Blinking Suppression and Anti-Bunching of Quantum Dots
as Single-Photon Sources

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ABSTRACT

We report here our study on suppression of fluorescence blinking of colloidal CdSe/ZnS quantum dots (QDs) for potential applications as high performance single-photon sources. Blinking is an interesting property for single QDs, but it is undesirable for their applications. We have demonstrated that by coupling these QDs to adjacent silver nanoprisms, we could not only completely suppress the blinking but also enhance the fluorescence quantum yield, and also increase the fluorescence decay rates. These single QDs also exhibit anti-bunching behavior which is a signature for a single-photon emitter. In addition, we have also achieved blinking suppression by embedded the QDs in agarose gel. The electrostatic environment around QDs due to negatively charged fibers of gel might strongly affect the extent of blinking suppression. The mechanisms of blinking suppression will be discussed in the frame work of diffusion-controlled electron transfer model.

Keywords: quantum dots, fluorescence blinking, anti-bunching, single-photon sources

I.   Introduction

During the last two decades there is a tremendous improvement in fabrication and imaging techniques involving nanomaterials. For example, semiconductors quantum dots (QDs) were developed that exhibit excellent fluorescence properties as compared to organic chromophores. Thus, QDs are being substituted for traditional organic dye molecules and are now widely used in biological labeling,[1] light-emitting diodes,[2] solar cells,[3] lasers[4] and single-photon sources.[5] Despite many advantages, the universal fluorescence blinking is a major drawback for their practical applications. The details of blinking mechanism are still much under debate, although some basic notions are widely accepted, such as inverse power-law waiting time distribution (blinking statistics) with a long-time bending tail showing size and excitation intensity dependence. One of the models

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called diffusion-controlled electron transfer (DCET) model was proposed by Tang and Marcus[6,7] to explain these phenomena. Blinking is attributed to the stochastic charge transfer and recombination of the photo-excited electron-hole pairs between the neutral light state and the dark charged state. Here is the sequence of the processes involved in blinking: (1) formation of an exciton at the neutral light state, then the electron could be transferred to the surface trap states and leaving a positive charge (hole) in the core of a QD; (2) subsequent photoexcitation of a second electron-hole pair in such a charged QD, trion could be produced; and (3) the excess charge carrier may decay via efficient nonradiative Auger recombination ($10^{10} \sim 10^{11}$ s^{-1}) instead of radiative emission ($10^8 \sim 10^9$ s^{-1}). In a QD, the Auger relaxation is enhanced due to size confinement and strong Coulomb electron-electron interactions.[8]

Just imaging a bicycle rider in darkness with no street light except a headlight blinking randomly, one can realize the nuisance for blinking in applications for QDs as fluorescence markers or single-photon sources,　Therefore, suppression of the blinking of single QDs has been an important issue for practical applications. One simple approach is to block the electron transfer either by attaching organic ligands to QD surface or by capping a thicker inorganic layer.[9,10] For the former case, the attached chemical ligands are unstable and they could be easily removed from the QD surface.[11] For the latter case, a multi-shell structure leads to an increase in the size of QD. More importantly, to avoid the large lattice mismatch between the CdSe core and the ZnS shell (~12%), CdS was chosen to form this thick shell because its smaller lattice mismatch. However, this approach leads to the formation of a type-II band structure,[12] with the hole localized within the core and an electron delocalized over whole core/shell materials. Due to less wave function overlap, such a structure should lead to a reduced quantum yield and a longer lifetime, thus degraded the performance of single-photon emission. In a recent study, QDs with an alloyed composition gradient from the core to the surface do not blink. Blinking suppression of single QDs could also be achieved via coupling these QDs to metal coated substrates.[13,14] These interactions including energy transfer ($10^{10} \sim 10^{14}$ s^{-1}) and localized surface plasmon resonance. In this paper, we provide two approaches to obtain blinking suppression by coupling QDs to Ag nanoprisms and encapsulating QDs in agarose gel.

