in the blinking of single CdSe/CdS core–shell nanocrystals. This state has a low quantum yield and connects the “on” and “off” states commonly observed in the photoluminescence blinking of individual nanocrystals. We find that the transitions between these two emitting states follow nearly single-exponential statistics. The transitions from the “on” state to this intermediate state result from changes in the surface passivation of the nanocrystal. The data are consistent with photoinduced, adsorption/desorption events that take place at the surface of the nanocrystals. The trion state leads to a reduction in photoluminescence in nanocrystals.

KEYWORDS: semiconductor nanocrystals · quantum dots · excitons · CdSe/CdS · photoluminescence · blinking · spectral diffusion · single molecule spectroscopy · trions

core–shell NCs exhibit unusual blinking dynamics involving three states. In addition to a bright state, we observe an intermediate state that has a low radiative quantum yield and facilitates the transition to the “off” state. We show that this intermediate state stems from radiative recombination from a positively charged NC, and we also provide evidence that incomplete surface passivation provides an efficient nonradiative decay channel that is activated/deactivated by adsorption/desorption of small atmospheric molecules. Furthermore, unlike the case of the commonly studied CdSe/ZnS NCs, the duration of both the bright and the dim state emission have a single (and well-defined) characteristic time constant.

RESULTS AND DISCUSSION

In Figure 1a we show a typical PL time-trajectory of a single CdSe/CdS NC (zoomed-in, 5 ms binning time, 300 s total observation time). The emission from this system is dominated by blinking, that is, it is often interrupted by periods of time where the total intensity drops to the background level. However, unlike previously reported data, the emission is dominated by

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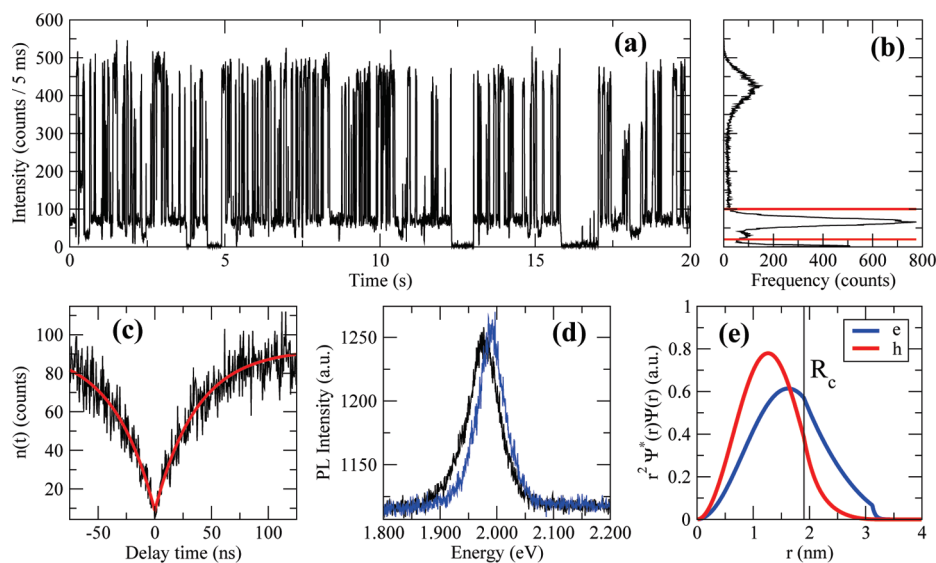


Figure 1. Photoluminescence from a single CdSe/CdS nanocrystal (core radius 1.9 nm, 3.5 ML of CdS): (a) intensity as a function of measurement time; (b) histogram of the measured intensity. It is clear in this figure that there are two well-defined emission levels above the background; (c) histogram of time delay between consecutive photons measured on a Hanbury–Brown and Twiss interferometer. The dip at zero delay time indicates that the photon emission is antibunched. (d) Representative emission spectra of a single CdSe/CdS NC measured with 1 s integration time at room temperature, due to spectral diffusion the emission peak position randomly shifts during the course of several seconds. The two spectra shown in the figure demonstrate the typical extent of these fluctuations. All the measurements were carried out under cw illumination at $\sim 200 \text{ W/cm}^2$. (e) Electron (blue) and hole (red) radial probability densities calculated for a CdSe/CdS NC within the effective mass approximation. The vertical line denotes the position of the core–shell interface R_c .

frequent, discontinuous jumps between *two well-defined levels* with occasional transitions to a dark state. In Figure 1a, the time trajectory is a superposition of events where (i) there is little emission (“off” events), (ii) events with an intermediate and well-defined emission level, and (iii) periods of short-lived fluorescence bursts with count rates well above the intermediate level. In sharp contrast to previous findings, the NC seems to spend most of the time experiencing transitions to and above the intermediate state, resulting in the sharp feature observed in the intensity histogram of Figure 1b. This emission pattern can be reproduced by a single NC for periods of observation longer than 600 s and is consistently observed for CdSe/CdS NCs drawn from different samples (see Supporting Information).

