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Surface Charge Control of Quantum Dot Blinking

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ⓢ *Supporting Information*

ABSTRACT: A characteristic property of colloidal semiconductor nanocrystal quantum dots (QDs) is their emission intermittency. Although a unifying theory of QD photoprocesses remains elusive, the importance of charged states is clear. We now report a new approach to directly study the role of surface charge on QD emission by adding metal ions to individual, core-only QDs immobilized in aqueous solution in an agarose gel. The CdTe QDs show very stable emission in the absence of metal ions but a dramatic and reversible increase in blinking due to the presence of trivalent metal ions. Our results support a charge-separation model, in which the major blinking pathway is the surface trapping of electrons; transiently bound metal ions close to the QD surface enhance this process.
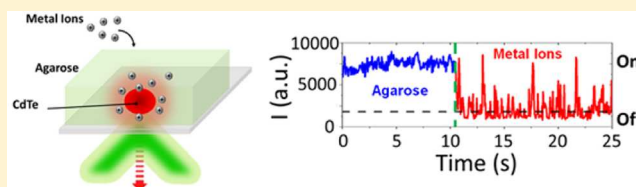
INTRODUCTION

Photoluminescence (PL) intermittency, also termed blinking, is a universal feature of emitters ranging from small molecular fluorophores,[1,2] fluorescent proteins,[3] and conjugated polymers[4] to nanoscale emitters such as semiconductor quantum dots (QDs)[5] and diamond nanocrystals.[6] Until recently, the blinking of QDs was primarily seen as a disadvantage, especially for applications such as particle tracking[7] and solar cells[8] where long-lived dark states are unwanted. In contrast, the emergence of super-resolution imaging techniques that utilize the stochastic switching of fluorescence between "on" and "off" states has meant that blinking QDs are also highly desirable.[9−11] The resistance to photobleaching, together with other desirable optical properties, gives blinking QDs a distinct advantage in such applications.

It is well established that the PL intensity for QDs randomly jumps between highly emissive "on" states and nonemissive "off" states under continuous excitation.[5,12,13] Rather than displaying two-state on/off dynamics, the on states display a continuous distribution of emissive states.[14] The distribution of on and off times span up to 6 orders of magnitude, corresponding to almost 9 orders of magnitude in probability density, which are generally assigned to power law kinetics.[15,16] Many studies have also reported truncated power law behavior,[17] though the exact form of on/off distributions is sensitive to the methods employed for data analysis.[18] There is also recent evidence that the apparent power law distributions are due to a superposition of exponential functions.[16]

Therefore, in spite of nearly two decades of experimental studies of the photophysical and charge transport properties of QDs, the mechanism of blinking in QDs is still the subject of vigorous debate.[13,16,19,20] It is possible that several different mechanisms are operating in parallel, depending on the particular sample, environment, and experimental conditions. Nevertheless, there has been an attempt to find a universal blinking mechanism. The first model that gained acceptance involved the long-time charging of a single QD core, with subsequent excited-state energy lost nonradiatively via Auger recombination.[21,22] However, various studies have questioned this model.[23−25] The recently developed multiple recombination centers (MRC)[26−28] model invokes multiple surface hole traps with fluctuating trapping rates. This has been recently extended to include additional electron trapping pathways,[16] in part to accommodate experimental evidence that QD blinking can be altered through surface or solution modifications.[29−31] More recent experiments[32,33] have confirmed the existence of delayed emission,[34,35] which can only be explained by long-lived charge-separated states; a modified version of the Auger quenching model was proposed, with a suggested assignment of the electron as the trapped carrier.[32,33]

