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Controlling fluorescence intermittency of a single colloidal CdSe/ZnS quantum dot in a half cavity

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We show that by placing a single CdSe/ZnS quantum dot (QD) near a high-reflective optical mirror, both the photoluminescence intensity and the blinking statistics can be modified significantly and controlled deterministically by changing the dot-mirror distance. The modified local optical mode density in proximity to the QD alters the internal dynamics of the QD, which controls its blinking behavior. Such external controls of single-QD blinking can help us to better understand the underlying mechanism of the blinking process and lead to interesting applications of such QDs.

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Fluorescence intermittency (blinking) is a universal property of single colloidal semiconductor quantum dots (QDs),[1] which can greatly affect the applications of QDs in biological labeling,[2] optoelectronic devices,[3] and single-photon sources.[4] Therefore, it is very important to find ways either to suppress or to control the blinking phenomenon in the QDs.[5–8] Efforts have been made to suppress the intermittency phenomenon by using chemical procedures, where the durations of the "on" time are increased considerably by surface passivation[5] or by increasing the shell thickness around the core[6] to modify the charge tunneling process.[7] An external modification of intermittency process was observed when the single CdSe/ZnS QD was placed in the proximity to a rough metal surface.[8]

When a light emitter is placed inside a small optical cavity, its emission properties, such as radiative lifetimes, emission spectra, and quantum statistical properties of the field, will be greatly modified, leading to an active field of research called cavity-quantum electrodynamics (cavity-QED).[9–12] If only one cavity mirror is present near the light emitter, the system is viewed as a half cavity with the light emitter coupling to a large number of field modes or can be considered as in the "low-Q" regime of cavity-QED.[10] Depending on the distance between the light emitter and the mirror, there are two regions for studying the emitter-mirror interactions. When the light emitter is far from the mirror with a distance in the order of tens of centimeters, the reflected light from the mirror is significantly delayed and the interaction processes become non-Markovian.[10] Interesting effects under this condition were studied by using a trapped Ba^+ ion placed long distance from a high-reflective mirror.[11,12] However, when a light emitter is placed very near the dielectric mirror (in the order of wavelength of the emitted light), the interaction processes are Markovian.[10] Modified average radiative lifetime was measured for an ensemble of CdSe/CdS QDs near a reflective surface with an oscillatory behavior as the average dot-mirror distance changed.[13]

In this Rapid Communication, we experimentally demonstrate that when a single CdSe/ZnS QD is placed near a highly reflective dielectric mirror (in the Markovian regime), not only the photoluminescence (PL) intensity is modified when the dot-mirror distance is changed but the PL intermittency behavior also gets significantly altered with an oscillatory change in its statistically evaluated diffusion correlation rate as a function of dot-mirror distance. The experiments were carried out at room temperature by placing the CdSe/ZnS QD sample (spin coated on quartz coverslip with less than 1 QD/μm^2) at a distance L away from the dielectric mirror [mounted on a piezoelectric transducer (PZT)], as shown in Fig. 1(a). The QDs have an average diameter of 3.2 nm with the emission-peak wavelength at 575 nm. PL images, spectra, and the blinking time sequences of the single-QD were obtained by using the conventional far-field confocal microscopic technique.[13,14] The excitation light was from the 488 nm line of an argon-ion laser, which was incident onto the sample through a microscope objective [200 × and numerical aperture =0.7] giving a spot size of ~560 nm and having an excitation intensity of 350 W/cm^2. This excitation intensity was used to give clear blinking signals as the dot-mirror distance was varied. The PL signals were collected by the same objective and sent into the spectrometer. The PL spectra and time traces of blinking events were recorded by using the water-cooled photomultiplier tube (PMT). The spatial PL images [Fig. 1(b)] were recorded

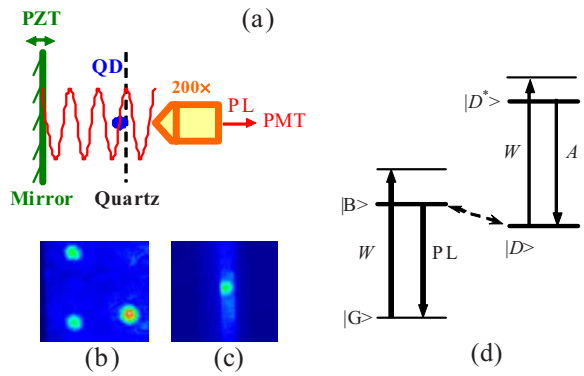

FIG. 1. (Color online) (a) Experimental setup with a single CdSe/ZnS QD placed at a distance L from an optical mirror. The mirror is mounted on a piezoelectric transducer to tune the QD-mirror distance. The QD excitation and PL collection are from the same objective. (b) PL images of single-QDs with a fully opened entrance slit of spectrometer. (c) PL image of an individual QD with a narrowed spectrometer slit. (d) Energy level diagram for single-QD from the DCET model.

