

Environmental effects on photoinduced electron transfer and fluorescence blinking of single semiconducting nanocrystals in various matrices

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ABSTRACT

In this report we explore how the surrounding environments around a single semiconducting nanocrystal affect the photoinduced electron transfer, charge trapping fluorescence lifetime and fluorescence blinking. Using the time-correlated single photon counting techniques combined with confocal microscopy, we investigated photoluminescence of single CdSe/ZnS quantum dots embedded in agarose gel and on conductive substrates as examples. Understanding of the underlying mechanisms would allow us to better control of the photoluminescence properties of nanoparticles and to improve their performance in biophotonics and optoelectronics applications such as fluorescence markers, single-photon sources, photovoltaics and quantum dot lasers.

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I. INTRODUCTION

With the development over the past two decades in nanofabrication and imaging techniques with nanometer resolution, researchers are empowered with tools to design nanomaterials with tailored optical, electrical, mechanical and thermal properties toward applications in important areas of global interests such as energy, environment and biomedicine.^{1, 2} Semiconductors quantum dots (QDs), for example, have attracted a lot of attention recently because of their superior photoluminescence properties as compared to organic chromophores.^{3, 4} QDs are now widely used in biomedical imaging, light-emitting diodes, solar cells, lasers and single-photon sources for improved performance. Despite better photostability and tunable emission wavelength as compared to the conventional organic chromophores, the blinking behavior commonly observed in single QDs is a major drawback in practical applications.⁵⁻⁷ In order to suppress the annoying blinking behavior it is necessary to improve the understanding of the mechanisms that cause blinking so that one could gain better control of blinking suppression.

Recently, several schemes to suppress blinking have been proposed. One approach is to mitigate Auger recombination rate by reducing quantum confinement by fabricating QDs with an alloyed composition gradient from the core to the surface.⁸ Several other approaches were proposed, including modified synthesis with an increase in shell thickness of QDs,⁹⁻¹¹ surface passivation with appropriate molecules,¹²⁻¹⁴ and surface plasmon effects via coupling QDs to metallic nanoparticles.¹⁵⁻¹⁸ Here, we will also discuss another approach recently demonstrated by us via embedding QDs in agarose gel to achieve blinking suppression. By changing the surrounding environment of QDs, one could influence the blinking behavior and the long-time exponential bending tail for the blinking statistics. Finally, we will offer some explanations about the effects of the gel concentration on the blinking behavior. Our other more recent study of QDs on conductive substrates and environmental effects will also be presented to illustrate that the energy and charger transfer between QDs and the conductive substrates could be responsible for the changes in the photoluminescence properties of QDs.

II. EXPERIMENTS

The colloidal CdSe/ZnS QDs used in our experiments were purchased from Evident Technology. The emitting wavelength is at 600 nm. We prepared agarose gel (Sigma-Aldrich) solutions with different concentrations (0.3 % to 1 % by weight) by first mixing it with a solution of QDs and then by spin-coating onto a glass substrate typically or onto other substrates. The experiments were performed using a scanning confocal microscope (MicroTime 200, PicoQuant) through a $\times 100$ objective lens (Olympus, N.A. = 1.4) based on time-correlated single-photon counting techniques to measure the fluorescence time traces and the fluorescence lifetimes. In sample preparation using spin coating, a very low concentration of QDs was chosen so that the mean separation between QDs was larger than the excitation laser spot so that only one single individual QD could be monitored at a time. Excitation of the sample was made by using a pulsed

diode laser (PDL 800-D) operating at 467 nm. The fluorescence from the sample was collected by the same objective lens and was guided to a confocal pinhole ($\sim 50 \mu\text{m}$) to block the out-of-focus light. After a pinhole, the fluorescence was split by a beam splitter cube into two beams, then filtered by passing through a 605/40 band-pass filter (D605/40; Chroma Tech), and detected by a pair of single-photon avalanche photon diodes (SPCM-AQR-14; PerkinElmer). Fluorescence images were then obtained by raster scanning with a piezo-driven nano positioning and scanning system (E-710; Physik Instrument). After obtaining the images of single QDs, we scanned each particle by moving consecutively the focal point of the objective lens to record the time evolution of the fluorescence intensity. To investigate antibunching behavior using photon correlation detection, TTL pulses from two APDs were fed into photon counting module (PicoHarp 300, PicoQuant) to perform cross correlation measurements.

