Antibunching Single-Photon Emission and Blinking Suppression of CdSe/ZnS Quantum Dots

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ARTICLE

ABSTRACT We demonstrated that by properly coupling to silver nanoprisms, single CdSe/ZnS semiconductor quantum dots (QDs) exhibited suppressed blinking behavior, an enhanced fluorescence intensity (~2.5 fold), increased radiative decay rates (~12.5 fold), and antibunching single-photon emission. All these modifications significantly promote the overall performance of the proposed single-photon sources based on colloidal semiconductor QDs.

KEYWORDS: blinking suppression · single-photon emission · photon antibunching · CdSe/ZnS quantum dots

A high performance single-photon source is essential in quantum cryptography.[1] To achieve such a goal, a variety of nanomaterials have been demonstrated, but all appear to suffer some deficiencies.[2−7] For example, epitaxially grown semiconductor QDs could be used extensively as such emitters, however, they are limited to low temperature operation.[8] Furthermore, low extraction efficiency and multiexcitonic state emission could degrade their practical performance. To improve single-photon emission, these QDs need to be incorporated into complex microcavities, but such a procedure is time-consuming and expensive.[9] Some single molecules with high quantum yields could also be used as single-photon sources at room temperature.[3] Unfortunately, their poor photostability is the main disadvantage. On the other hand, color centers in diamond bulk or nanocrystals have also been demonstrated as single-photon sources.[4,10] However, their broad emission spectra and several emissive sites located inside the sample are unfavorable.[11]

Recently, colloidal semiconductor QDs have attracted much attention due to their excellent fluorescence properties, including size-dependent emission, large absorption cross section, high quantum yields at room temperature, and excellent photostability.[12] Consequently, they are expected to have potential applications in biological labeling,[13] light emitting devices,[14] and single-photon sources.[5,15] However, the universal fluorescence blinking is a fatal disadvantage for their practical applications.[16,17] The detailed mechanism for blinking has been addressed by many researchers but remains unsettled.[18,19] It is widely accepted that the dark state represents a QD with a positive charge inside the core and an electron trapped in some surface states or surrounding matrix.[20] In this case, the exciton energy can be transferred to the core carrier by efficient Auger processes, instead of photon emission.[21] This Auger process not only quenches fluorescence but it also suppresses multiexcitonic emission.[21] Therefore, even at high-power excitation close to saturation, only single exciton emission occurs.[21,22]

Suppression of the fluorescence 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[23,24] or by capping a thicker inorganic layer.[25,26] For the former case, the attached chemical ligands are not temporally stable and could be removed from the QD surface. For the latter case, a multishell structure leads to increase the size of QDs. More importantly, to avoid large lattice mismatch between the CdSe core and ZnS shell (~12%), CdS was chosen to form this thick shell because of its smaller lattice mismatch. However, this approach also leads to the formation of a type-II band structure,[27] with the hole localized within the core and an electron delocalized over whole core/shell materials. Owing to less wave function overlap, such a structure should lead to reduced quantum yields and longer lifetimes, thus degrading the performance of single-photon emission.

Blinking suppression of single QDs could also be achieved by coupling these QDs to metal-coated substrates.[28,29] These interactions, including energy transfer (ET) and localized surface plasmon resonance (LSPR), could modify