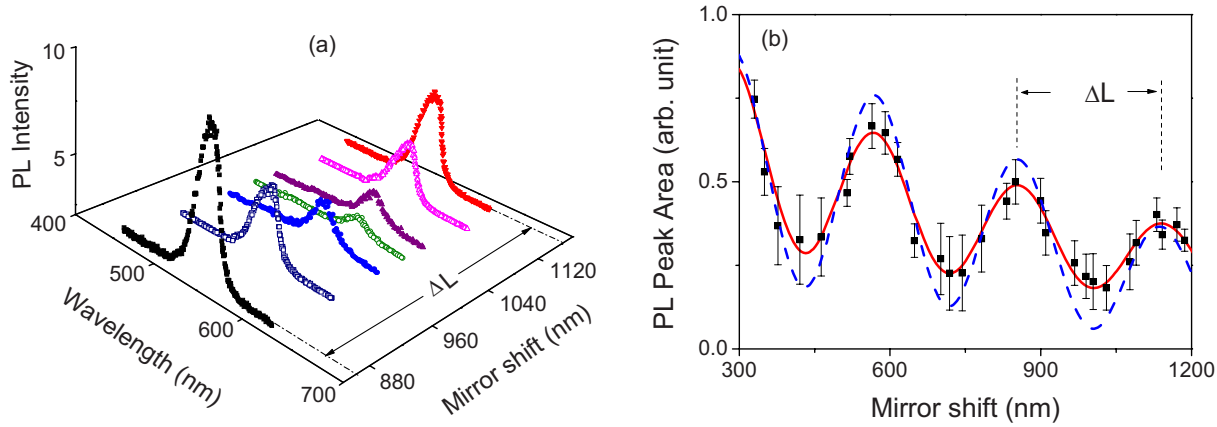

FIG. 2. (Color online) (a) PL emission spectra of a single-QD at dot-mirror separations of 849 nm (solid square), 909 nm (empty square), 967 nm (solid circle), 1003 nm (empty circle), 1030 nm (solid triangle), 1090 nm (empty triangle), and 1141 nm (solid reverse triangle). (b) PL areas under the spectra as a function of dot-mirror distance. Square points are the experimental data. The solid and dashed lines are the fits to Eq. (1) with Lorenzian and Gaussian correlation functions, respectively. (a) corresponds to the ΔL region of (b).

by a liquid-nitrogen-cooled charge-coupled device (with an integration time of 10 s). One-dot image was obtained by further closing the slit of the spectrometer, as shown in Fig. 1(c).

Figure 2(a) shows the PL spectra of the single-QD, which are recorded at different dot-mirror distances. Enhanced and inhibited PL intensities are observed while the dot-mirror distance is increased from 846 to 1029 nm successively along with certain spectral shifts.[15] When the areas under the PL spectra are plotted as a function of the dot-mirror distance [data points in Fig. 2(b)], a clear oscillatory behavior is observed. Such an oscillation in PL intensity near the mirror can be understood as the interference between the light field emitted by the QD directly [denoted as $E(t)$] and the retarded field reflected from the mirror with a time delay τ [denoted as $E(t+\tau)$]. The reflectivity of the dielectric mirror is $\sim 99\%$ at 575 nm wavelength. The small reflectivity (few percent) at the surfaces of the quartz coverslip can be neglected since its distance from the QD is fixed. Under the perfect reflection condition, the stochastic and time averaged total signal intensity is given by

$$I(\tau) = \langle |E(t) + E(t+\tau)|^2 \rangle = 2\langle |E(t)|^2 \rangle (1 + \mathrm{Re}[g^{(1)}(\tau)]). \tag{1}$$

The first-order correlation function $g^{(1)}(\tau)$ can be written either as $g^{(1)}(\tau) = \langle E(t)E^*(t+\tau)\rangle / \langle |E(t)|^2 \rangle = \exp(-\alpha|\tau|)\exp(-i\omega\tau)$ for the Lorentzian PL line shape or as $g^{(1)}(\tau) = \exp[-(\alpha\tau/2\sqrt{\ln 2})^2]\exp(-i\omega\tau)$ for the Gaussian PL line shape, with $\tau = 2kL/\omega = 2L/c$, where k is the wave vector of the emitted light. α is proportional to the linewidth of the PL spectrum, which corresponds to the decay rate Γ_B of the excited state $|B\rangle$ [Fig. 1(d)]. We fitted the data with both Lorentzian and Gaussian fluctuating fields in Fig. 2(b) and found that the fit to the Gaussian is definitely not as good as to the Lorentzian line shape, which indicates that the emission lines are more Lorentzian in shape.[16] The damping in oscillation in Fig. 2(b) is mainly determined by α. The oscillatory behavior in PL intensity can be explained by the modification of the photon mode density (PMD) at the location of the QD due to the presence of the mirror. When $kL = n\pi$, the reflected (retarded) field $E(t+\tau)$ from the mirror is in phase with $E(t)$; therefore there is an antinode of field strength at the QD location, which enhances the PL. When $kL = (n+1/2)\pi$, $E(t+\tau)$ is out of phase with $E(t)$ and there is a node in the field strength at the QD location, which inhibits the PL. Due to this field intensity change as a function of dot-mirror distance, the decay rate of the "bright" state ($|B\rangle$ to $|G\rangle$) and the transition frequency are also modified.[10]

