# *Challenge to the Charging Model of Semiconductor-Nanocrystal Fluorescence Intermittency from Off-State Quantum Yields and Multiexciton Blinking*

# Challenge to the Charging Model of Semiconductor-Nanocrystal Fluorescence Intermittency from Off-State Quantum Yields and Multiexciton Blinking

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Semiconductor nanocrystals emit light intermittently; i.e., they ''blink,'' under steady illumination. The dark periods have been widely assumed to be due to photoluminescence (PL) quenching by an Auger-like process involving a single additional charge present in the nanocrystal. Our results challenge this long-standing assumption. Close examination of exciton PL intensity time traces of single CdSe(CdZnS) core (shell) nanocrystals reveals that the dark state PL quantum yield can be 10 times less than the biexciton PL quantum yield. In addition, we observe spectrally resolved multiexciton emission and find that it also blinks with an on/off ratio greater than 10:1. These results directly contradict the predictions of the charging model.

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Since the discovery of fluorescence intermittency (blinking) in single colloidal semiconductor nanocrystals (NCs), also known as quantum dots (QDs) [1,2], significant effort has been devoted to understanding the mechanism of its dynamics with the aim of control by a judicious choice of materials. Blinking plays an important role in the performance of NCs in a variety of applications. For example, QD LED brightness [3–7] and NC lasing [8] efficiency are compromised if a significant fraction of nanocrystals are not emissive at a given moment, and the use of single NCs both as biological trackers [9–11] and as single photon sources [12–15] is also limited when the NC blinks off. The dark periods have long been thought to be the result of the NC's charging with a single delocalized carrier [16], but to date there has been no direct experimental evidence supporting this assumption. The results presented here challenge the charging hypothesis.

Although blinking suppression has been recently reported in CdSe(CdS) core(shell) NC samples [17,18], rational design requires understanding the blinking mechanism. Originally, it was proposed that the off-state NC is in fact a charged NC [1,16,19] with the charge delocalized in a QD electronic state (as opposed to trapped on the surface). In the presence of this additional carrier, say a hole, any photogenerated electron-hole pair could efficiently recombine and simultaneously promote the extra hole deep into the valence band via a single energy-conserving Coulomb interaction. Experiments on multiexciton (MX) population dynamics have shown that Auger processes are very efficient in NCs [15,20,21]. Many physical pictures have been developed since to explain the intriguing statistics of the blinking process [22–26]. The fundamental element of the original off-state mechanism remains widely accepted today. Regardless of how the NC is thought to become charged, it is the Auger relaxation mechanism activated by the delocalized charge that is believed to render the NC nonemissive.

In this work we test the charging model by examining the fluorescence intermittency of NCs with comparatively slow MX Auger decay rates due to their large size [15]. We use the fact that charged exciton states (i.e., ''trions'') and normal MX states share the Auger process as a common fluorescence quenching mechanism to estimate the ''on''-''off'' intensity ratios for exciton (X) and MX emission within the charging model framework. We measured experimental on-off ratios of X and MX emission, and we found them both to be significantly larger than would be predicted by the charging model. We conclude that the off nonradiative decay pathway is too fast to be explained by Auger processes involving just a single additional carrier. We discuss possible modifications and extensions of existing models that would be compatible with our findings.

For single NC experiments, a dilute solution of 5 nm core radius CdSe(CdZnS) core(shell) NCs (synthesized by our group or from Quantum Dot Corp.) and polymethylmethacrylate was spun onto a cover glass (Electron Microscopy Sciences). Single NCs were excited through a 100× 1.40 NA oil immersion objective (Nikon) with a pulse-picked Ti:sapphire laser frequency-doubled to 400 nm (3.1 eV) at 4.75 MHz, a pulsed diode laser at 414 nm (3.0 eV) (PicoQuant) at 5 MHz, or continuous $Ar^+$ laser at 514 nm (2.4 eV). The emission was collected through the same objective and directed with a beam splitter onto two avalanche photodiodes (Perkin Elmer) in a Hanbury Brown–Twiss geometry. Bandpass filters transmitting $650 \pm 20$ nm (1.85–1.97 eV) and $610 \pm 5$ nm (2.02–2.05 eV) were used to isolate X and biexciton (BX) emission at one avalanche photodiode (channel 1) and MX $1P_e$ emission at the other (channel 2). Photon cross correlation and intensity time traces of both channels were measured with a Timeharp200 (Picoquant) and pulse counters (National Instruments). A portion of the NC emission was dispersed on a charged coupled device (Pentamax, Princeton Instruments) for spectral monitoring.