III. RESULTS AND DISCUSSION

Here we first present the experimental results on single QDs in agarose gel. These gel molecules contain negatively charged fibers so that the induced electrostatic environment could significantly influence the charge transfer processes in photoexcited QDs. The work on single QDs on conductive substrates will be discussed later. Figure 1 shows the fluorescence intensity trajectories of single CdSe/ZnS QDs on a glass substrate, in mixtures of 0.3% and 1% agarose gel, respectively. The stochastic fluctuation between fluorescent “on” level and dark “off” level was observed for QDs on glass and also for QDs embedded in 0.3% gel. The photon count distribution of two distinguishing intensity levels related to the “on” and “off” states is displayed on the right of the intensity trajectory. In contrast, the time trace for single QDs in 1% gel exhibits essentially continuous emission without dark periods (Figure 1c), i.e., blinking was suppressed in this case.

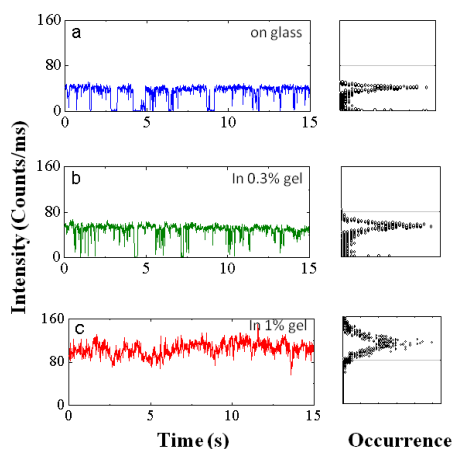


Figure 1. Fluorescence intensity trajectory and its corresponding photon count histogram from single CdSe/ZnS QDs spin-coated on a glass substrate (subplot a), in a 0.3% gel mixture (subplot b), and in 1 % gel (subplot c).

To help understand the porous nature of agarose gel at various concentrations, we show in Figure 2 the SEM images of agarose gel with the concentrations of 0.3 % and 1%. The comparison illustrates the influence of the gel concentration on the pore sizes.

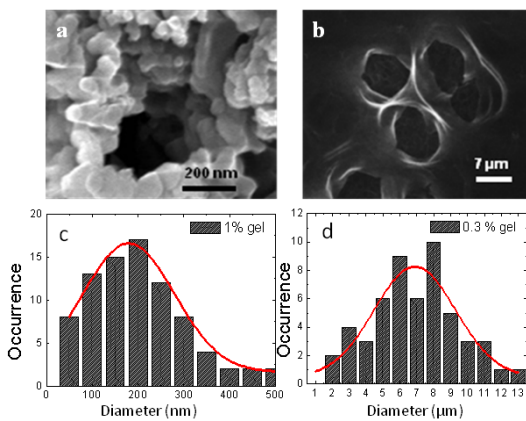


Figure 2. (a) SEM cross-sectional view of 1% agarose gel at 50000 \times . (b) SEM cross-sectional view of the 0.3% agarose gel at 1600 \times . (c) The pore diameter distribution for 1% gel obtained from the SEM images. The majority of the pore diameters are around 200 nm. (d) The pore diameter distribution for 0.3% gel obtained from the SEM images. The majority of the pore diameters are around 8 μ m.