One of the reasons that it has been so difficult to develop a detailed blinking mechanism for QDs is the difficulty in correlating bulk charge distributions with specific surface processes. Important previous studies have involved adjusting the bulk solution environment with a change in pH,[36] via electrochemical methods,[37,38] by intraparticle charge transfer[39] by altering the bulk matrix,[40−42] by adding a shell[30] or capping ligands,[29,31] or by applying external electric fields.[43] In this work, we describe a new experimental approach to directly probe the effect of surface-localized charge on the QD emission by immobilizing core-only QDs in agarose gel and adding metal ions in aqueous solution (Figure 1a). We attribute the blinking to the occupation of surface traps enabled by kinetically labile positive metal ions bound to the agarose close to the QD surface. Our data are consistent with a model in which blinking results from the surface trapping of electrons.[32,33]
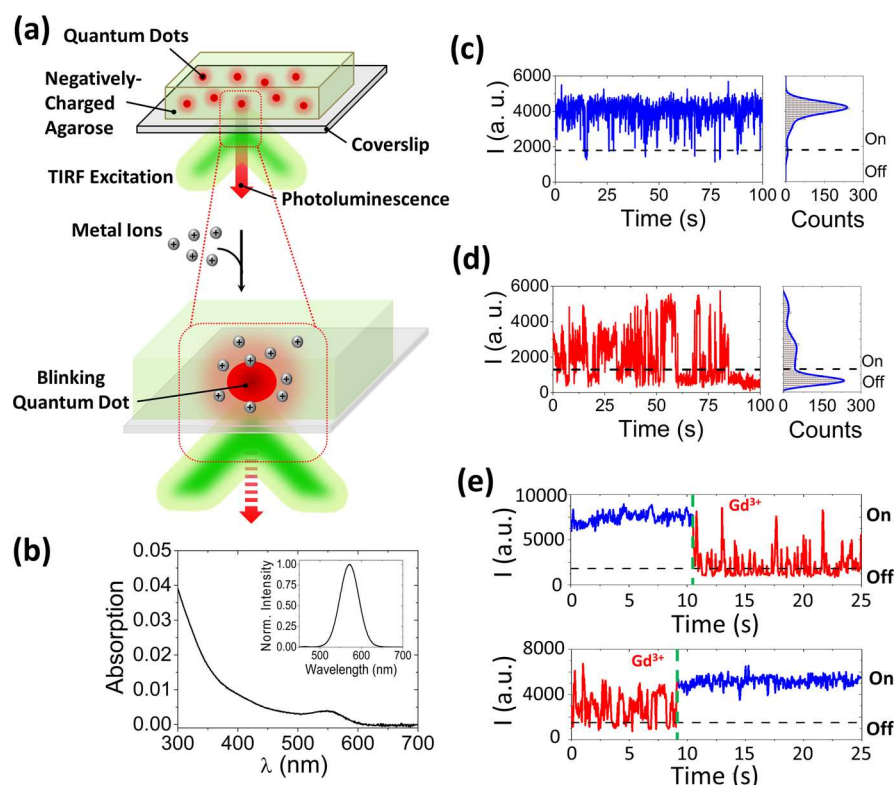
Figure 1. Surface charge control of CdTe quantum dot blinking. (a) Experimental design of single-particle imaging to visualize CdTe QDs immobilized within a 1% (w/v) agarose gel at pH 8 using wide-field o-TIRF microscopy (upper panel). The injection of trivalent ions, introduced as metal nitrates changes the emission properties (lower panel). (b) Absorption spectrum of CdTe QDs (25 nM) at pH 8; inset shows the fluorescence emission spectrum with λ_{exc} = 400 nm. (c) Typical intensity trajectory of a single CdTe QD immobilized within 1% agarose gel at pH 8 with 532 nm excitation and (d) after injection of 10 μM Gd^{3+} ions. (e) The upper panel shows a single CdTe QD intensity trace in 1% agarose gel as Tris-HCl buffer containing 10 μM Gd^{3+} was injected at ca. 10 s (green dashed line). The lower panel demonstrates the reverse scenario where Gd^{3+} buffer was washed away by injecting 20 mM Tris-HCl (pH 8) buffer after ca. 10 s.

## ■ RESULTS AND DISCUSSION

Hydrophilic CdTe QDs (λ_{em} = 580 nm), which are capped with mercaptocarboxylic acids, were first characterized using ensemble spectroscopy in aqueous solution (Figure 1b). The QDs were stable at the concentrations and pH used for sample preparation (Figures S1 and S2). For single-particle experiments, the QDs were rapidly diluted to the 1−10 pM level. Immobilization of QDs in agarose was achieved by adapting protocols used previously for immobilizing enzymes and proteins in an aqueous environment.[44] Gels were prepared by adding 1−10 pM CdTe QDs to a buffered (pH 8), molten 1% (w/v) agarose solution at 26−30 °C. A small volume of the molten solution was added to a precleaned glass coverslip and allowed to cool and form a gel. The concentration of the QDs in solution was adjusted to give good surface density for single-particle experiments. Emission trajectories of several hundred QDs in parallel were acquired using objective-type total internal reflection fluorescence (oTIRF) microscopy. All single-particle measurements were acquired with an excitation wavelength of 532 nm and excitation intensity of 130 W/cm^2.