We measured interphoton arrival times, under continuous wave excitation, with a Hanbury–Brown and Twiss interferometer.¹⁵ The absence of coincidence counts at zero interarrival time in the histogram of Figure 1c [*i.e.*, $n(0) \approx 0$], shows that this multistate emission displays photon antibunching, thus unambiguously demonstrating that the three-state pattern of Figure 1a stems from the emission of individual photons from a single NC.^{16–18}

Despite the clear observation of more than one emission intensity level in the time transient of Figure 1a, the emission spectra (at room temperature) only consist of a single peak, as shown in Figure 1d, with no additional features at either higher or lower energies, thus indicating that the two emission states do not stem from eigenstates of different energy of the NC

(within spectral-diffusion-limited resolution,¹⁹ at room temperature [see ref 20]).

We found the emission intensity to be strongly correlated with the PL decay lifetime, as shown in Figure 2. For the high intensity events, the PL decay time was monoexponential with a decay time of $\sim 44 \text{ ns}$, which is almost twice as large as that reported for CdSe/ZnS NCs,^{21,22} and attributable to the lowered electron–hole wave function overlap in the pseudo-Type II heterostructure [see Figure 1e] in agreement with the recent results of Mahler *et al.*²³ On the contrary, the PL decay of the photons originating from the intermediate level were well-described by double-exponentials with average decay times of $\sim 5.2 \text{ ns}$. As discussed by Schlegel *et al.*²² and by Fisher *et al.*,²¹ such a correlation of PL lifetimes with emission intensities suggests that the nonradiative decay rate k_{nr} is fluctuating; furthermore, given the shape of the histogram of Figure 1b, these data imply that there must be an almost binary fluctuation of k_{nr} values.

Given these observations, and as first discussed by Zhang *et al.*,²⁴ it is obvious that an analysis of blinking in terms of a binary (on/off) process is inaccurate, and instead, for CdSe/CdS, blinking statistics should be analyzed in terms of transitions that occur among a set of (at least) three states, namely, an “off” state [with intensities lying below the (arbitrary) line L in Figure 1b], an intermediate intensity level (events with intensities within the bounds of the lines U and L in Figure 1b) and a high intensity level (events with intensities above line U); in other words, we extend the traditional

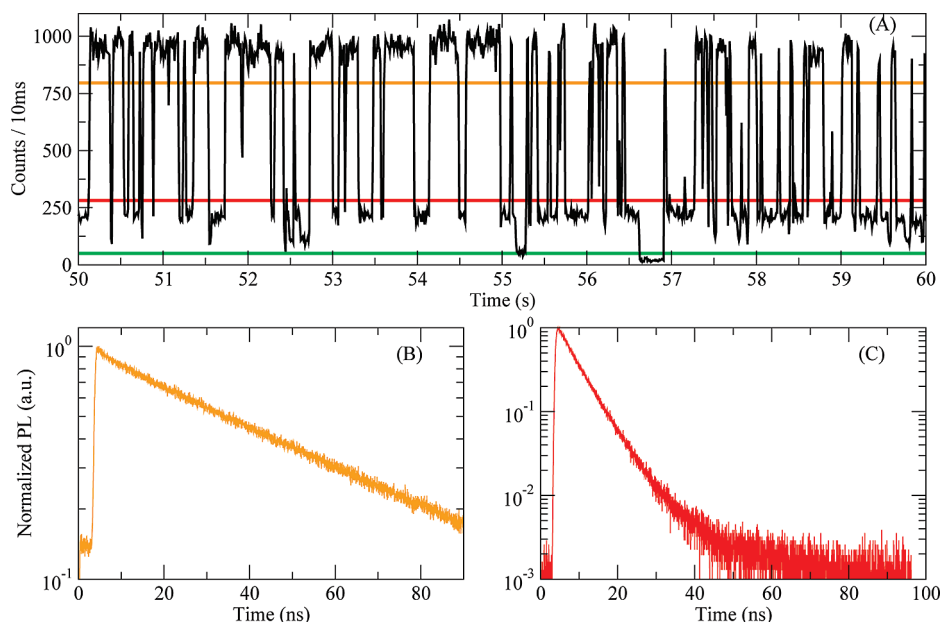


Figure 2. (A) Emission time transient from a single CdSe/CdS nanocrystal (core radius 1.9 nm, 3.5 ML of CdS). Each horizontal line indicates the intensity threshold employed to discriminate the high-intensity against the medium intensity events. (B) Photoluminescence time decay of the photons that originate from the high intensity level (those above the orange line) plotted on a log–linear scale. (C) Photoluminescence time decay of the intermediate intensity photons (those that were selected between the green and red lines in panel A). Excitation with pulses of ~ 73 ps width, 466 nm at a repetition rate 10 MHz.

on/off intensity-threshold analysis⁶ to account for three states. Using this approach, we can compile histograms of the duration of these three types of events from which we obtain the results of Figure 3a–c (times spent in the “off”, intermediate-, and high-intensity states, respectively). Here, it is important to point out that a more robust identification of both the number and magnitude of the intensity levels accessible to the NC, can be achieved by using the change-point method of Watkins and Yang.²⁵ However, the main point that we wish to highlight is that the data presented here strongly indicate that the number of such states is finite (unlike the case of CdSe/ZnS NCs that display a continuous distribution²⁴) and bigger than two (i.e., binary blinking).