The averaged pore diameter of the 1% gel structure was found to be \sim 200 nm, and for 0.3% gel the averaged pore diameter was around 8 μ m. In a previous work the pore diameter was found to increase as the agarose concentration decreased and that the wide pore diameter distribution became narrower as the gel concentration was increased.¹⁹ Such observation agreed with our results. Agarose gel fibers were known to be inherently negatively charged, and a sufficient amount of charged groups, such as pyruvate, sulfate, and methoxy groups, are present in commercially prepared agarose.²⁰⁻²² We suggested that blinking could be suppressed by blocking the transitions from the light state to the dark state due to a higher activation energy. In addition, the negative charges on the pore surface. Such blocking could reduce the tunneling rate of the electron to the surface. Therefore, the negative charges on agarose gel fibers could play an important role in this blinking suppression behavior.

Figure 3a shows the decay profiles of single QDs on a glass substrate and in 1% agarose gel. We observed that the negative charges inherent with gel fibers could affect the fluorescence decay. The average fluorescence lifetime of QDs embedded in 1% agarose gel is around 19 ns, which is faster than that of QDs on glass (28 ns). Also, fluorescence quantum yield of QDs is enhanced with an increase of gel concentration. Figure 3b shows the dependence on the gel concentration for the total photon counts from the fluorescence time traces. The photon counts were obtained by summing up over 20 QDs at a light intensity set at 0.67 KW/cm². The result demonstrates that the photon counts are linearly related to the gel concentration. Generally, the quantum yield of a natural emitter is given by $Q = \Gamma / (\Gamma + k_{nr}) = \Gamma \times \tau$, where Γ , k_{nr} and τ are the radiative, non-radiative, and measured fluorescence lifetimes, respectively. Therefore, we can estimate nearly 3.8-fold increase in the radiative rate for QDs embedded in 1% agaroses gel than QDs on glass.

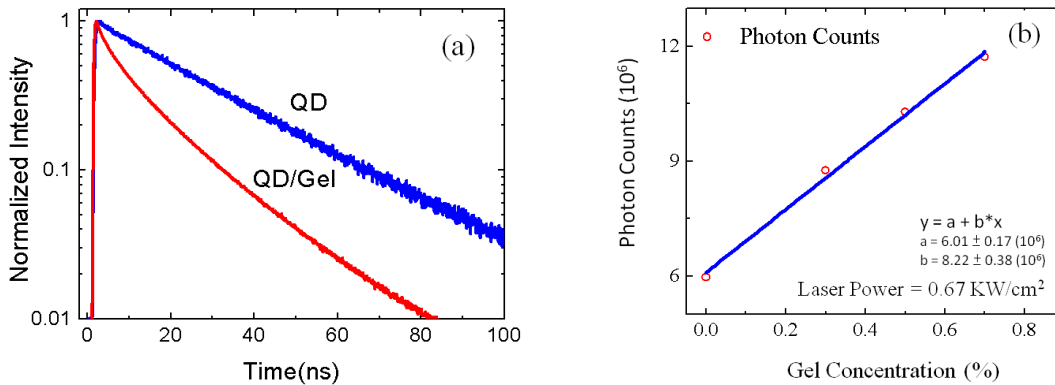


Figure 3. (a) Fluorescence decay profiles for single QDs on a glass substrate and embedded in 1% agarose gel. (b) The dependence on the gel concentration for the total photon counts for the fluorescence time traces by summing up over 20 QDs.

Fluorescence traces of aggregated QDs in a region smaller than the wavelength limit could also appear as non-blinking. We could assure that the observed non-blinking in agarose gel was not due to aggregation of QDs by photon correlation measurements. Second-order intensity autocorrelation function, $g^2(\tau)$, for single QDs embedded in 1% agarose gel is shown in Figure 4. The data were acquired around 30 min and binned with 400 ps time intervals. In general, $g^2(\tau)$ function can be approximated as $g^2(\tau) \cong 1 - \exp[-\tau(W_P + \Gamma_R)]/N$, where N , W_P , Γ_R , are the number of independent emitters, excitation rates, and fluorescence recombination rates, respectively. The value of $g^{(2)}(\tau)$ in our case is around 0.23, which is still less than 0.5 (the value of $g^{(2)}(\tau)$ is 0.5 for two independent emitters). The residual $g^{(2)}(\tau)$ value could be attributed to agarose gel which yields a low fluorescence background. Therefore, this photon anti-bunching behavior is the hallmark for single photon emission from an individual QD rather than emission from aggregated QDs.