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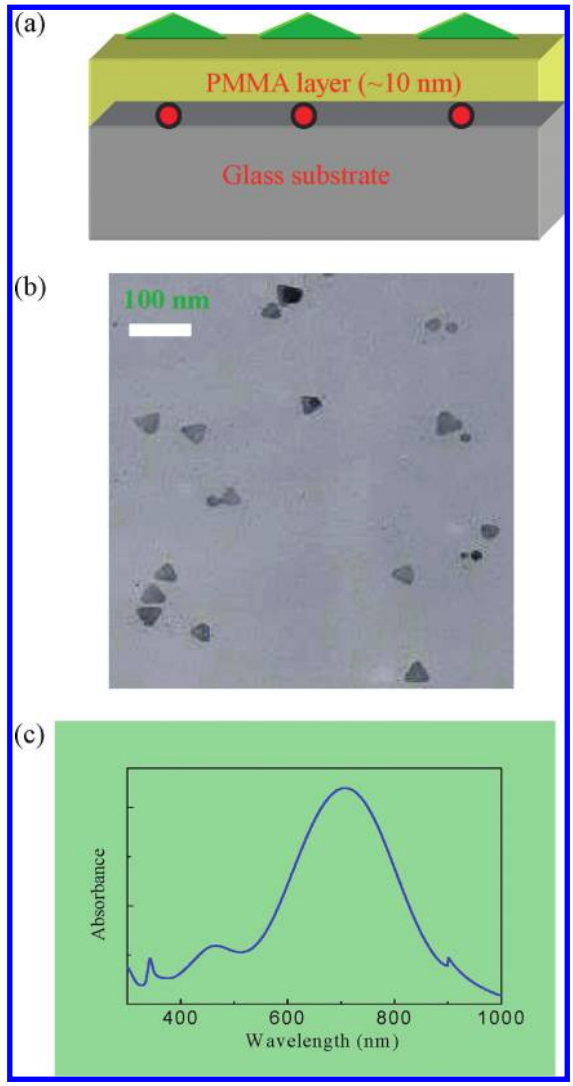

Figure 1. (a) The sample configuration of silver nanoprisms coupled single CdSe/ZnS QDs. (b) TEM image of silver nanoprisms. (c) Absorption spectrum of silver nanoprisms.

the single-QD fluorescence properties dramatically. It is well known that both ET and LSPR interactions are strongly dependent on the separation between the exciton and the plasmon.[30] Therefore, we optimized the coupling condition by fine-tuning the exciton−plasmon separation.

In this work, we presented a facile approach to concurrently suppress fluorescence blinking and enhance their fluorescence intensity. Moreover, we demonstrated a high performance single-photon emitter at room temperature based on colloidal QDs properly coupled to silver nanoprisms.

RESULTS AND DISCUSSION

To couple silver nanoprisms to single QDs with suitable separation, a simple structure was prepared, as shown in Figure 1 a. In this case, single colloidal CdSe/ZnS QDs emitted at ~600 nm were utilized as single-photon emitters. Plasmonic effects can be provided by upper silver nanoprisms. The TEM image of Ag nanoprisms with an edge length of ~47 nm is shown in Figure 1b and the corresponding absorption spectrum is shown in Figure 1c. In addition, a PMMA polymer layer with optimized thickness (~10 nm) was used to minimize energy transfer from QDs to silver nanoprisms. Therefore, based on this configuration, dominant interactions should be the plasmonic effects instead of energy transfer.

Figure 2a shows the fluorescence image ($6 \times 6\ \mu m^2$) of CdSe/ZnS semiconductor QDs coupled to silver nanoprisms. For general blinking QDs, the fluorescence intensity image exhibits non-Gaussian patterns due to fluorescence blinking that occurred during the course of scanning. In contrast, a complete Gaussian spot was observed for most of the coupled QDs. Figure 2b shows the typical fluorescence time traces with 10 ms bin time for reference and coupled QDs. To avoid the heterogeneity within the ensemble QDs, more than 30 QDs were measured and averaged for further data analysis and comparison. Generally, with a bin time of 10 ms, ~78% QDs within the ensemble samples exhibited continuous emission without long-lived dark states, but with some intensity fluctuation, rather than typical on/off blinking behavior. Furthermore, 2.5-fold fluorescence enhancement on average was observed for coupled QDs compared to the on-state of blinking QDs. Figure 2c shows a histogram of fluorescence intensity for more than 30 QDs. Because of the use of the spin-coating technique, the relative location between QDs and silver nanoprisms could not be exactly controlled, thus not all QDs could be coupled to silver nanoprisms. This blinking suppression and accompanied fluorescence enhancement could be attributed to the coupling of single QDs to its adjacent metal nanostructures with the excitation of LSPR.[28,31−33] The detailed mechanism is still under investigation. In current status, we thought that accelerating the radiative decay rates by coupling to silver nanoprisms to compete with Auger processes could play an important role in the blinking suppression and accompanied with enhanced fluorescence intensity.