The resulting histogram of off-times spans almost four decades in time and is linear on a log–log scale, indicative of an inverse power-law distribution.²⁶

Consistent with previous reports, these statistics were also found to be insensitive to pump power^{1,7,27} and pump energy²⁸ as shown on Figure 4 and Figure 5, where we show a representative set of blinking statistics obtained by illuminating a single CdSe/CdS nanocrystal with different excitation powers (at 488 nm cw excitation) and excitation energies. On the contrary, the histograms of the other two types of events were found to be described by stretched-exponentials (the lines in Figure 3b–c) with a parameter β that for the high-intensity events, frequently reached a value of unity, thus indicating that the rate of depletion of this state has a well-defined time scale (~ 24 ms). For the histograms of the times spent at the intermediate-intensity level the values of β were ~ 0.7 and the average decay times were in the order of 15 ms. These decay times were found to depend on both pump power and energy, as shown in Figures 4 and 5, indicating that the

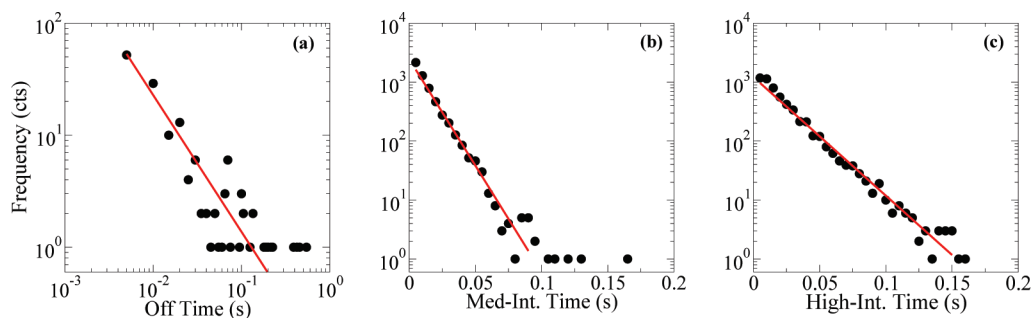


Figure 3. Histograms of the lengths of time the CdSe/CdS nanocrystal (core radius 1.9 nm, 3.5 ML of CdS) spent in (a) the off-level on a log–log scale; (b) in the intermediate intensity level; (c) and in the higher intensity level in log–linear scales. In panel a the line is a fit to an inverse power-law At^{-m} , with $m = 1.45 \pm 0.02$, whereas in panels b and c the data was fitted to stretched exponentials $y = A \exp -(t/\tau)^\beta$.

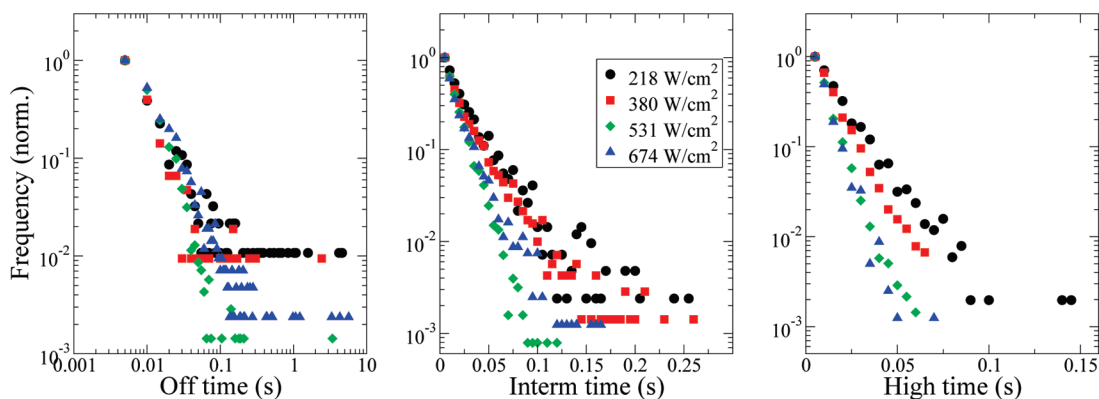
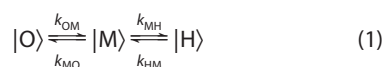


Figure 4. Effect of the excitation power on the blinking statistics of a single CdSe/CdS nanocrystal. The histograms correspond to the off times (left), the intermediate-level times (center), and the times spent at the high-intensity level (right). Excitation wavelength: 488 nm (cw).