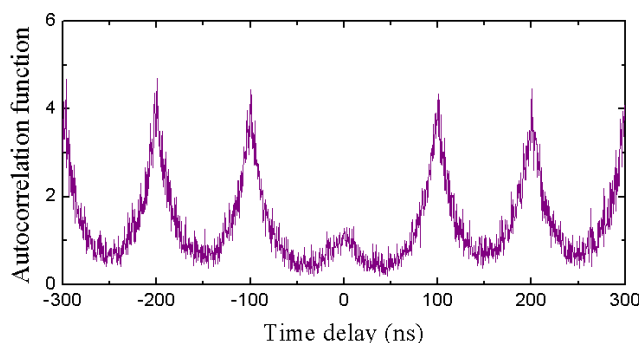


Figure 4. Photon correlation measurements of QDs embedded in 1% agarose gel, exhibiting anti-bunching behavior as a characteristic signature of single-photon emission from a single QD.

The on-time distribution $P_{on}(t)$ of single QDs on glass, in 0.3%, 0.5% and 0.7% gel are shown in Figure 5. It presents an inverse power-law distribution at shorter times but then deviates from this distribution at longer times, exhibiting an exponential bending tail. The distribution was fitted by using $P(t) \sim ct^m \exp(-\Gamma t)$, where c is an unimportant scaling constant, m is the power-law exponent, and Γ is the bending rate. In our cases, m is typically around 1.0-1.5.

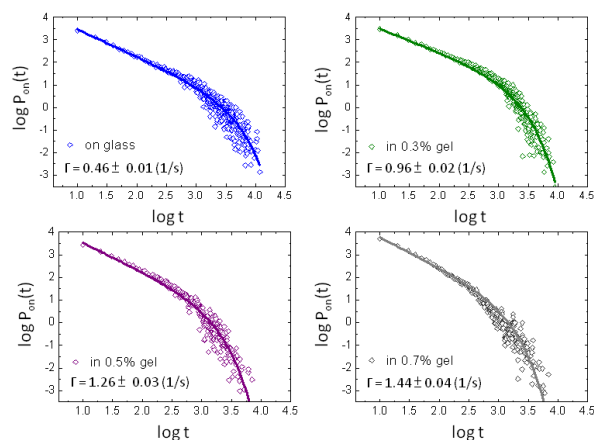


Figure 5. On-time blinking statistics of single QDs on glass, in 0.3%, 0.5% and 0.7% gel showing an increase of the bending as the gel concentration increases.

As shown in Figure 6 the bending rate Γ becomes greater as the gel concentration increases by comparing to QDs on glass. We have presented such findings in a recent report.²³

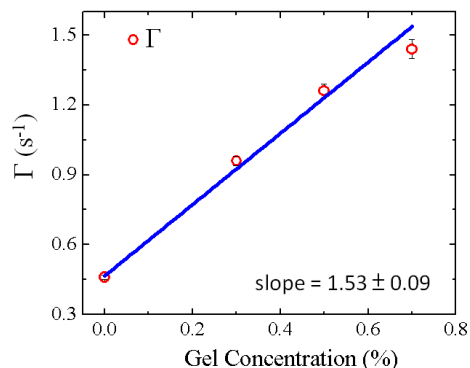


Figure 6. Plot of the fitted exponential bending rate Γ vs. the gel concentration showing a linear dependence, indicating a linear dependence of the activation for the charge transfer on the gel concentration.

The diffusion-controlled electron transfer (DCET) model of Tang and Marcus²⁴⁻²⁷ demonstrates that Γ increases with the activation energy for electron transfer from the light state to the dark state. In our case, we observed that the activation energy also increased with the gel concentrations. Therefore, the activation energy might be too large for the charge transfer or for the blinking to occur at a much higher concentration. Comparing with the on-events, the occurrence of the dark events is less frequent for QDs in gel, and becomes completely absent for the case with 1% gel. Therefore, the noise level of the waiting time distribution during the dark events would be too high for a meaningful analysis.