Figure 3 shows the fluorescence decay profiles for reference QDs and the QDs coupled to silver nanoprisms. For reference QDs, the decay is single-exponential with a time constant of ~25 ns. Such a fluorescence lifetime is similar to those reported previously.[34] In contrast, the fluorescence decay profile for coupled QDs deviates slightly from a single-exponential decay with a shortened averaged lifetime of ~5 ns. The fluorescence intensity is described as

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

where Γ, k_{nr}, and τ stand for the radiative decay rate, the nonradiative decay rate, and the measured fluorescence lifetime, respectively. Therefore, by comparing the reference QDs with the coupled QDs according to

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

we deduced ~12.5 enhancement of the radiative decay rates. Although, the radiative decay rates can be enhanced by ~12.5-fold, the nonradiative decay rates also increased,

thus only 2.5-fold fluorescence enhancement was achieved.

To demonstrate single-photon emission behavior, photon correlation measurements were performed for QDs coupled to silver nanoprisms. Figure 4a reveals the second-order autocorrelation function under pulsed laser excitation with 10 MHz repetition rates. Obviously, a peak with a reduced height is found at zero delay time. This photon antibunching behavior is a signature for single-photon emission. Although, this photon antibunching dip did not go down to zero, its value of ~0.2 is still smaller than 0.5 (the value of autocorrelation function at zero delay for two independent emitters). This nonzero height could be attributed to the background fluorescence from silver nanoprisms. Actually, fluorescence has been found in nanometer-sized metal nanoparticles.[35,36] This fluorescence is attributed to radiative emission of LSPR. To estimate the contribution from the background fluorescence to the autocorrelation function, we measured the fluorescence spectra of single QDs coupled to silver nanoprisms, as shown in Figure 4b. This implies that the corrected autocorrelation function is about 0.04 upon subtracting the background contribution. Here, we cannot block the background fluorescence completely only by using interference filters due to spectral overlap between QDs and silver nanoprisms, which exhibits a broad plasmon band caused by multiple plasmonic modes, as shown in Figure 1b.[37] Fortunately, this plasmon-induced fluorescence has a relatively short emission lifetime.[35] Therefore, specific photons with very different lifetimes could be distinguished on the basis of time-gated techniques.

