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Blinking suppression of single quantum dots in agarose gel

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Fluorescence blinking is commonly observed in single molecule/particle spectroscopy, but it is an undesirable feature in many applications. We demonstrated that single CdSe/ZnS quantum dots in agarose gel exhibited suppressed blinking behavior. In addition, the long-time exponential bending tail of the power-law blinking statistics was found to be influenced by agarose gel concentration. We suggest that electron transfer from the light state to the dark state might be blocked due to electrostatic surrounding of gel with inherent negatively charged fibers. © *2010 American Institute of Physics*. [doi:10.1063/1.3280386]

Colloidal semiconductor quantum dots (QDs) have attracted extensive attention in scientific studies and technological applications recently because of their unique optical and electric properties.[1,2] One potential application is their use as fluorescence labels in biological system studies.[3,4] Despite of the good photostability and tunability of the emission wavelength, the blinking of QDs is an undesirable feature like driving a car in darkness with blinking headlights.[5–7] Therefore, it is important to improve the understanding of the physics involved in blinking in order to gain better control of blinking suppression.[8]

Although the details of blinking mechanism are still under debate, some notions are widely accepted. Following the formation of an exciton in the neutral light state, the electron could be transferred to the surface trap states. The dark state is generally attributed to the formation of such a charged QD with a hole in the core and an electron trapped in the surface states.[9,10] In this case, the excitation energy of the singly charged QD could be transferred to the excess charge carrier via efficient nonradiative Auger recombination instead of photon emission. In QDs, Auger relaxation is very efficient due to strong quantum confinement in nanosize space.[11] To suppress blinking, one simple approach is to inhibit Auger recombination by reducing quantum confinement. In a recent study QDs with an alloyed composition gradient from the core to the surface do not blink.[12] Several ideas were also offered to suppress blinking, such as modified synthesis,[13] an increase in shell thickness of QDs,[14–16] surface passivation with appropriate molecules,[17–19] and surface plasmon effects via coupling to metallic nanoparticles.[20–22]

As an example, by synthesizing type-II semiconductor QDs, one could obtain nonblinking QDs.[23] Unfortunately, such an approach often leads to reduced wave function overlap between the electron and the hole. As a result, such QDs exhibit quenched fluorescence and longer fluorescence lifetimes, which yields degraded performance of photon emission. More recently, we demonstrated an approach to concurrently maintain strong quantum confinement and blinking suppression by coupling the QDs to metal nanoparticles.[22] The interactions between plasmonic nanostructures and single emitters are rather complex and remain elusive.

Encapsulation of QDs has been made into some dielectric materials, such as silica, exhibiting many interesting phenomena, including modification of fluorescence intensity and photostability.[24] In this work, we will discuss blinking suppression and antibunching behavior of single CdSe/ZnS QDs in agarose gel. By changing the surrounding environment of QDs, we could influence blinking and the long-time exponential bending tail of the blinking statistics.

Colloidal CdSe/ZnS QDs (water-soluble, hydrophilic, nonfunctional) with 6 nm in diameter and emission ~600 nm were purchased from Evident Technology. Agarose gel (Sigma-Aldrich) solutions with different concentrations (0.3%, 0.5%, 0.7%, and 1% by weight) were mixed with QDs solution and then spin-coated on glass. The experiments were conducted using far-field laser scanning confocal microscope (MicroTime 200, PicoQuant). A pulsed diode laser at 467 nm was focused to a diffraction limited spot by an oil-immersion objective (Olympus, N.A.=1.4). The fluorescence was collected by the same objective and guided to a confocal pinhole to reject out-of focus light. For photon correlation measurements, TTL pulses from two APDs were fed into a photon counting module (PicoHarp 300, PicoQuant) to perform second-order correlation.

The fluorescence intensity trajectories of single CdSe/ZnS QDs on glass substrate, in 0.3% and 1% agarose gel are shown in Fig. 1. For QDs on glass and in 0.3% gel stochastic fluctuation between fluorescent "on" level and dark "off" level was observed. In contrast, the time trace for single QDs in 1% gel exhibits essentially continuous emission without dark periods. Previous research showed that agarose gel fibers were found to be inherently negatively charged because the backbone is substituted with sufficient amount of charged groups, such as pyruvate, sulfate, and methoxy groups, are present in commercially prepared agarose.[25–27] If the transitions from the light state to the dark state could be blocked, blinking could be suppressed. Moreover, the negative charges around the gel surface could reduce the tunneling rate of the electron to the surface.

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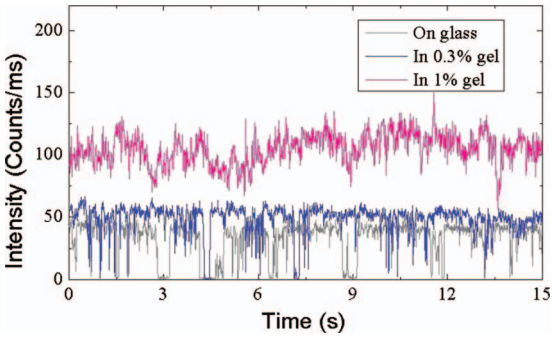

FIG. 1. (Color) Fluorescence intensity trajectory from single QDs on a glass substrate, in 0.3%, and 1% gel, respectively.