II.　Experiments

Water-soluable CdSe/ZnS core/shell QDs with non-functional groups were purchased from Evident Technology (emission at ~600 nm). In this study, blinking suppression of single QDs could be achieved by either coupling these QDs to Ag nanoprisms or encapsulating QDs in agarose gel. In the former case, the Ag nanoprisms with an edge length of ~43 nm were prepared by following reported method with miner modification (Fig. 1a).[15] For single-QD experiments, a diluted solution of QDs was spin-coated on the glass coverslip. A ~10 nm PMMA polymer layer was capped onto the QDs, then silver nanoprisms were directly deposited onto the top of the PMMA layer. Fig. 1b shows a schematic diagram outlining the sample configuration of silver nanoprisms coupled to CdSe/ZnS QDs. For the latter case, the QD solution was mixed with wt. 1% agarose gel.
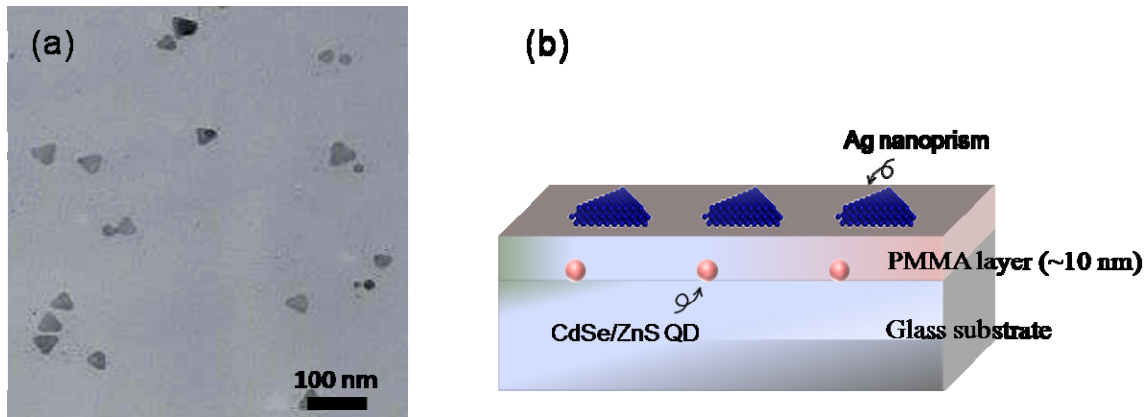
Fig. 1 (a) TEM image of silver nanoprisms. (b) Schematic illustration of the sample configuration.

Single QD detection was carried out with a far-field laser scanning confocal microscope (Micro-Time 200, PicoQuant). The excitation of CdSe/ZnS QDs in this study is at 460 nm by a pulsed diode laser, which is focused through an oil–immersion object (Olympus, N.A.=1.4) down to a diffraction limited spot. The fluorescence was collected by the same objective and lead to a confocal pinhole to reject out-of focus light. For photo correlation measurement, TTL pulses from two APDs were fed into a photon counting module (PicoHarp 300, PicoQuant) to perform second-order correlation.

III.   Results and Discussion

The major interactions between QDs and metal nanoparticles are energy transfer and plasmonic effects. They can quench or enhance the fluorescence of single QDs. These two effects are competing with each other, and the overall results are strongly dependent on the separation between the QD and the metal nanoparticles.   In this study, we control the separation by tuning the thickness of PMMA polymer layer. We will also discuss the QDs in agarose gel.

3.1 Blinking Suppression of CdSe/ZnS QDs by coupling to silver nanoprisms

The time traces of photoluminescence intensity of a single CdSe/ZnS QD with and without coupling to Ag nanoprisms were shown in Fig. 2. It is noticed that the PMMA polymer layer is absent in this sample. A typical binary blinking characteristic was observed for QDs on the glass. On the contrary, a nonblinking time trace with stochastic intensity fluctuation was found for coupled CdSe/ZnS QDs on silver nanoprisms coated substrates. More than 75% of individual QDs within the ensemble samples exhibit this nonblinking behavior and dark periods have vanished. We selectively display two cases for coupled QDs with different intensities for comparison were also shown in Fig. 2. It is likely that each QD couples to nearby Ag nanoprisms differently, since the distance to nanoprisms could vary from dot to dot.
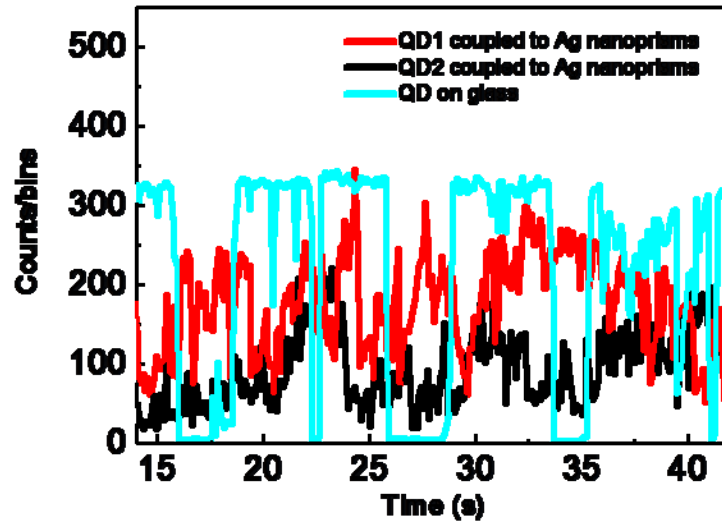
Fig. 2 Time trace of photoluminescence intensity of a single CdSe/ZnS quantum dot with (QD1 and QD2) and without coupling to Ag nanoprisms, respectively.