A schematic of the DCET model,²⁴⁻²⁷ is presented in Figure 7. Generally, the power-law exponent, m , for “on” and “off” times equals to 1.5 exactly for normal diffusion but deviation occurs for anomalous diffusion. However, the exponential bending rate Γ is related to the activation energy for the electron transfer process from the light state $|L^*\rangle$ to the dark state $|D\rangle$. We suggest here that the negative charges from gel fibers surrounding the QDs could cause an energy up-shift of $|D\rangle$ with respect to $|L^*\rangle$, and would result in an increased activation energy. Therefore, the transition rate from the neutral light state to the charged dark state could be reduced.

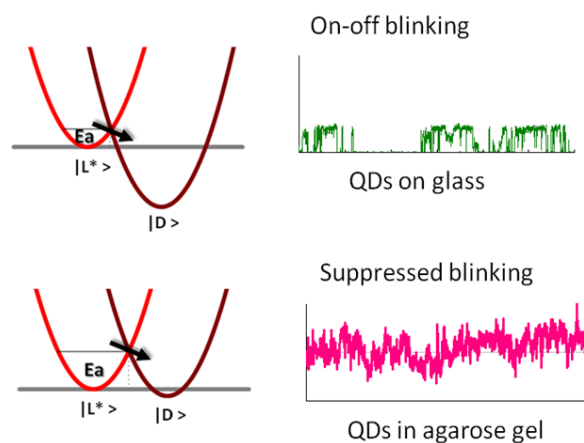


Figure 7. The DCET model describing the effects of the gel concentration on the activation barrier height.

Now we will discuss in the following section our recent studies of single QDs on conductive substrates to explore the environmental effects on photoluminescence properties of QDs. When single colloidal QDs were deposited on noble metal substrates (Au or Ag), their blinking behavior can be modified dramatically due to complex interactions between them, including plasmonic interactions, energy and charge transfer processes.^{18, 28-30} As an example, when single colloidal QDs were directly deposited onto Ag nanoprisms, their blinking behavior could be suppressed.¹⁸ Other conductive substrates, taking the ITO substrate as an example, are also important and interesting materials to test how they influence the single-QD blinking behavior.³¹

Typically, there existed two types of fluorescence time trajectories for single colloidal CdSe/ZnS QDs on ITO substrates, as shown in Figures 8 (a) and (b). In the first type the behavior is similar to the conventional QDs with typical blinking behavior. In contrast, for the second type of QDs, these nanoparticles exhibited relatively continuous emission without long-lived dark states. Such a phenomenon has also been found for single colloidal QDs on smooth gold surfaces. In addition, their fluorescence intensity is usually lower than that of the on-state of the blinking QDs.

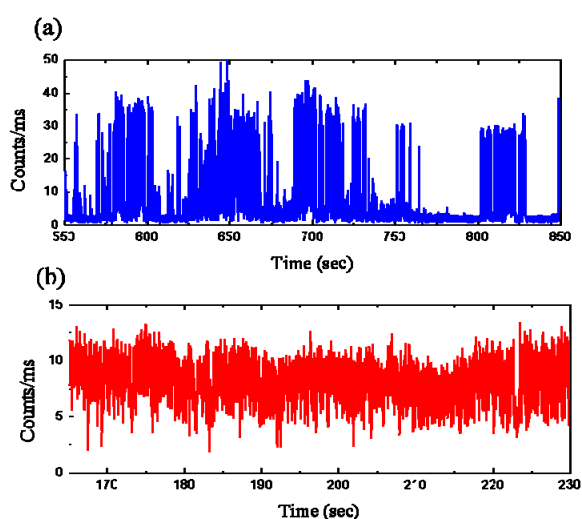


Figure 8. Fluorescence time traces for two distinctive types of QDs, one exhibiting typical on-off blinking behavior, and the other displaying a nonblinking pattern.