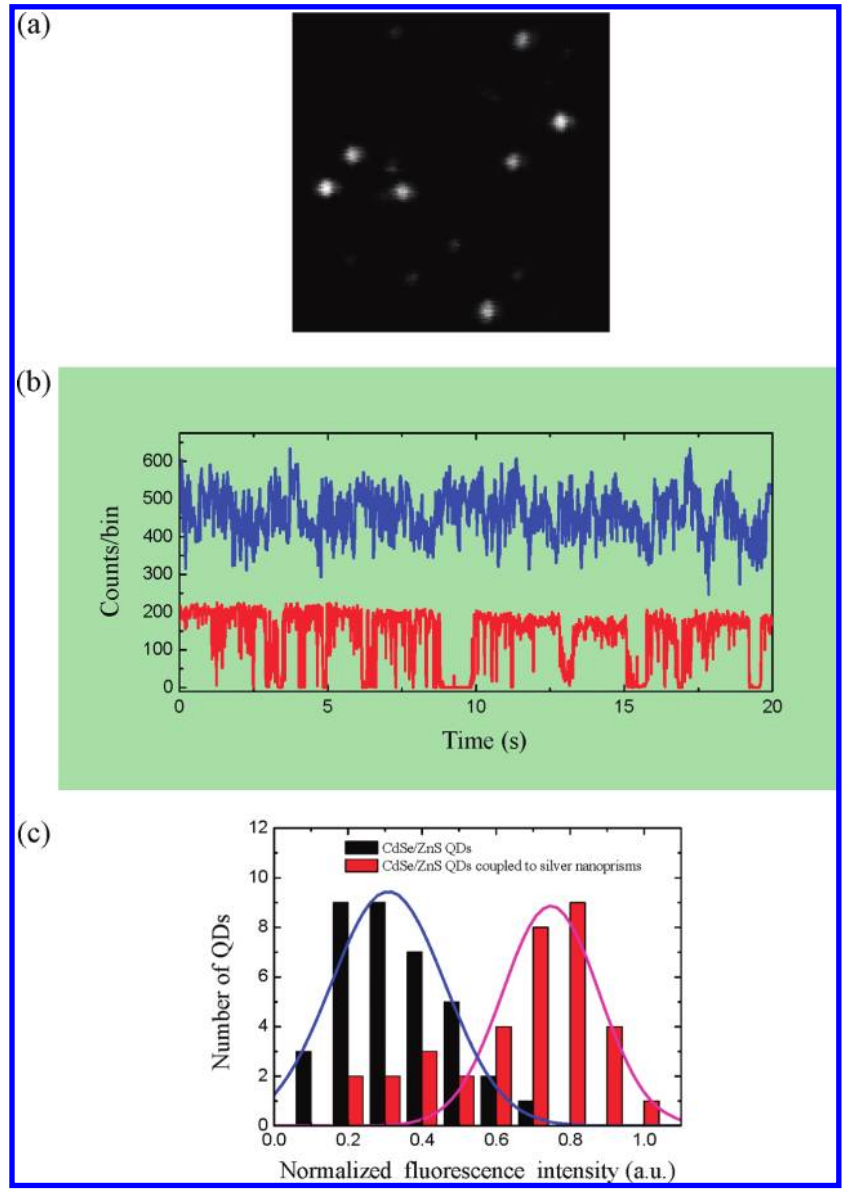

Figure 2. (a) Confocal fluorescence image (6 × 6 μm²) of CdSe/ZnS QDs coupled to silver nanoprisms. (b) Fluorescence time traces with 10 ms bin time for usual QDs on glass and coupled QDs to silver nanoprisms. (c) Histogram of fluorescence intensity for more than 30 reference QDs and coupled QDs.

In the following we summarized some advantages for our proposed single-photon emission configuration: (1) No issues on low photon extraction efficiency due to the surrounding matrix with a high refractive index. Such a problem always occurs for epitaxially grown QDs.[38] In our case, most of the emitted photons could direct to the detectors.[15] (2) Photon emission is relatively continuous instead of stochastic on/off blinking. (3) High fluorescence intensity at room temperature. (4) An enhanced radiative decay rate. (5) Facile to formation of QD/silver nanoprism hybrids by chemical binding.[31,32] (6) Better photostability. (7) No multiexcitonic states emission.[15,22] (8) Type-I band structure is still preserved. Despite many advantages, the main drawback is the relatively high background contribution from metal nanostructures.[35,36] As mentioned ear-

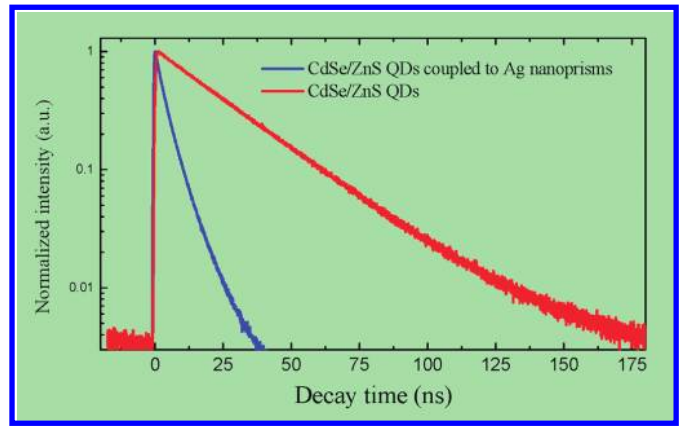

Figure 3. Fluorescence decay profiles for usual QDs on glass and QDs coupled to silver nanoprisms.