 

Transient photoluminescence (PL) spectra of NCs in hexane under 1 kHz 3.1 eV excitation from an amplified Ti: sapphire laser were obtained by dispersion on a streak camera (Hamamatsu C5680). All measurements were performed at room temperature.

Under both continuous and pulsed excitation, blinking on/off ratios of $>100{:}1$ have been observed in a number of commercial and homemade single NCs. Figure 1 shows a representative blinking trace of a single NC excited at 3.1 eV, 10 $\mu J \cdot cm^{-2}$ (calculated assuming a diffraction limited spot size, same below) [27]. The on and off count rates of the band edge emission in Fig. 1(a) are $\approx$46 000 cps and $\approx$300 cps, indicating that the off X quantum yield (QY) is less than 0.01 relative to the on X. On/off ratios exceeding 100:1 were also found using $\approx$30 ps pulse width 3.0 eV excitation and 2.4 eV continuous excitation [28], and in samples of CdSe(CdZnS) core (shell) NCs prepared in our group [28]. For comparison, we note that the BX QY of the NC in Fig. 1 is estimated as $\approx$12% using a method described in a separate study based on photon cross correlation [29], consistent with a previous ensemble transient PL estimate of 11% [15].

Figure 2 illustrates our MX blinking experiment. In CdSe NCs, MXs starting from the triexciton (TX) onwards, in addition to emitting at the band edge 1S-1S transition, also emit at a blueshifted band because of electron occupation of the $1P_e$ level [15,30–32]. With the choice of appropriate spectral filters and given our sample's relatively long MX lifetimes [15], we have been able to separate the band edge emission (channel 1) from the $1P_e$ emission of MXs (channel 2).

The principal challenge in the MX emission experiment was to detect MX emission from single NCs and quantify how well it has been isolated from the X emission. By using short acquisition times, simultaneously monitoring the NC PL spectrum to make sure the peak shifts less than $\pm$5 nm, and periodically checking the NC's behavior under low fluence, we ensure the integrity of the NC during the course of the MX experiments.

We verified that the channel 2 signal is primarily due to MX emission and not X leakage at high excitation powers by two independent methods. The first is based on the $g^{(2)}$ correlation data of the two channels and the second is estimated from the PL time traces we simultaneously collect. Figure 2(c) shows the channel 1-channel 2 cross correlation histogram. Unlike the X signal autocorrelation, which is completely symmetric [28], the channel 1-channel 2 cross correlation is markedly asymmetric. The asymmetry of the side peaks of the cross correlation shows that the

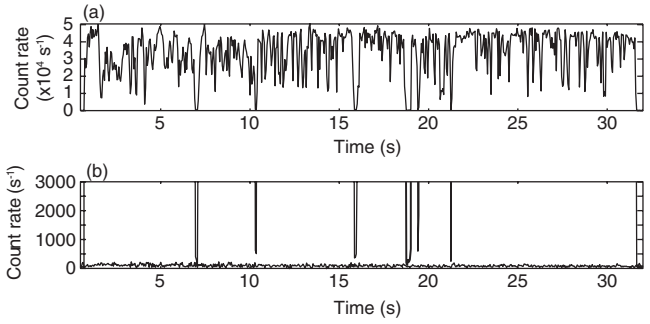


FIG. 1. (a) Blinking time trace of a single NC and (b) an expanded view of the baseline showing off periods with count rate as low as ~300 cps.

