

Anti-bunching and luminescence blinking suppression from plasmon-interacted single CdSe/ZnS quantum dot

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Abstract: CdSe/ZnS colloidal quantum dots generally exist as blinking phenomena during the luminescence process that remarkably influences its applications. In this work, we used the surface plasmonic effect to effectively modulate single quantum dots. Obvious contrasts have been observed by comparing single quantum dots on silica and gold films. The surface plasmon is shown to obviously suppress the blinking of single quantum dots. With further demonstrated second-order correlation measurements, an anti-bunching effect was observed. The anti-bunching dip gives the smallest value of $g^{(2)}(0) = 0.15$, and the lifetime of the exciton has been reduced. This method presents the application's potential towards tunable high-emitting-speed single photon sources at room temperature.

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OCIS codes: (270.5290) Photon statistics; (240.6680) Surface plasmons; (030.5260) Photon counting.

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1. Introduction

Quantum dots (QDs), which have atomic-level structures, are widely studied and have been utilized in areas of quantum information technology [1, 2, 3], bioactive fluorescent sensing [4], cavity quantum electrodynamics [5], and fundamental physics [6] for years. The core/shell structured CdSe/ZnS colloidal QDs with strong electron-hole-binding energy are controllable in fabrications, and hence can conveniently work at room temperature (RT) [7]. Furthermore, colloidal QDs can be easily manipulated to couple with other elements such as microcavities[5] and nanowires [8]. That quality provides advantages in complicated applications. Still, for colloidal QDs it is found that the phenomenon of blinking is a common feature in most of them, and the mechanism for this phenomenon is as yet unclear. In recent years, research has found that the surface plasmonic effect can influence QD dynamic processes through localized electromagnetic interaction, which brings forward a feasible way to suppress the quenching process within luminescence blinking [9, 10]. Simultaneously, the transition of QDs would also be modified, hence a possible method to tune the photon emission rate could be realized when a QD is

studied as a single photon source.

In this work we report on the enhanced single photon emission from a surface-plasmon-interacted CdSe/ZnS QD on gold film that has successfully suppressed the blinking of luminescence. The single photon emission is further demonstrated using second-order correlation measurement, and the anti-bunching gives the smallest value of $g^{(2)}(0) = 0.15$, which is much smaller than the value for normal QDs provided. We also show that coupling QDs to surface plasmons has greatly reduced the lifetime of an exciton compared to QDs on a silicon substrate out of a surface plasmon.

2. Experiment and analysis

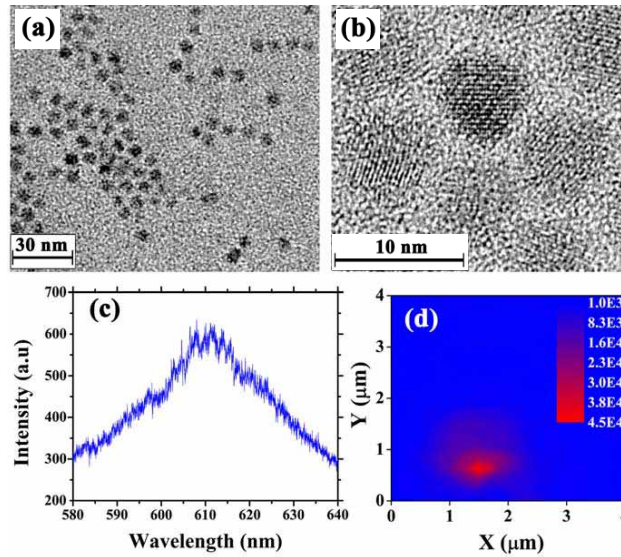


Fig. 1. (a),(b) TEM images from CdSe/ZnS QDs at different scales. (c) Photoluminescence spectrum of CdSe/ZnS QDs assembling at RT. (d) Confocal scanning image shows a single QD on gold film within the area.