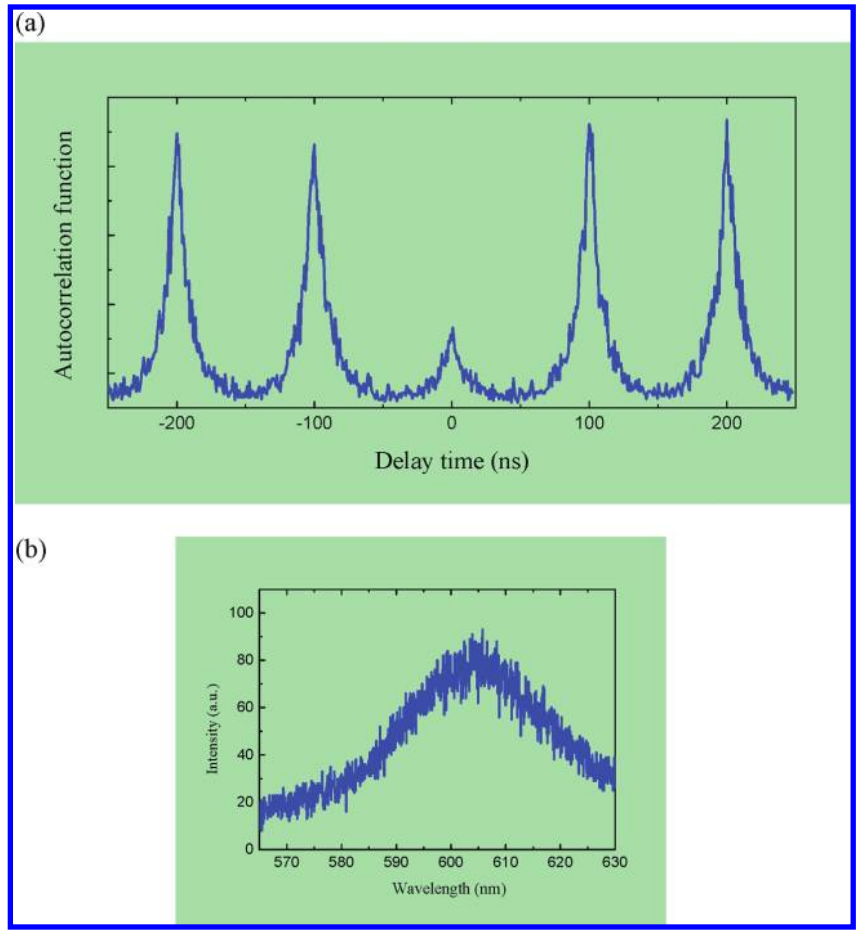

Figure 4. (a) Second-order autocorrelation function showing antibunching signature for CdSe/ZnS QDs coupled to silver nanoprisms. (b) Fluorescence spectrum of CdSe/ZnS QDs coupled to silver nanoprisms.

lier, such a drawback could be overcome by time-gated techniques to distinguish photons with very different fluorescence lifetimes.

CONCLUSION

We demonstrated a facile approach to achieve blinking suppression and enhancement of fluorescence intensity concurrently. With such a configuration based on CdSe/ZnS QDs coupled to silver 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. All these improved characteristics would make the proposed scheme a better alternative for a high performance single-photon emission.

EXPERIMENTAL SECTION

Colloidal CdSe/ZnS QDs in water emitted at ~600 nm were purchased from Evident Technology (detailed information can be found in the Supporting Information). The Ag nanoprisms were synthesized in our laboratory according to published methods with minor modifications (detailed information can be found in the Supporting Information).[39] For single-QD experiments, a dilute solution (10^{-9} M) was dispersed onto a glass coverslip by spin coating techniques. Upon a few minutes, a PMMA (in toluene) polymer layer with ~10 nm thickness (optimized condition) was capped onto the QDs as a spacer layer to minimize the energy transfer from the exciton to the plasmon so that fluorescence quenching can be reduced.[30,40] The thickness of PMMA layer was controlled by tuning the PMMA concentration (see Supporting Information). Note that when PMMA layer is smaller than ~5 nm, quenched fluorescence were observed for most of QDs. Finally, silver nanoprisms (10^{-6} M) were directly deposited onto the top of the PMMA layer. In this case, the mean separation between QDs is larger than the excitation laser spot (~300 nm), thus an individual QD could be monitored by a far-field laser scanning confocal microscope (MicroTime 200, PicoQuant). For better comparison, we also prepared a reference sample with the same procedure as mentioned before but without silver nanoprisms.

For excitation, a pulsed diode laser at ~460 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. After a pinhole, the fluorescence was split by a beam splitter cube into two beams, then filtered by suitable band-pass filters and finally detected by a pair of single-photon avalanche photon diodes. For photon correlation measurements, TTL pulses from two APDs were fed into a photon counting module (PicoHarp 300, PicoQuant) to perform second-order correlation function.[41]

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Supporting Information Available: Detailed information including sample configuration, synthesis of silver nanoprisms, and sample preparation. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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