We also performed TTTR measurements during the course of single QD detection to clarify the origins. Fig. 3a shows the fluorescence decay curves of QDs on glass and coupled to Ag nanoprisms, respectively. The fluorescence decay of QDs on glass is single exponential with a lifetime of ~ 25 ns, but is biexponential with two time constants of ~ 5 ns and ~ 20 ns for coupled QDs to Ag nanoprisms. Here, we also combined the time-correlated single-photon counting technique and the maximum likelihood estimation analysis to obtain fluorescence lifetime distributions. As shown in Fig. 3b, most of the coupled QDs reveal two peaks centered at 10-20 ns and ~5 ns, respectively. The longer component varies from dot to dot, but the shorter component remains mostly unchanged at ~ 5 ns.
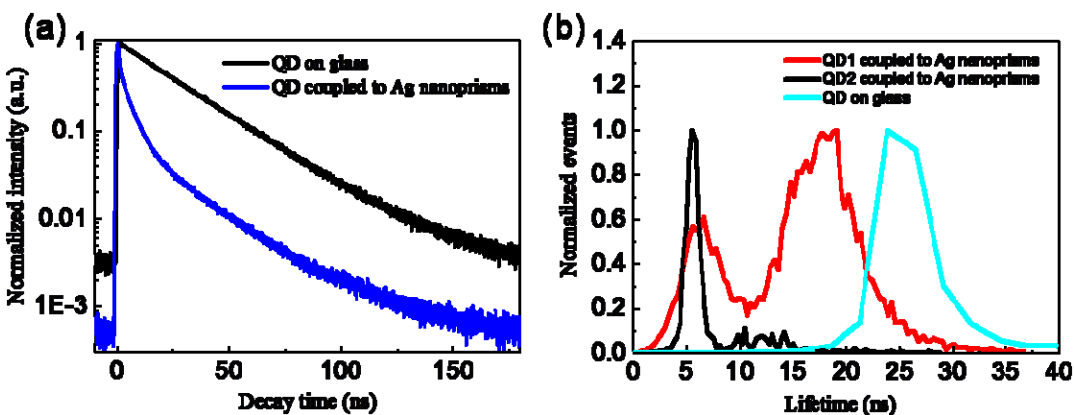

Fig. 3 (a) Fluorescence decay curves of QDs on glass and coupled to Ag nanoprisms, respectively. (b) Fluorescence lifetime distribution of a single QD with (QD1 and QD2) and without (QD) coupling to Ag nanoprisms, respectively.