The colloid CdSe/ZnS QDs in the experiment are chemically synthesized core/shell QDs as the transmission electron microscopy (TEM) pictures demonstrate in Figs. 1(a) and 1(b) at different scales. At RT, QD luminescence has the emitting peak centered at 610 nm [Fig. 1 (c)]. To prepare the sample, QDs were dispersed in toluene, then spin-coated on the substrates. In a homemade confocal scanning system, the samples were placed on a three-dimensional piezoelectric transition (PZT) stage and excited by an Nd:YAG continuous-wave laser ($\lambda = 532$ nm) through an objective (NA = 0.85). Photons from QDs were collected by the same objective. After that, the photon was detected by a standard Hanbury-Brown and Twiss (HBT) setup [11] before which the bandpass filters were used. The atomic-force microscope inspected the substrates given the roughness of around 5 nm for both silica and gold films. The average distribution density of QDs on each substrate was controlled at around $0.2/\mu\text{m}^2$, as can be noted in the confocal scanning image shown in Fig. 1 (d).

In an open environment without isolating material, the luminescent process of a single CdSe/ZnS QD would usually be intensively quenched, leading to a dark state. Many mechanisms have been proposed to explain the phenomenon; for example, the defects in the surrounding variance [12] or the Auger ionization [13]. Generally, the bright period of time (on-time)

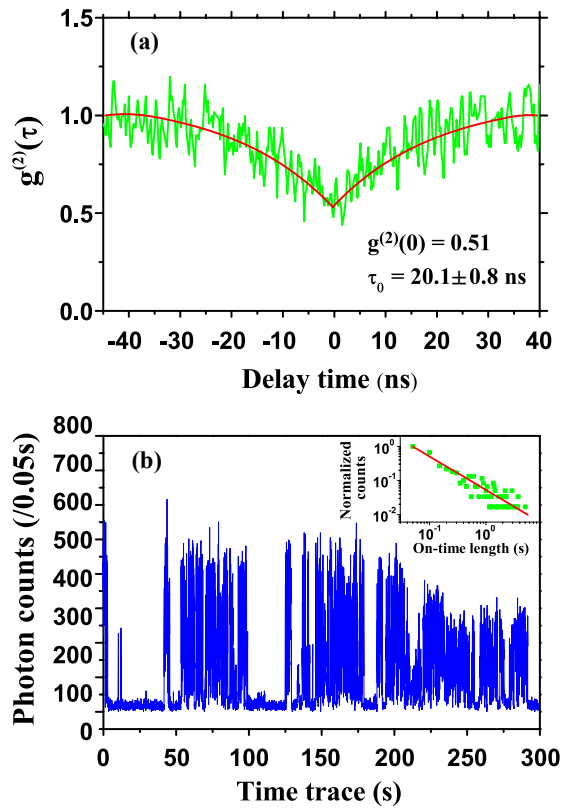


Fig. 2. (a) $g^{(2)}(\tau)$ for a single QD on silica substrate. (b) The corresponding QD's fluorescence intensity variation in the 300 s range. The inset is a statistic of on-time length, and real measured data (scatters) follow Eq. (1) (red line) with $\alpha = 1.22$.

obeys the self-similar inverse power law [14, 15],

$$P_{on} = P_0 t^{-\alpha}, \quad (1)$$

where α is a parameter characterizing the event of blinking under a certain condition. In Fig. 2, we present a typical blinking phenomenon of a single QD on silica with a 20 Hz acquisition rate. It can be seen that a large scale of luminescence intensity dropped to the level of background noise, even though the dark state lasted over 25 s. The inset of Fig. 2(b) gives the distribution of on-time length from this period. Using Eq. (1) the optimized fitting takes $\alpha = 1.22$, consistent with typical conditions [14].

Under the same condition, a dramatic difference can be observed for the CdSe/ZnS QD on the gold film owing to surface plasmonic influence. In this situation, the gold film has generated a strong surface plasmonic field during the photoluminescence excitation process. Non-blinking fluorescence was sustained for a long time scale, as shown in Fig. 3(b). The background noise (N) is marked with the QD signal (S) simultaneously, which is explicitly lower than the QD luminescence in almost 300 s of detecting time. This clearly indicates that there is no obvious quenching of luminescence appearing through the long excitation time. In detail, as is demonstrated in the inset of Fig. 3(b), the emission is stable during most of the selected 25 s. However, it does not mean the blinking is completely eliminated. We can observe the dark state of the QD