The QD immobilization was found to be pH dependent. QDs added to agarose in pH 7 buffer did not immobilize and were seen to be freely diffusing. Increasing the pH increased the number of fixed QDs, with 100% bound at pH 8. We attribute this to Coulombic interactions of the QD with the agarose, which contains negatively charged substituents (particularly pyruvate and sulfate).[45] Under dilute single-molecule conditions, the labile QD capping ligands can dissociate; bulk

studies demonstrate slow aggregation (on a time scale of several minutes for a 10-fold dilution), which we attribute to ligand loss, as discussed previously (Figure S3).[46] Addition of metal ions to such concentrated QD solutions leads to rapid aggregation (Figure S4 and Table S1). Such conditions have previously been used to study the effects of metal ions on QDs,[47] but we believe that it is not possible to unambiguously assign diffraction limited spots to single QDs under such conditions. Our method of rapid dilution and immobilization in agarose avoids issues of aggregation.

Single-particle imaging of immobilized QDs was performed in the absence and presence of M(NO$_3$)$_3$(aq), where M = Al^{3+}, Y^{3+}, and Gd^{3+} (Figure 1a). We chose these metal ions because they are all tripositive, have large differences in ionic radius, and include both diamagnetic (Al^{3+} and Y^{3+}) and paramagnetic (Gd^{3+}) ions. In 1% (w/v) agarose gel at pH 8, the emission intensity of CdTe QDs displayed a notable lack of blinking observed on the time scales investigated (Figure 1c and Figure S5). Core−shell QDs (CdSe/ZnS) have been studied in agarose previously, and the observed reduced blinking has been attributed to the negatively charged polysaccharide.[48] In the presence of trivalent ions, however, we observed that the blinking of the CdTe QDs was greatly enhanced (Figure 1d). For example, for QDs incubated with 10 μM Gd^{3+}, the majority of traces analyzed (70%) displayed significantly higher levels of blinking, with only 3% in total remaining entirely photostable over the 100 s measurement time window. Notably, the predominant effect was to modulate the blink frequency rather
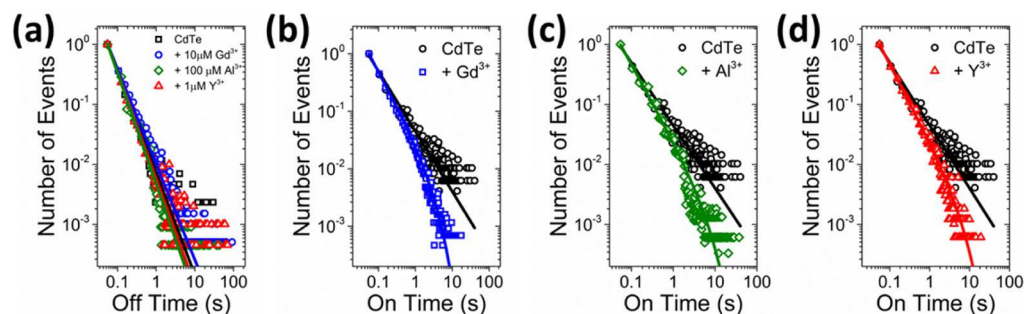
Figure 2. Statistics of on- and off-dwell times. (a) Normalized off-time histograms of CdTe immobilized within a 1% (w/v) agarose gel (pH 8) in the absence (black) and presence of 10 μM Gd^{3+} (blue), 100 μM Al^{3+} (green), and 1 μM Y^{3+} (red) ions. The solid lines represent power law fits of the form $y = Ct^{-\alpha}$, where C is a constant, with similar exponents (α = 1.70 (black), 1.59 (blue), 1.83 (green), and 1.75 (red)). Normalized on-time histograms of immobilized CdTe in the absence (black) and presence of (b) 10 μM Gd^{3+} (blue), (c) 100 μM Al^{3+} (green), and (d) 1 μM Y^{3+} (red) are also shown. The solid black lines represent power law fits with α = 1.04. The solid blue, green, and red lines represent truncated power law fits ($y = Ct^{-\alpha}e^{-\Gamma t}$, where C is a constant) with similar exponents and truncation factors (α = 1.20, Γ = 0.30 s^{-1} (blue); α = 1.27, Γ = 0.13 s^{-1} (green); α = 1.27, Γ = 0.14 s^{-1} (red)).

than the peak intensity. The effect of the trivalent ions appears to be instantaneous on our measurement time scale, since the blinking behavior was immediately altered as soon as they were injected into the sample (upper trace in Figure 1e). We found that this process could be reversed by flushing the QDs with buffer at pH 8 (lower trace in Figure 1e). There is no change in pH upon adding the metal salts, ruling out this as a cause of the increased blinking.