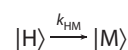
transitions between bright and dim states are at least partially of photophysical origin.

Careful analysis of time trajectories such as that of Figure 1 revealed that almost all of the discrete jumps in emission intensity occur between the high and intermediate levels ($\sim 92\%$ of the total number of jumps). Furthermore, the transitions to the off-state occur predominantly from the intermediate level (3.7% of total number of transitions) and likewise the recovery of the PL seems to be mediated by transitions between the "off" state and the intermediate level (3.8%). This indicates that the three-state pattern of Figure 1a results from the following transitions:



where $|H\rangle$ denotes a state assumed to be the (lowest state) exciton where the NC has a high emission QY with a monoexponential PL decay and is coupled to a state $|M\rangle$ that has a lower emission QY, and is in turn coupled to an off-state $|O\rangle$. In this empirical representation, the rates that connect $|H\rangle$ and $|M\rangle$ are much larger than those connecting $|M\rangle$ and $|O\rangle$ since the NC spends most of the time experiencing jumps between the bright and dim states. Further-

more, the exponential character of the histogram of Figure 3c indicates that



is a single-rate process, further supporting the assignment of $|H\rangle$ as a discrete emission state. The observed power-law distribution of off-times in Figure 3a implies that the transition $|O\rangle \rightarrow |M\rangle$ occurs *via* a manifold of kinetic pathways⁶ that must result from the existence of a distribution of states associated with $|O\rangle$ which in reference¹² we hypothesized to arise from unsaturated surface atoms in the NC (see also ref.⁸ where the traps are considered to be distributed in the surrounding matrix). We note that the kinetics of the state $|M\rangle$ are influenced by both $|H\rangle$ and $|O\rangle$, explaining why the histogram of Figure 3b deviates from a pure monoexponential.

In Figure 6, we present the PL time trajectory of a single CdSe/CdS NC, measured under alternating atmospheric conditions. In this figure, a drastic change in the emission pattern is immediately observed when the gaseous environment of the sample is changed from air to dry nitrogen and finally to wet nitrogen. In the dry nitrogen case, the PL is seen to continuously change

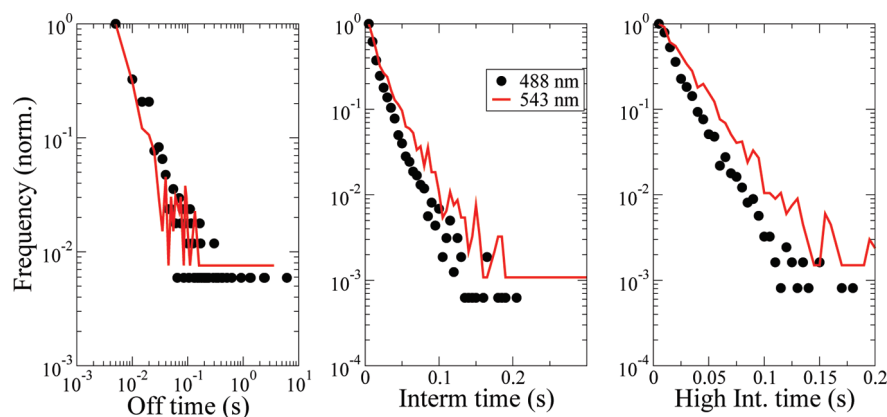


Figure 5. Effect of excitation energy on the statistics of blinking in a single CdSe/CdS nanocrystal. Histogram of off-times (left), times spent at the intermediate level (center), and times spent in the high intensity level (right). The dots correspond to excitation with cw laser light at 488 nm, whereas the line corresponds to 543 nm.

its intensity to and above the background level with lowered emission intensity, and without the pattern observed in Figure 6a. However, a three-state pattern appears after the introduction of $\text{H}_2\text{O}_{(\text{g})}$, indicating that the three-state blinking is only observable when the surface of the NCs is passivated, in this case, by oxygen and water.^{29,30} Notably, a lowered emission intensity was measured under $\text{N}_{2(\text{g})}/\text{H}_2\text{O}_{(\text{g})}$ which can be ascribed either to the lack of oxygen molecules which are known to influence the PL intensity³¹ or to a photodissociative adsorption process discussed by Ladizhansky *et al.*³² and Cordero *et al.*,³³ whereby physisorbed $\text{H}_2\text{O}_{(\text{g})}$ coexists with chemisorbed $-\text{OH}$, which might lead to irreversible photo-oxidation of the NC.