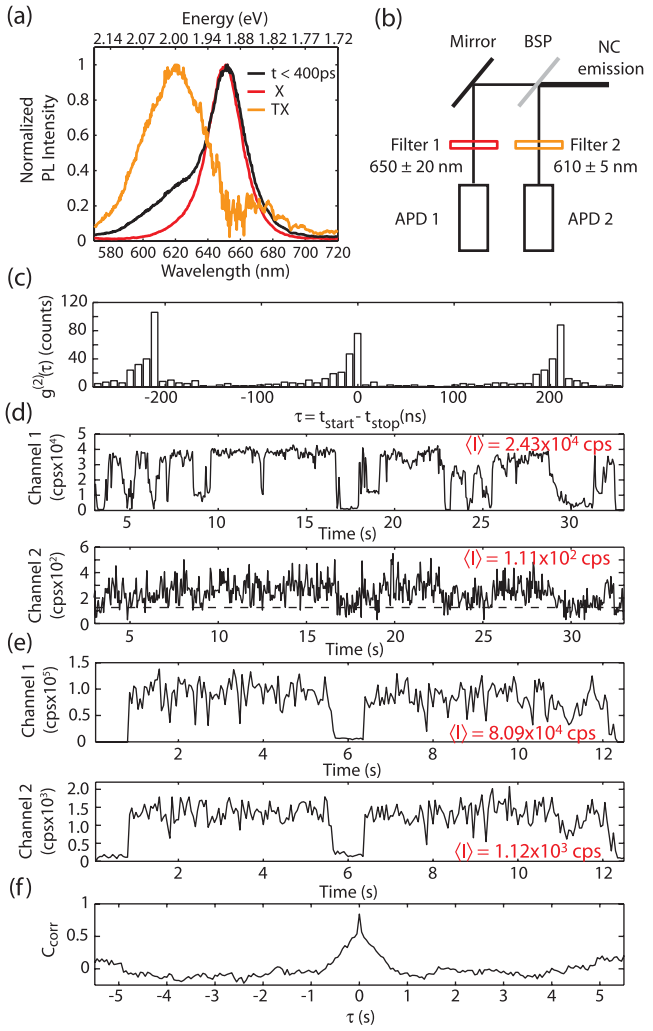


FIG. 2 (color online). (a) Transient PL of ensemble CdSe(CdZnS) core(shell) NCs in hexane. The black spectrum is averaged over the first 400 ps after the excitation pulse, containing both $1P_e$ and band edge emission. The red spectrum is averaged over 750 ps after 1 ns delay following the excitation pulse, and is only from the X band edge emission. The orange spectrum is obtained by subtracting the X emission contribution from the black spectrum, representing the $1P_e$ emission. (b) Schematic illustration of the experimental setup. (c) Cross correlation of signals in the two channels. (d)–(e) PL traces of a single NC excited at (d) 10 $\mu J \cdot cm^{-2}$ and (e) 400 $\mu J \cdot cm^{-2}$. The black dashed line in the channel 2 trace in (d) denotes the average background counts at the same excitation power. The average count rate of each time trace after background subtraction is labeled in red. The integrated intensity ratio channel 2 to 1 is 0.46% in (d) and 1.38% in (e). (f) Correlation coefficient of the time traces in (e).

channel 2 signal has a much shorter lifetime than that of channel 1, a clear signature of MX detection. Such asymmetric peaks would be impossible if the majority of the signal was due to X leakage. Furthermore, Fig. 2(d) shows the PL intensity time traces collected in both channels from a single NC under an excitation fluence of 10 $\mu J \cdot cm^{-2}$. At such low power, MX populations are negligible and the signal in both channels is from X emission. At a high excitation power of 400 $\mu J \cdot cm^{-2}$, [Fig. 2(e)] the PL intensity ratio of channel 2 to channel 1 increases to 1.38% from 0.46%, a factor of 3 increase from the low fluence data directly resulting from the MX contribution.

Quantitative analysis of the cross correlation peak asymmetry and the time trace intensity ratios in Fig. 2 independently estimate that at least 50% of the channel 2 signal at high power originates from MX $1P_e$ emission [28]. The similarity of the two time traces shows that MX emission blinks and its blinking is correlated with the band edge emission intermittency. The correlation coefficient $C_{\mathrm{corr}}$ of the two time traces is calculated with periodic boundary conditions and plotted in Fig. 2(f) [33]. We estimate a MX emission on/off ratio greater than 10:1 from the observed $\sim$1600 cps (>800 cps from MX) and $\sim$50 cps channel 2 on and off levels after background subtraction. Similar MX on/off ratios were observed on a variety of NCs.