Figure 4 shows the time trace of photoluminescence intensity of a single CdSe/ZnS QD coupled to Ag nanoprisms in observation time of 5-10 s. Since it exhibits stochastic fluctuations without a long stay in the dark state, the fluorescence decay curves have to be constructed by selecting a specific time gate region. As shown in Fig. 4b, the distinct lifetimes of the fluorescence decay curve depend on high (cyan area) and low (blue area) fluorescence intensity in Fig. 4a, respectively. Similarly, lifetime distributions were recorded for overall high (green area) and low (red area) intensity regions were shown in Fig. 4c. There are two lifetime distribution peaks for the high and low intensities, which coincide with time gate results. These observations further support the existence of two distinctive states for single QDs coupled to Ag nanoprisms. In this case, there is no significant energy shift of an emitted photon. Therefore, we attributed this nonblinking behavior to energy transfer from a QD to Ag nanoprisms. The QD emission can be easily coupled to the silver nanoprisms, which has broad absorption caused by multiple plasmonic modes. Here, it provides an efficient process of energy transfer from a QD to Ag nanoprisms to compete with Auger ionization, then the transition to dark state can be reduced.[16]
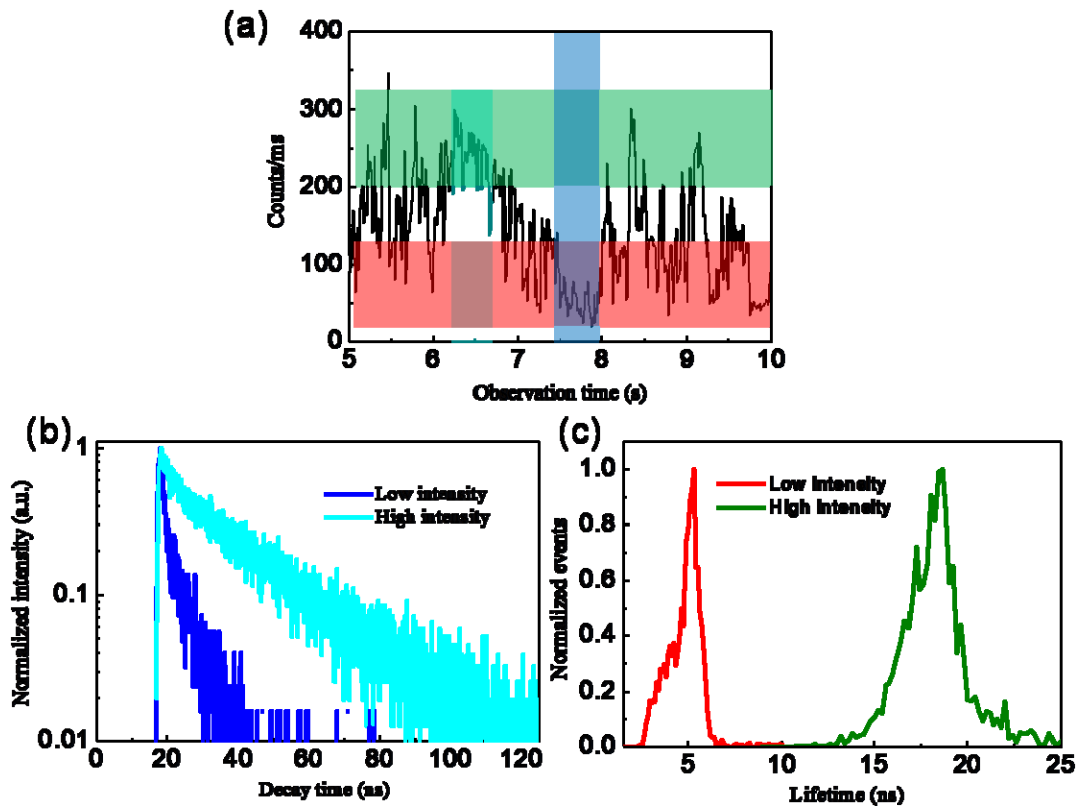

Fig. 4 (a) Time trace of photoluminescence intensity of a single CdSe/ZnS QD coupled to Ag nanoprisms in observation time of 5-10 s. (b) Fluorescence decay curves for specific time gate of high (cyan area in a) and low (blue area in a) fluorescence intensities, respectively. (c) Fluorescence lifetime distribution for specific count gate of low (red area in a) and high (green area in a) fluorescence intensities, respectively.