To explain these experimental observations, several scenarios must be considered: First, fast blinking events cannot be responsible for the observed three state blinking, since it is highly unlikely that such a random process would result in the histograms of Figure 1b and in the difference in PL decay lifetimes observed in Figure 2. The model proposed by Efros and Rosen² is expected to result in binary modulation of the PL, since according to their postulates, transitions occur from a neutral to a charged state (and vice versa), accordingly activating (deactivating) the Auger nonradiative decay channel. This results in discrete “on-off” blinking, clearly not accounting for the dim state. However, in a recent work by Jah and Guyot-Sionnest,³⁴ it was found that in films of CdSe/CdS NCs, the emission quantum yield of a trion (a multiparticle state consisting of either a positively T^+ or negatively charged T^- exciton) was in the $\sim 10\%$ to 15% range, which could account for the dim state reported here.

In CdSe/CdS NCs the hole wave function is localized in the core, whereas that of the electron is delocalized over the entire structure²⁷ (see Figure 1e). Consequently, it is likely that the species responsible for the dim state is due to reversible electron trapping in surface states. This results in a positively charged NC (*i.e.*, hole delocalized in the core). In this configuration, due to subsequent photoexcitation, a positively charged exciton, or a T^+ trion can exist in the NC. Nonradiative Auger recombination now competes with exciton recombination, resulting in a lowered QY. Thus, we postulate that in eq 1, $|H\rangle$ stems from exciton radiative recombination and $|M\rangle$ to T^+ radiative decay, and therefore the transitions $|H\rangle \rightleftharpoons |M\rangle$ would correspond to (discrete) electron transfer events between a quantum-confined energy state of the NC and a trap state.

This mechanism explains most of the key new observations, namely, the discrete nature of the jumps in emission intensity (the transition from a neutral exciton to a trion involves a discrete fluctuation in charge), and (at least qualitatively) the decrease in PL decay lifetime that occurs from $|H\rangle$ to $|M\rangle$. However, this model should also account for the observed complete quenching of the PL (*i.e.*, the “off” events) and sensitivity of

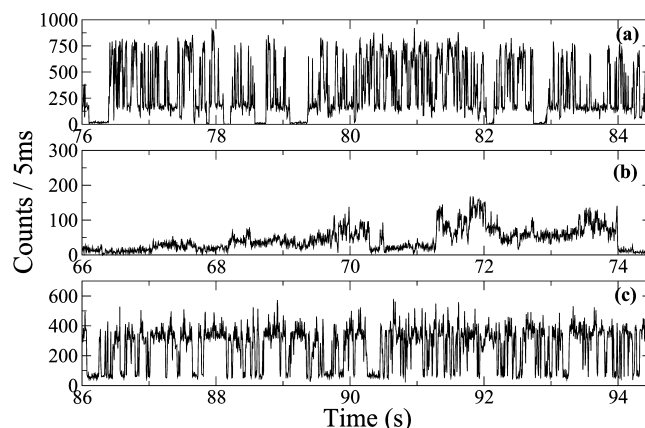


Figure 6. Effect of air exposure on the three-level blinking of a single CdSe/CdS nanocrystal. The sample was mounted in a chamber that could be flushed with dry nitrogen gas or ambient air. When this chamber was flushed with dry $\text{N}_{2(\text{g})}$ for 30 min (to ensure saturation), the three-state emission pattern changed to an on/off blinking (b). When the $\text{N}_{2(\text{g})}$ is bubbled through water, a three-state pattern was recovered during the course of photoexcitation (c). The lowered emission intensity in panel c can be related to the lack of $\text{O}_{2(\text{g})}$ molecules that are also known to bind and enhance the PL from single NCs.³⁰

blinking to the atmospheric environment, as we now discuss.

Large, passivating molecules such as primary alkyl amines and phosphine oxides, that adsorb to the NC surface during chemical synthesis cannot bind to every surface atom in the CdS shell due to steric hindrance, and this results in the presence of a number of surface states that can trap photoexcited electrons, generating a nonradiative decay channel that has a detrimental effect on the PL.^{35–37} Smaller molecules, such as $\text{H}_2\text{O}/\text{O}_2$, can reversibly bind to these sites thereby providing a means to complete the surface passivation.^{32,33} Surface passivation modifies the energetic distribution of surface states,^{12,37,38} since it results in a net shift (in energy) of these states away from the middle of the band gap toward the quantum-confined energy levels of either the electron or hole.³⁸ We have shown that the presence of these small atmospheric molecules is essential for both $|H\rangle$ state emission, and the observation of the transitions between the bright and dim states. Their absence not only results in a decreased PL QY but also in a loss of the discrete nature of the intensity jumps. To account for the $|M\rangle \rightleftharpoons |O\rangle$ transitions, we postulate that desorption of $\text{H}_2\text{O}/\text{O}_2$ molecules from the NC surface increases the number and broadens the distribution of surface traps, creating a kinetically and energetically broad pathway for the electron transfer events that control the exciton- T^+ trion transitions. If the surface is poorly passivated and multiple charge carriers are able to be accommodated in surface traps, the NC becomes dark as Auger recombination quickly dominates over radiative recombination. The intermediate state is recovered after incremental surface passivation (as in the case of Figure 6c). Importantly, this model predicts that the switching between bright and dark states can be completely reversible and explains