In the charging model an off NC is a singly charged NC with charge in a delocalized QD electronic state, and its low QY is entirely due to Auger recombination. The QY is given by the ratio of the radiative rate to the total radiative rate $\eta = k_{\mathrm{rad}}/k_{\mathrm{tot}}$. By counting the total number of recombination pathways of a CdSe NC, it can be shown that the charged exciton radiative rate is half that of a BX $k^{\mathrm{rad}}_{\mathrm{X}^{\pm}} \approx \frac{1}{2} k^{\mathrm{rad}}_{\mathrm{BX}}$ in the high temperature limit [28]. The total decay rate of both species is dominated by the nonradiative Auger decay, so $k_{\mathrm{tot}} \approx k_{\mathrm{nr}}$. The off X decay rate $k^{\mathrm{nr}}_{\mathrm{Xoff}}$ is either $k_{\mathrm{X}^+}$ or $k_{\mathrm{X}^-}$ depending on whether the extra charge is assumed positive or negative. The BX can decay by promoting either one of the two holes or either of the two electrons to higher kinetic energy states. In the strong electronic confinement limit [34], the rates of the hot electron and hot hole pathways are the same as in negatively and positively charged excitons and $k^{\mathrm{nr}}_{\mathrm{BX}} = 2k_{\mathrm{X}^+} + 2k_{\mathrm{X}^-}$ [35,36]. Then:

$$\frac{\eta_{\mathrm{X}^{\pm}}}{\eta_{\mathrm{BX}}} \approx \frac{k_{\mathrm{X}} + k_{\mathrm{X}^-}}{k_{\mathrm{X}^{\pm}}} \geq 1. \tag{1}$$

The charging model therefore predicts that the off-state $X$ cannot have a lower emission QY than a BX state. This conflicts with our finding that $\eta^{\mathrm{off}}_{\mathrm{X}} < 0.01$ (Fig. 1) for NCs with $\eta_{\mathrm{BX}} \approx 0.1$ [15]. The factor of 10 discrepancy points to an inability of the traditional Auger mechanism to account for off-state PL quenching [37]. Our finding is consistent with a recent report on the optical properties of charged ensemble CdSe/CdS NC thin films by Jha and Guyot-Sionnest which suggested that negative charging of the NC films may not lead to sufficient PL quenching to explain blinking [36].

The charging model also predicts a very specific modification of MX QY during blinking off periods. We consider first a TX state and a charged $\mathrm{TX}^{\pm}$ state (as shown in Figs. 3(c) and 3(d)) [30,32]. For similar reasons as in the $\mathrm{BX}/\mathrm{X}^{\pm}$ comparison, the radiative rate for $1P_e$ band emission is faster for the charged TX than for the neutral TX. The nonradiative rates can be estimated by noting that $k^{\mathrm{nr}}_{\mathrm{TX}} < k^{\mathrm{nr}}_{\mathrm{TX}^{\pm}} < k^{\mathrm{nr}}_{\mathrm{QX}}$ where QX is a $4e$-$4h$ configuration. From our ensemble transient PL data, we derive an experimental upper bound of $k^{\mathrm{nr}}_{\mathrm{QX}}/k^{\mathrm{nr}}_{\mathrm{TX}} \approx 3.8$ given by the ratio of fast to slow rates observed in the $1P_e$ emission dynamics. This gives us a bound on the relative quantum yields of on- and off- TX states:

$$1 > \frac{\eta_{\mathrm{TX}^{\pm}}}{\eta_{\mathrm{TX}}} > \frac{k^{\mathrm{nr}}_{\mathrm{TX}}}{k^{\mathrm{nr}}_{\mathrm{QX}}} \approx 0.26. \tag{2}$$

The charged/neutral QY ratio is expected to be larger still for higher multiexcitons. Our conservative estimate also does not factor in the larger radiative rate of a $\mathrm{TX}^{\pm}$ state relative to a TX state. The charging model therefore predicts that the MX $1P_e$ emission on/off ratio should not exceed $\sim$4. Instead, our data show a 10:1 MX emission on/off ratio. This finding, like our observation that the BX QY is significantly larger than the off-state X QY, supports a general conclusion that the off nonradiative decay pathway is too fast to be explained by a traditional Auger process involving just a single additional delocalized carrier [39].