3.2 Anti-Bunching Single-Photo Emission of CdSe/ZnS QDs by coupling to silver nanoprisms

For minimization of energy transfer from QDs to Ag nanoprisms, a PMMA polymer layer ~10 nm was used (see Fig. 1b) and the plasmonic effect would be dominant in this configuration. The time traces of photoluminescence intensity of a single CdSe/ZnS QD on glass and coupled to Ag nanoprisms were shown in Fig. 5. Generally speaking, with a bin time of 10 ms, ~78% coupled QDs within ensemble samples shows continuous emission without long-lived dark state. The fluorescence image of coupled QDs was shown in the inset of Fig. 5. A complete Gaussian spot was observed for most coupled QDs, rather than QDs on glass. In addition, 2.5 times fluorescence enhancement on average was observed for coupled QDs compared to the on state of blinking QDs on glass. This blinking suppression and accompanied fluorescence enhancement could be attributed to the coupling of single QDs to its adjacent Ag nanoprisms with the excitation of LSPR.
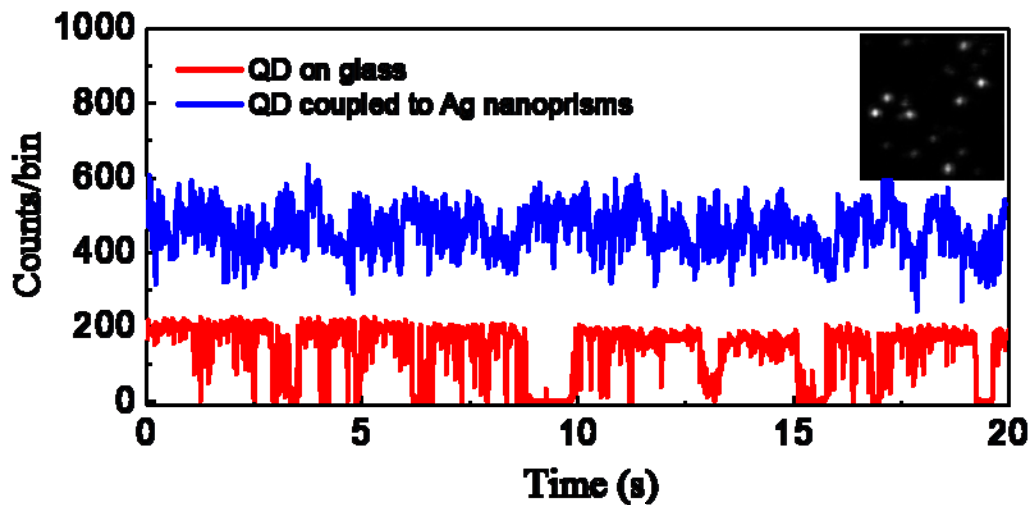

Fig. 5 Time trace of photoluminescence intensity of a single CdSe/ZnS QD on glass and coupled to Ag nanoprisms, respectively. Inset is the confocal fluorescence image (6 x 6 μm^2) of single QDs coupled to Ag nanoprisms.

The fluorescence decay curves of QDs on glass and coupled to Ag nanoprisms were also obtained (data not shown). The lifetime of QDs on glass and coupled QDs exhibit single exponential decay with a time constant of ~ 25 ns and ~5 ns, receptively. The fluorescence intensity can be described by

$$QYs = \frac{\Gamma}{\Gamma + k_{nr}} = \Gamma \times \tau$$

where Γ is the radiative rate and k_{nr} is the nonradiative rate for the QDs. The measured fluorescence lifetime of the QD is $\tau = (\Gamma + k_{nr})^{-1}$. Therefore, by comparing the reference QDs with the coupled QDs one has

$$\frac{QY_{Ag-QDs}}{QY_{QDs}} = \frac{\Gamma_{Ag-QDs}}{\Gamma_{QDs}} \times \frac{\tau_{Ag-QDs}}{\tau_{QDs}}$$

And we deduced ~12.5 enhancement of radiative decay rate. To demonstrate single-photon emission behavior, photon correlation measurements were performed for QDs coupled to Ag nanoprisms. The second-order autocorrelation function under pulsed laser excitation with 10 MHz repetition rates was shown in Fig. 6. This photon antibunching behavior is a signature for single-photon emission, where a peak with a reduced height (~0.2) was found at zero delay time. The nonzero height could be attributed to the background fluorescence from silver nanoprisms. In this single-photon source configuration, photon emission is relatively fast and continuous instead of stochastic on/off blinking, and high fluorescence intensity at room temperature.[17]
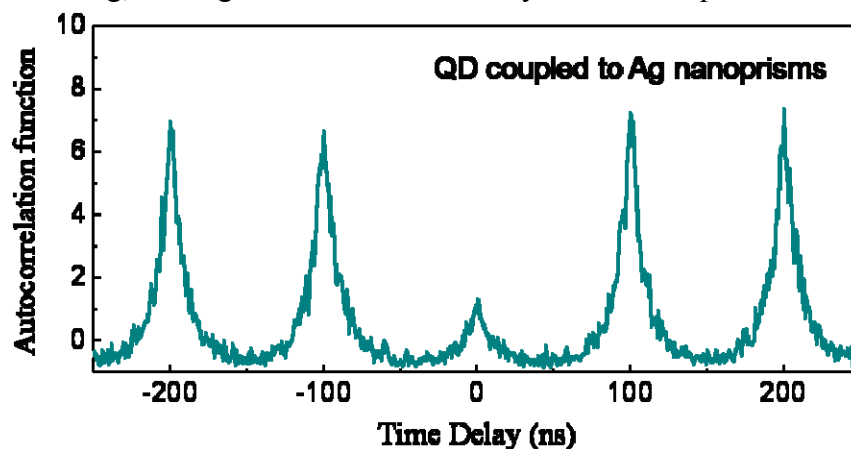