the fact that no photodegradation occurs despite extensive cycling between the bright, dim, and dark states of the nanocrystal. These postulates are supported by the recent results of Mahler *et al.*²³ and Chen *et al.*³⁹ who used CdSe/CdS NCs with thicker shells under similar experimental conditions and found the $|O\rangle \Rightarrow |M\rangle$ transition could be suppressed, while retaining similar $|H\rangle \Rightarrow |M\rangle$ transitions to those reported here. In these systems the electron is prevented from interacting with the surface, which clearly points to the overlap of the electron wave function with active surface states as a route to blinking in these materials. In previous studies of similar CdSe/CdS NCs, such as the one by Banin *et al.*²⁷ and Gómez *et al.*,¹² these discrete jumps in emission intensity were not observed. In both such studies, the NCs were synthesized by using organometallic precursors which are known to result in an increased number of structural defects in the NCs, consequently resulting in lower emission efficiencies. On the contrary, the CdSe/CdS NCs of the work presented here, were grown by use of less reactive precursors that result in a reduction in the number of such structural defects, translating into NCs with improved emission efficiencies.

CONCLUSION

We have observed fast and discrete fluctuations in the PL blinking in single CdSe/CdS NCs, dominated by

population of an intermediate dim state of lowered QY. For this type of blinking, the statistics describing the residence time of the NC in these emitting states were exponential, indicating that the transitions between these states occur *via* a single-rate process. The dim state facilitates the transition to the “off” state and stems from incomplete surface passivation that results in an increase of nonradiative relaxation due to the formation of a trion T^+ . The transitions to and from such trion states are controlled by the availability of surface traps, which is controlled, partially, by surface passivation.

NOTE

Recently, in a study of similar CdSe/CdS structures (thicker CdS shells), Spinicelli *et al.*⁴⁰ observed periods of low intensity emission with a QY of 19%, which they attributed to emission from a T^+ state. In this study it was argued that radiative recombination from such states was allowed in these pseudo type-II structures, due to a decrease in the Auger nonradiative recombination rate. Longer PL decay time constants were also observed, a result attributable to the presence of thicker CdS shells (lowered electron–hole wave function overlap). However, in this study the role of surface passivation in controlling this $|M\rangle$ state was not addressed.

METHODS

The CdSe NC cores were synthesized according to literature methods.⁴¹ These were overcoated with monolayers of CdS following a modified selective ion layer adsorption and reaction method.⁴² For the detection of the PL of individual NCs, we employed a confocal microscope in the epi-illumination configuration.¹² The PL was excited and collected with an oil-immersion objective (Olympus, PlanApo NA = 1.4) and the excitation sources consisted of the 488 nm line of an Ar⁺ laser (Melles–Griot), a HeNe laser operating at 543 nm and a pulsed laser diode ($\lambda = 466$ nm, 10 MHz repetition rate, PicoQuant, LDH-P-C-470). After passing through the confocal optics, the signal of interest was sent to an imaging spectrometer equipped with a liquid-nitrogen-cooled CCD for spectral measurements (Horiba JY, TRIAX 550) or to a Hanbury–Brown and Twiss interferometer comprising a nonpolarizing 50/50 beamsplitter and two avalanche photodiodes (Perkin–Elmer, SPCM-AQR-15). For (cw) antibunching measurements, the outputs of these detectors were connected to the start and stop channels of a photon counting card (PicoQuant, TimeHarp 200), which after the introduction of an electronic delay (about 80 ns) in one of the detector outputs, allowed for the measurement of photon interarrival times. The measurements of the PL decay times of individual NCs were carried out with the photon-counting card in time-tagged time-resolved mode (TTTR). Following the procedure described by Fisher *et al.*,²¹ from this TTTR data, it was possible to bin the “macro” times yielding the time trajectory of Figure 2a, and by using a threshold discrimination of the intensity (*i.e.*, number of photon counts in the “macro” time trajectory), we obtained the data presented as histograms in Figure 2b,c. For the case of cw excitation, the trajectories of the detected photon counts were measured with a counter-timer card (NI, PCI-6602). The samples for single NC detection were prepared by spin coating small amounts of a dilute dispersion of the NCs in chloroform on top of clean glass coverslips.