In order to further clarify the underlying mechanism of such modified blinking behavior, we also performed time-resolved fluorescence measurements for these two types of QDs, as displayed in Figure 9. Interestingly, they exhibited distinct decay behavior even on the same ITO substrates. For blinking QDs, a pure single decay profile with ~ 11 ns lifetime was generally observed upon subtracting the background noise. On contrary, for QDs with relatively continuous emission, much fast decay dynamics with an averaged lifetime of ~ 3 ns was found. This finding implies that the modification of blinking behavior is correlated to the change of the fluorescence decay processes.

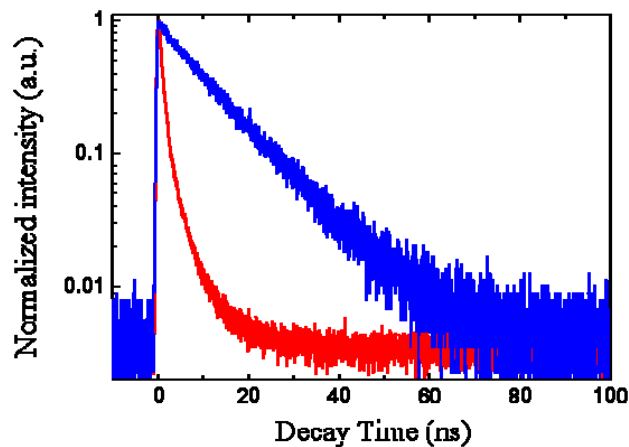


Figure 9. Fluorescence decay curves for two distinctive types of QDs, with one showing a normal and slow decay and another showing a much fast decay.

According to the previous reports, extra efficient energy transfer processes could prevail over Auger recombination to prevent QDs from entering into dark states. Therefore, dipole and image-dipole induced energy transfer from colloidal QDs to TIO conductive substrates could be used to explain our experimental observation, including reduced fluorescence intensity, shortened fluorescence lifetimes, and continuous emission behavior. Indeed, we also observed a fraction of QDs with typical blinking behavior on the same substrate. Their fluorescence characteristics are similar to that of QDs on insulating glass substrates, implying no interactions between them.

In order to monitor the photon statistics, we also performed photon correlation measurements based on Hanbury Brown Twiss experimental setup. Figure 10 shows the second-order autocorrelation function for typical blinking QDs (a) and continuous emission QDs (b). For blinking QDs, photon antibunching behavior was observed, indicating their single-photon emission characteristic. On contrary, such typical behavior disappeared for less blinking QDs. Here, we exclude the possibility of QD aggregation. If aggregation of QDs occurred, fluorescence intensity would have been increased, rather than quenched. In addition, their fluorescence lifetimes should be similar to those of single QDs. At present, the exact mechanism is still under investigation and further experiments are needed.

In general, the ITO substrate is comprised of 90% In_2O_3 and 10% SnO_2 , and then deposited on glass by spin coating. Therefore, surface heterogeneity is unavoidable and it would cause distinct nano environments around QDs, thus would display different blinking behavior.

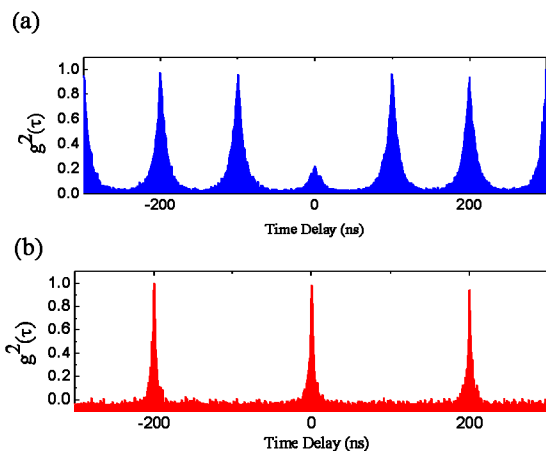


Figure 10. Results from photon correlation measurements showing (a) antibunching behavior (blue) for blinking QDs, in comparison with (b) absence of antibunching (red) for nonblinking QDs.

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