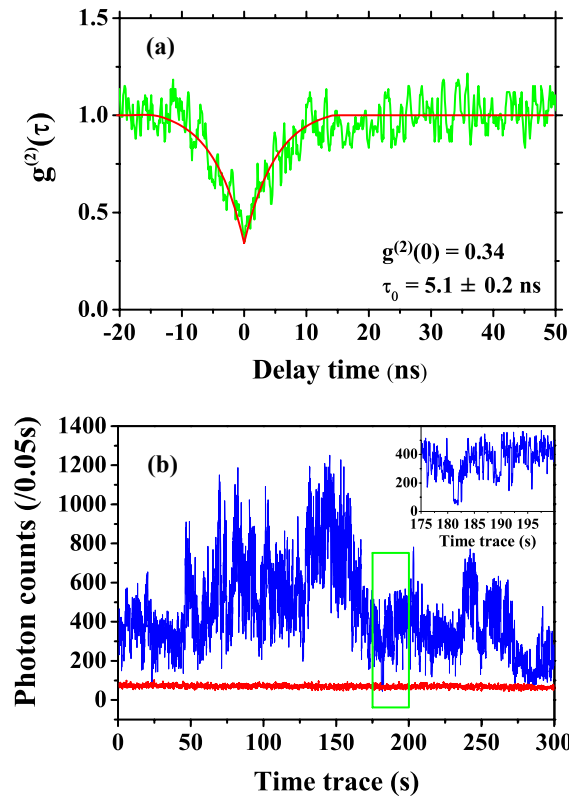


Fig. 3. (a) $g^{(2)}(\tau)$ for a single QD on gold substrate. (b) The same QD's fluorescence intensity variation detecting time is 300 s, and background noise is shown as red scatter for clarity. The inset is a magnified time trace.

emission happening in a short time range at the magnified image. The luminescence quenching mechanism still exists, but the surface plasmon has greatly reduced the possibility of the effect. The mean fluorescence intensity ($\bar{S} + N$) for the 300 s period shows a striking difference from the sample on silica. The QD on gold is 460 counts/50 ms, and the QD on silica is 122 counts/50 ms. Removing the noise signal, a luminescence enhancement factor of 3.8 can be extracted.

The enhancement of fluorescence is mainly due to the localized plasmonic excitation from the gold film [16]. Within the raised emission intensity the plasmon-enhanced excitation field is believed to be dominant [17, 18], since there is a large internal quantum yield of the CdSe/ZnS QD and the weak excitation light (4 Kw/cm^2) that is well below saturation intensity in our experiment [19]. Based on the electromagnetic model [20], a QD can be treated as a dipole adjacent to the gold film surface. The surface plasmon is excited by the incident light, which generates a localized electromagnetic field in the region and draws the radiating process into an increased frequency [21]. A direct consequence would be a dramatic reduction of the exciton lifetime. The radiation rate of the QD is $\gamma = |f(\omega)|^2 \gamma_0$; here, γ_0 is the radiative rate of bare QDs, while $f(\omega)$ depicts electromagnetic enhancement [22, 23]. In addition, the coupling of QDs and plasmons changes the electric environments of QDs, and the energy transfer in the quenching period will be modified [9]. Therefore, when the luminescence of QDs is blocked, the strong electric field generating from the gold film propels the QD to escape the quenched

state, thus the blinking of a QD is naturally suppressed.

Within this picture, a QD under surface plasmonic interaction is expected to provide a variable photon emitting distribution. Accordingly, the second-order correlation functions $g^{(2)}(\tau)$ are presented. The anti-bunching state has been found for both QDs on silica (Fig. 2) and gold (Fig. 3) substrates. Under a steady excitation power, they were used for comparison. Based on our exciting conditions, all the data can be fitted using a single exponential function [24],

$$C(t) = C_0 + A \exp(-t/\tau_0), \quad (2)$$

where the lifetime τ_0 is determined by the upper level lifetime of the CdSe/ZnS QD, and C_0 is the contribution from background light. Depending on the above results from Figs. 2(b) and 3(b), the mean signal-to-noise ratios $\bar{\rho} = \bar{S}/(\bar{S} + \bar{N})$ are at the levels of 0.71 and 0.84, respectively. Therefore the background noise would add $g^{(2)}(0)$ up to $1 - \rho^2$ from zero [25], which are 0.496 and 0.294, and the resulting values are close to the fitted data in Figs. 2(a) and 3(a). In a practical system, since background noise is inevitable, a higher signal-to-noise ratio is preferred to reach lower $g^{(2)}(0)$ so as to maintain a better quantum character at RT.