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Supporting Information Available: Representative blinking time trajectories; nanocrystal synthesis; effective mass model for the electron/hole wavefunctions. 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. Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals. *Nature* **1996**, *383*, 802–804.
- Efros, A. L.; Rosen, M. Random Telegraph Signal in the Photoluminescence Intensity of a Single Quantum Dot. *Phys. Rev. Lett.* **1997**, *78*, 1110–1113.
- Gómez, D. E.; Califano, M.; Mulvaney, P. Optical Properties of Single Semiconductor Nanocrystals. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4989–5011.
- Frantsuzov, P.; Kuno, M.; Janko, B.; Marcus, R. A. Universal Emission Intermittency in Quantum Dots, Nanorods, and Nanowires. *Nat. Phys.* **2008**, *4*, 519–522.
- Krauss, T. D.; Brus, L. E. Charge, Polarizability, and Photoionization of Single Semiconductor Nanocrystals. *Phys. Rev. Lett.* **1999**, *83*, 4840. Erratum: *Phys. Rev. Lett.* **2000**, *84*, 1638.
- Kuno, M.; Fromm, D. P.; Johnson, S. T.; Gallagher, A.; Nesbitt, D. J. Modeling Distributed Kinetics in Isolated Semiconductor Quantum Dots. *Phys. Rev. B* **2003**, *67*, 125304/1–125304/15.

7. Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G. Blinking Statistics in Single Semiconductor Nanocrystal Quantum Dots. *Phys. Rev. B* **2001**, *63*, 205316/1–205316/5.
8. Verberk, R.; van Oijen, A. M.; Orrit, M. Simple Model for the Power-Law Blinking of Single Semiconductor Nanocrystals. *Phys. Rev. B* **2002**, *66*, 233202/1–233202/4.
9. Cichos, F.; Martin, J.; von Borczyskowski, C. Emission intermittency in Silicon Nanocrystals. *Phys. Rev. B* **2004**, *70*, 115314.
10. Issac, A.; von Borczyskowski, C.; Cichos, F. Correlation between Photoluminescence Intermittency of CdSe Quantum Dots and Self-Trapped States in Dielectric Media. *Phys. Rev. B* **2005**, *71*, 161302/1–161302/4.
11. Xia, X.; Silbey, R. Fluorescence Intermittency of a Single Quantum System and Anderson Localization. Arxiv preprint cond-mat/0601092 (2006).
12. Gómez, D. E.; van Embden, J.; Jasieniak, J.; Smith, T. A.; Mulvaney, P. Blinking and Surface Chemistry of Single CdSe Nanocrystals. *Small* **2006**, *2*, 204–208.
13. Frantsuzov, P. A.; Marcus, R. A. Explanation of Quantum Dot Blinking without the Long-Lived Trap Hypothesis. *Phys. Rev. B* **2005**, *72*, 155321/1–155321/10.
14. Tang, J.; Marcus, R. A. Mechanisms of Fluorescence Blinking in Semiconductor Nanocrystal Quantum Dots. *J. Chem. Phys.* **2005**, *123*, 054704/1–054704/12.
15. Hanbury-Brown, R.; Twiss, R. Q. Correlation between Photons in Two Coherent Beams of Light. *Nature* **1956**, *177*, 27–29.
16. Michler, P.; Imamoglu, A.; Mason, M. D.; Carson, P. J.; Strouse, G. F.; Buratto, S. K. Quantum Correlation among Photons from a Single Quantum Dot at Room Temperature. *Nature* **2000**, *406*, 968–970.
17. Lounis, B.; Bechtel, H. A.; Gerion, D.; Alivisatos, P.; Moerner, W. E. Photon Antibunching in Single CdSe/ZnS Quantum Dot Fluorescence. *Chem. Phys. Lett.* **2000**, *329*, 399–404.
18. Messin, G.; Hermier, J. P.; Giacobino, E.; Desbiolles, P.; Dahan, M. Bunching and Antibunching in the Fluorescence of Semiconductor Nanocrystals. *Opt. Lett.* **2001**, *26*, 1891–1893.
19. Empedocles, S. A.; Bawendi, M. G. Influence of Spectral Diffusion on the Line Shapes of Single CdSe Nanocrystallite Quantum Dots. *J. Phys. Chem. B* **1999**, *103*, 1826–1830.
20. Gómez, D. E.; van Embden, J.; Mulvaney, P. Spectral Diffusion of Single Semiconductor Nanocrystals. The Influence of the Dielectric Environment. *Appl. Phys. Lett.* **2006**, *88*, 154106/1–154106/3.
21. Fisher, B. R.; Eisler, H.-J.; Stott, N. E.; Bawendi, M. G. Emission Intensity Dependence and Single-Exponential Behavior in Single Colloidal Quantum Dot Fluorescence Lifetimes. *J. Phys. Chem. B* **2004**, *108*, 143–148.
22. Schlegel, G.; Bohnenberger, J.; Potapova, I.; Mews, A. Fluorescence Decay Time of Single Semiconductor Nanocrystals. *Phys. Rev. Lett.* **2002**, *88*, 137401/1–137401/4.
23. Mahler, B.; Spinicelli, P.; Buil, S.; Quelin, X.; Hermier, J.-P.; Dubertret, B. Towards Non-blinking Colloidal Quantum Dots. *Nat. Mater.* **2008**, *7*, 659–664.
24. Zhang, K.; Chang, H.; Fu, A.; Alivisatos, A. P.; Yang, H. Continuous Distribution of Emission States from Single CdSe/ZnS Quantum Dots. *Nano Lett.* **2006**, *6*, 843–847.
25. Watkins, L. P.; Yang, H. Detection of Intensity Change Points in Time-Resolved Single-Molecule Measurements. *J. Phys. Chem. B* **2005**, *109*, 617–628.
26. Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. Nonexponential Blinking Kinetics of Single CdSe Quantum Dots: A Universal Power Law Behavior. *J. Chem. Phys.* **2000**, *112*, 3117–3120.
27. Banin, U.; Bruchez, M.; Alivisatos, A. P.; Ha, T.; Weiss, S.; Chemla, D. S. Evidence for a Thermal Contribution to Emission Intermittency in Single CdSe/CdS Core/Shell Nanocrystals. *J. Chem. Phys.* **1999**, *110*, 1195–1201.
28. Knappenberger, K. L.; Wong, D. B.; Romanyuk, Y. E.; Leone, S. R. Excitation Wavelength Dependence of Fluorescence Intermittency in CdSe/ZnS Core/Shell Quantum Dots. *Nano Lett.* **2007**, *7*, 3869–3874.
29. Koberling, F.; Mews, A.; Basche, T. Oxygen-Induced Blinking of Single CdSe Nanocrystals. *Adv. Mater.* **2001**, *13*, 672–676.
30. Müller, J.; Lupton, J. M.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. Air-Induced Fluorescence Bursts from Single Semiconductor Nanocrystals. *Appl. Phys. Lett.* **2004**, *85*, 381–383.
31. Kippeny, T. C.; Bowers, M. J., II; Dukes, A. D., III; McBride, J. R.; Orndorff, R. L.; Garrett, M. D.; Rosenthal, S. J. Effects of Surface Passivation on the Exciton Dynamics of CdSe Nanocrystals As Observed by Ultrafast Fluorescence Upconversion Spectroscopy. *J. Chem. Phys.* **2008**, *128*, 084713/1–084713/7.
32. Ladizhansky, V.; Hodes, G.; Vega, S. Solid State NMR Study of Water Binding on the Surface of CdS Nanoparticles. *J. Phys. Chem. B* **2000**, *104*, 1939–1943.
33. Cordero, S. R.; Carson, P. J.; Estabrook, R. A.; Strouse, G. F.; Buratto, S. K. Photo-Activated Luminescence of CdSe Quantum Dot Monolayers. *J. Phys. Chem. B* **2000**, *104*, 12137–12142.
34. Jha, P. P.; Guyot-Sionnest, P. Trion Decay in Colloidal Quantum Dots. *ACS Nano* **2009**, *3*, 1011–1015.
35. Jasieniak, J.; Mulvaney, P. From Cd-Rich to Se-Rich—The Manipulation of CdSe Nanocrystal Surface Stoichiometry. *J. Am. Chem. Soc.* **2007**, *129*, 2841–2848.
36. Fomenko, V.; Nesbitt, D. J. Solution Control of Radiative and Nonradiative Lifetimes: A Novel Contribution to Quantum Dot Blinking Suppression. *Nano Lett.* **2008**, *8*, 287–293.
37. Jones, M.; Lo, S. S.; Scholes, G. D. Quantitative Modeling of the Role of Surface Traps in CdSe/CdS/ZnS Nanocrystal Photoluminescence Decay Dynamics. *Proc. Natl. Acad. Sci.* **2009**, *106*, 3011–3016.
38. Li, S.; Steigerwald, M. L.; Brus, L. E. Surface States in the Photoionization of High-Quality CdSe Core/Shell Nanocrystals. *ACS Nano* **2009**, *3*, 1267–1273.
39. Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. “Giant” Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J. Am. Chem. Soc.* **2008**, *130*, 5026–5027.
40. Spinicelli, P.; Buil, S.; Quélin, X.; Mahler, B.; Dubertret, B.; Hermier, J.-P. Bright and Grey States in CdSe-CdS Nanocrystals Exhibiting Strongly Reduced Blinking. *Phys. Rev. Lett.* **2009**, *102*, 136801.
41. van Embden, J.; Mulvaney, P. Nucleation and Growth of CdSe Nanocrystals in a Binary Ligand System. *Langmuir* **2005**, *21*, 10226–10233.
42. van Embden, J.; Jasieniak, J.; Gómez, D. E.; Giersig, M.; Mulvaney, P. Review of the Synthetic Chemistry Involved in the Production of Core/Shell Semiconductor Nanocrystals. *Aust. J. Chem.* **2007**, *60*, 457–471.