We suggest two classes of models that may be compatible with our experimental findings. Recent reports on the blinking of single CdSe(CdS) core(shell) NCs show a clearly defined intermediate emission (''grey'') state with a faster radiative rate than the on state [40,41], which suggests that at least in those materials charging occurs when the NCs blink. On the other hand, our study has shown that a single charge is not sufficient to explain the off-state PL quenching of the CdSe(CdZnS) NC samples we studied. However, if off NCs contained several charges, the Auger mechanism can readily ensure that both $\eta^{\mathrm{off}}_{\mathrm{X}} \ll \eta^{\mathrm{on}}_{\mathrm{BX}}$ and $\eta^{\mathrm{off}}_{\mathrm{MX}} \ll \eta^{\mathrm{on}}_{\mathrm{MX}}$. Gómez *et al.* have invoked multiple charging as a possible explanation of the completely dark off states occasionally visited by their CdSe(CdS) NCs [41]. The microscopic model developed by Frantsuzov and Marcus [26], for example, can be extended to allow for rapid charge buildup within an NC. In their model, the NC blinks off when a large number of surface hole traps become simultaneously active, and several charges can accumulate in the NC volume. When the NC blinks back on the trapped holes recombine with the electrons and the NC fluorescence efficiency fully recovers.

Another class of models would involve trap-assisted instead of Auger-mediated recombination. Upon absorbing a photon during an off state, either the photogenerated hole or electron is trapped in a defect site either at the outer interface of the NC, at the core-shell interface or within the core-shell structure itself. The remaining carrier soon after recombines with the trapped carrier, completing a cycle that returns the NC to a neutral state. On-off transitions

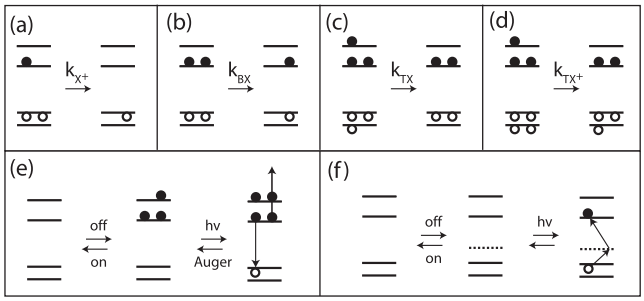


FIG. 3. (a)–(d) Schematics of the various recombination processes of interest for our experiment: (a) charged $X$ (''trion'') Auger decay as in the off state of blinking NCs; (b) neutral BX; (c) neutral TX; (d) charged TX. (e)–(f) Schematics of alternative blinking mechanisms: (e) trapping multiple charges; (f) trap-assisted recombination.

would occur when access to the trap is opened or closed. From the measured X blinking on/off ratio, the trap rate has to be at least 100 times faster than the radiative rate of the NC to account for the low $\eta_X^{\text{off}}$. Generally, microscopic models based on spectral diffusion-controlled access to traps, such as the one proposed by Shimizu *et al.* [22] and extended by Tang and Marcus [25,42], and recently by Frantsuzov *et al.* [43] could take a trapping-recombination form if the recombination rates are rapid enough.

We have investigated MX emission blinking of single NCs and compared the luminescence efficiency of the off-X and on-BX states. The QY of the off X state is found to be at least 10 times smaller than would be predicted by the charging model of blinking in the strong confinement limit. MX $1P_e$ emission shows strong 10:1 on/off blinking in coincidence with the band edge intermittency, whereas the charging model predicts only weak blinking. We believe that our results point to a need for a deeper look into the off-state PL quenching mechanism in CdSe NCs.

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