To make sure that the observed nonblinking in agarose gel is not due to aggregation of QDs, photon correlation measurements were performed. Figure 2 shows second-order intensity autocorrelation function $g^2(\tau)$ for single QDs in 1% agarose gel. The data was acquired for ~30 min and binned with 400 ps time intervals. Note that the value of $g^{(2)}(\tau)$ in our case is about 0.23, which is still less than 0.5 [the value of $g^{(2)}(\tau)$ is 0.5 for two independent emitters]. This photon antibunching behavior is the hallmark for single photon emission from an individual QD rather than emission from aggregated QDs. The residual $g^{(2)}(\tau)$ value is likely attributed to agarose gel, which yields a low fluorescence background.

The gel has very low but detectable background fluorescence as seen from the antibunching measurement. However, we think that the large amplitude fluctuations of the fluorescence intensity in 1% gel is not due to the background fluorescence from gel itself, but most likely due to the fluctuating electrostatic environment surrounding the QDs in presence of negatively charged gel fibers. Details of the mechanism need to be explored in the future.

Figure 3 shows on-time distribution $P_{on}(t)$ of single QDs on glass, in 0.3%, 0.5%, and 0.7% gel. It demonstrates an inverse power-law distribution at shorter times but it deviates from this distribution at longer times, exhibiting an exponential bending tail. The distribution was fitted 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. Comparing to QDs on glass, Γ becomes greater as the gel concentration increases. According to the model of Tang and Marcus,[28] Γ increases with the activation energy for electron transfer from the light sate to the dark state. Therefore, our data suggests that the activation energy also increases with the gel concentrations. At a much higher concentration, the activation energy might become too large for the charge transfer or blinking to occur. We suggest that the negative charges surrounding the quantum dots might play an important role in controlling charge transfer and blinking suppression. Unlike the on-events, the occurrence of the dark events is less frequent for QDs in gel, and becomes 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.

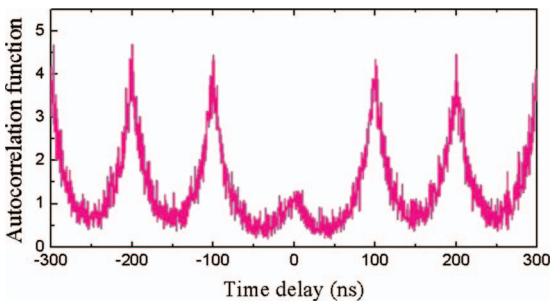

FIG. 2. (Color) Photon correlation measurements of QDs in 1% agarose gel, exhibiting antibunching behavior which is a signature of a single-photon emitter.

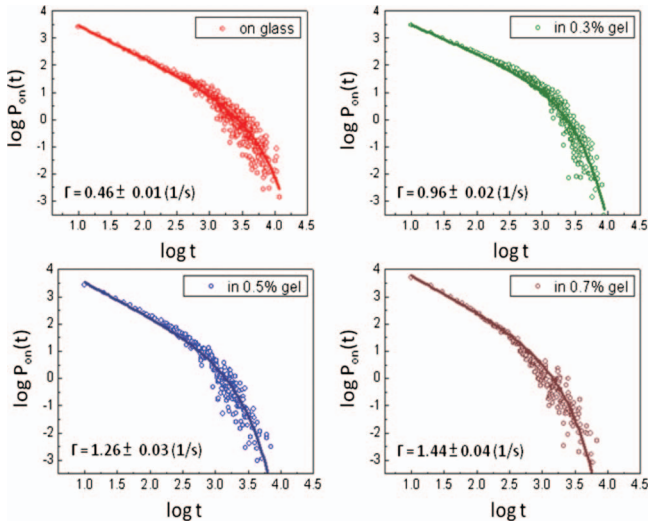

FIG. 3. (Color) On-time blinking statistics of single QDs on glass, in 0.3%, 0.5%, and 0.7% gel, respectively, showing an increased bending rate as the gel concentration increases.

In conclusion, we demonstrated blinking suppression of single QDs in agarose gel at 1% concentration. We observed that the long-time exponential bending tail has an increasing bending rate for single QDs as the gel concentration increases from 0.3% to 0.7%. Moreover, the antibunching behavior indicates that the fluorescence time trace is due to single-photon emission from one single QD and not from an ensemble of QDs. Due to the negative charges inherent with gel fibers and the electrostatic surrounding around QDs, electron transfer from the light state to the dark state might be blocked, leading to blinking suppression of QDs in agarose gel.

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