Fig. 6 Autocorrelation function showing antibunching which is a signature for a single CdSe/ZnS QD coupled to Ag nanoprisms.

3.3 Blinking Suppression of CdSe/ZnS QDs in Agarose Gel with Charged Fibers
Recently, we have also achieved blinking suppression by embedding the QDs in in agarose gel. Time trace of photoluminescence intensity of a single CdSe/ZnS QD on glass and a single QD in 1% agarose gel were shown in Fig. 7. A typical binary blinking characteristic was observed for single QDs on glass. In contrast, a nonblinking time trace with fluorescence enhancement was found for CdSe/ZnS QDs in agarose gel. According to previous studies, the commercial agarose gel could have some inherent negatively charged fibers.[18] Based on our preliminary studies, we think that the charge distribution of gel fibres around QDscould strongly affect the blinking suppression of QDs.
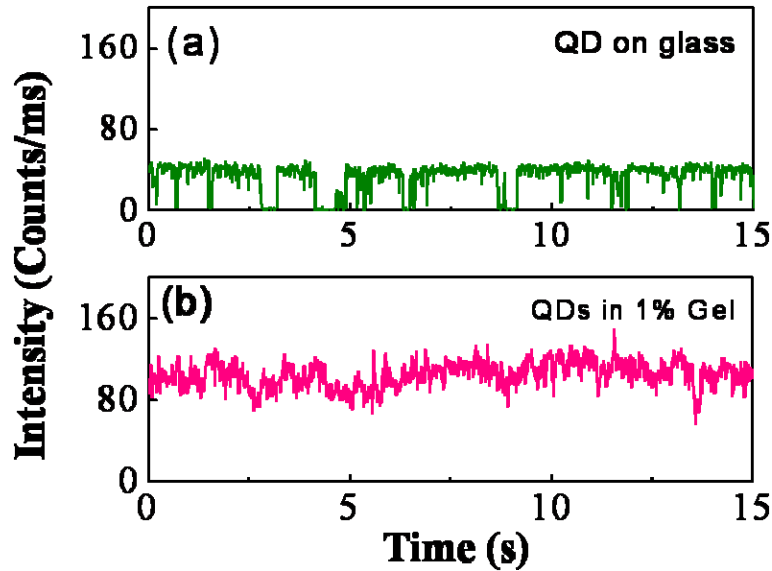
Fig. 7 Time trace of photoluminescence intensity of a single CdSe/ZnS QD on glass and in o1% agarose gel, respectively.

IV.   Conclusion

In this work, we report two different approaches to achieve blinking suppression and enhancement of fluorescence intensity of CdSe/ZnS QDs, namely, by coupling QDs to Ag nanoprisms and QDs in gel. The fluorescence time trace for most coupled QDs shows a constant intensity level with small intensity fluctuations but no presence of the dark events, clearly indicating suppressed blinking. For QDs coupled to Ag nanoprisms, we not only achieved blinking suppression but also obtained ~2.5-fold fluorescence enhancement and ~12.5-fold increase for the radiative decay rate via fine tuning the separation between QDs and Ag nanoprisms. We think that energy transfer and plasmonic effects by adjacent silver nanoprisms is responsible for the suppression of the charge transfer to the trap states and thus prevents the transitions to the dark states. All these improved characteristics would make the proposed scheme a better alternative for a high performance single-photon source. On the other hand, QDs in gel with a negative charge distribution on the inner surface could also inhibit the charge transfer to the surface trap states of QDs, leading to blinking suppression.

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