To analyze the modification of the emission rate, a QD with suppressed blinking generated a different transition process. Figures 2(a) and 3(a) have already demonstrated changing of lifetime τ by using Eq. (2). The reduction of lifetime is estimated to be $20.1/5.1 = 3.94 \pm 0.3$. We exhibit a serial of a single QD's lifetime getting from the second-order function in Fig. 4(a). The interesting aspect is that the surface plasmonic effect can greatly reduce the lifetime of the exciton. QDs on silica take average $\tau_0 \sim 19.8$ ns which is inconsistent with the theoretical calculation from the first-principle empirical pseudopotential method [26]. The fluctuation of τ_0 on silica is very small, which excludes the influence from excitation power drifting. Meanwhile, for QDs on gold film, the localized electric field can greatly change the exciton transition of a QD. For all of our samples we obtained the shortest lifetime to 4.9 ns, about 1/4 of the original time. Due to the surface feature's fluctuation, even the surface roughness is fabricated to be similar; it is impossible to reach an identical environment for each QD. This adds up to changing the electromagnetic field for coupling with QDs, and a constant effect cannot be kept. As a result, the fluctuation of the surface plasmons determined an unequal lifetime of QDs on gold, as we observe in Fig. 4(a).

Figure 4(b) is the corresponding $g^{(2)}(0)$ of the QDs in Fig. 4(a), where the left part represents the value of QDs on silica, and the right region is the QD's lifetime with gold substrate. The $g^{(2)}(0)$ from silica are close; besides, the average value is 0.52. However, the value is much lower from gold film. The smallest $g^{(2)}(0)$ we have obtained is 0.15. The lower $g^{(2)}(0)$ is promising for the practical application of a single photon source, especially in quantum cryptography [27]. In our experiment, all the data were detected under the same conditions, so the variation of $g^{(2)}(0)$ for QDs on gold still indicates that multi-photon emission from a single CdSe/ZnS QD could be influenced under plasmonic interaction at RT. Related mechanics in this process should be further studied.

Notice an important fact that although the plasmon-assisted luminescence could weaken the blinking, the phenomenon has not been thoroughly inhibited. That may be related to the sample preparation method [28]. Nevertheless, for practical applications such as using CdSe/ZnS QDs to be a single photon source [29], usually a faster single-photon emission rate is needed because multiple advantages can be achieved such as higher repetition frequency of the system. Owing to that, plasmon tuning may satisfy the requirement, not only for QDs but also in other luminescence materials like diamond crystals.

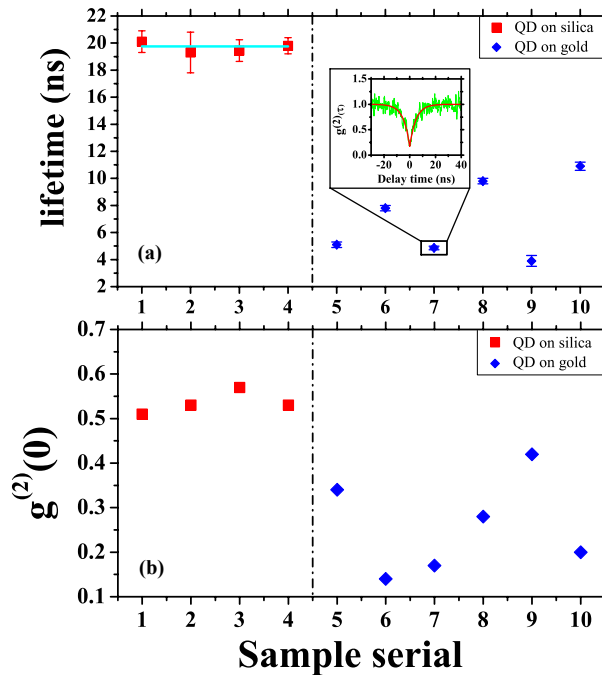


Fig. 4. (a) Lifetime of exciton for QDs on silicon and golden substrates. (b) Corresponding $g^{(2)}(0)$ for the anti-bunching effect.

3. Conclusion

In summary, we have studied the effect of surface plasmonic modification on the optical properties with CdSe/ZnS colloidal QDs at room temperature. Through the comparison of a single QD on different substrates, it has been found that the surface plasmon can effectively suppress the blinking of single quantum dots. The second-order correlation showed that the anti-bunching effect achieved a smaller value on gold, which is prominent for keeping the quantum property of a photon source. At the same time, the surface plasmon has greatly reduced the lifetime of the exciton. This result paves the way for potential applications towards single photon sources with tunable emission rates at room temperature.

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