To quantitatively analyze blinking, the on- and off-time distributions were obtained for immobilized QDs in the absence and presence of aqueous solutions of the trivalent ions. Blinking was analyzed by sampling the emission time trajectories using 50 ms time binning, and data were analyzed using algorithms in which the on- and off-states were distinguished using a threshold intensity level (see Supporting Information). For each measurement condition, dwell time histograms of on- and off-states were generated using data acquired from approximately 1200 QDs, and we were careful to avoid potential artifacts when analyzing on- and off-time distributions (see Supporting Information and Figures S6 and S7).[18] All data were processed in an identical fashion to ensure a fair comparison between different measurement conditions. The off-time distributions in agarose before and after addition of metal ions displayed a very similar power-law dependence (Figure 2a and Table S2). In contrast, a substantial shortening of the on-time was observed upon addition of all three metal ions, and the distributions followed a truncated power law (Figure 2b–d and Table S2). Such truncated power laws have been observed many times, and most blinking models have incorporated this behavior.[17]

Although all three metal ions could induce similar blinking behavior, they required different concentrations to achieve the same effect. While 10 μM Gd^{3+} induced rapid blinking (Figure S8), identical experiments using 10 μM Al^{3+} only resulted in minor changes to the on-times (Figure S9). However, as the Al^{3+} concentration was raised to 100 μM, the on-times shortened with similar fitting parameters to those observed in the presence of 10 μM Gd^{3+} (Figure 2c). In contrast, the injection of 10 μM Y^{3+} induced QD displacement from the gel. Reducing the Y^{3+} concentration to 1 μM, however, resulted in immobilized QDs and similar blinking to 10 μM Gd^{3+} and 100 μM Al^{3+} (Figure 2d).

To evaluate whether the presence of metal ions could alter the blinking statistics of QDs surrounded by a protective shell, the emission trajectories of single CdSe/ZnS core−shell QDs immobilized within a 1% (w/v) agarose gel were evaluated before and after addition of Gd^{3+}. In contrast to the core-only CdTe QDs, no blinking enhancement was observed, and the off- and on-rates remained unchanged after Gd^{3+} addition (Figure S10), though we note that the core materials are different in these samples (CdTe vs CdSe).

Our results have shown that trivalent metal ions are able to reversibly induce blinking, with very similar on-time distributions and little change in the off-time distribution (Table S2). It is clear that blinking depends on the metal, not the nitrate counterion; otherwise, we would not have a dependence of blinking on the salt concentration. The reversibility of the interaction in aqueous solution supports a labile ionic interaction rather than substitution of surface atoms.[49] Furthermore, the difference in blinking observed for different metal ions is not due to variations in the bulk dielectric constant for a particular metal salt solution, as dielectric constant is primarily dictated by the charge of the cation.[50]

Instead, we attribute the blinking to the binding of the tripositive metal ions to the negatively charged agarose in the vicinity of the QD. In fact, the binding of trivalent metal ions to an anionic polysaccharide has been reported and ascribed to ionic interactions.[51] Furthermore, the minimum concentration of trivalent metal ion needed to form gels varied widely in this same study, with an order of magnitude increase in concentration of Al^{3+} required, in comparison to Y^{3+} and heavier metals (including Gd^{3+}). Similarly, our results suggest that the binding constants for interaction with the agarose also depend on the metal ion (Y^{3+} > Gd^{3+} > Al^{3+}). Although the metal ions are quite different in size, this is unlikely to be the cause of the different abilities to induce blinking (i.e., due to different ion−QD distances), since the effective sizes of hydrated trivalent metal ions (from Al^{3+} to Ln^{3+}) are essentially identical.[52] Since the QD binds to the anionic agarose, it might be expected that binding of a sufficient number of positive metal ions to the agarose would disrupt this interaction and lead to QD loss, which is exactly what we observed on addition of 10 μM Y^{3+}.

■ CONCLUSIONS

In summary, we have developed a new approach to probe the effect of surface charge on the blinking of colloidal core-only QDs. Embedding the core-only CdTe QDs in agarose leads to

very stable emission because the negatively charged agarose suppresses blinking by slowing electron trapping to surface sites (e.g., by reducing the rate of tunneling or by filling the electron trap sites). Similar explanations have been used to explain the effects of QD capping ligands.[29,31] Trivalent metal ions can bind to the agarose leading to a reduction in the local negative charge in the vicinity of the QD and promoting the electron transfer pathway. The strong effect on the on-time distribution but negligible change in the off-time distribution suggests that the same process is responsible for the blinking dynamics with and without the metal ions, which supports the modified version of the long-time charging model.[32] By studying a simple and reproducible system (core-only QD in an aqueous agarose system), we have been able to directly correlate blinking with QD surface charge. We believe that this work will contribute to the debate on emission intermittency and will encourage the use of similar approaches to directly probe the role of surface charge in this phenomenon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07779.

Experimental methods, Figures S1−S10, and Tables S1 and S2 (PDF)

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Notes
The authors declare no competing financial interest.

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