Several time traces (60 s) of PL intermittency are shown in Fig. 3 for the single-QD with different dot-mirror separations. The PL intensity of the on states changes periodically with distance (which is consistent with the corresponding spectral measurements given in Fig. 2). From Fig. 3, it is clear that the on or off statistical properties are also altered at different dot-mirror distances. The blinking events occur much more frequently in Figs. 3(a) and 3(e) (corresponding

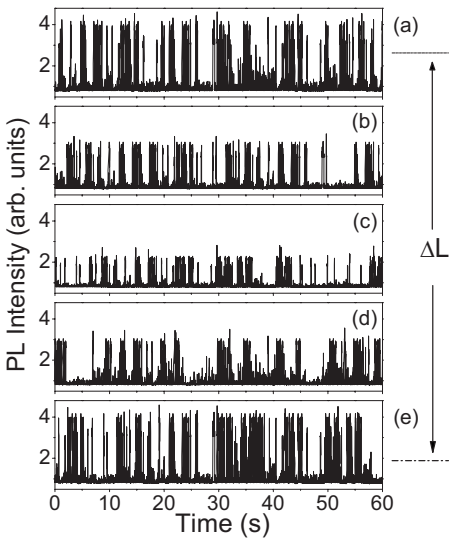

FIG. 3. Photon-counting trajectory segments of PL intensity for an isolated QD at dot-mirror separations of (a) 849 nm, (b) 909 nm, (c) 1003 nm, (d) 1090 nm, and (e) 1141 nm, respectively, corresponding to the ΔL region of Fig. 2(b).

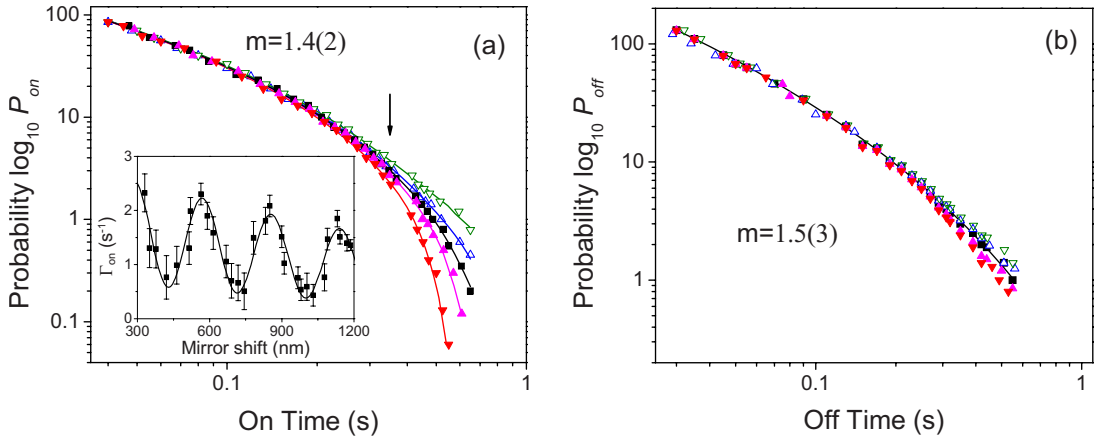

FIG. 4. (Color online) (a) Experimentally measured on-time probabilities for the dot-mirror separations of 849 nm (solid reverse triangle), 899 nm (solid triangle), 909 nm (square), 967 nm (empty triangle), and 1003 nm (empty reverse triangle). The solid curves are fits to the DCET model. The arrow indicates the start of the truncation point. Inset: measured variation in the diffusion correlation rate Γ_{on} for the on state as a function of the dot-mirror distance (data points). The solid line is a fit to the data. (b) Experimentally measured off-time probabilities for the same dot-mirror separations as in (a).

to the antinode positions in the interference fringe) than in Fig. 3(c) (corresponding to the node position in the interference fringe).

The modified QD intermittency is caused by the change in optical environment with the half cavity in proximity to QD.[9–12] To quantitatively describe such modifications of the QD's internal dynamics with the mirror, we adopted the light-driven four-state diffusion-controlled electron transfer (DCET) model,[17] which has been used successfully to explain the spectral diffusion and the blinking statistics that follow the power-law behavior.[15,17] The basic energy-level diagram of this DCET model is shown in Fig. 1(d). The neutral bright states involve the conduction state $|B\rangle$ and valence state $|G\rangle$. The "dark" states involve the decay between charge-separated excited $|D^*\rangle$ and ground $|D\rangle$ states through the nonradiative Auger process (labeled as A). W is the photoexcitation rate. When time t is longer than the critical time constant $t_{c,i}$ but shorter than the effective diffusion time constant τ_i, the blinking statistical probabilities $P_{on}(t)$ and $P_{off}(t)$ for the on events and off events are given by[17]

$$P_i(t) \approx at^{-m} \exp(-\Gamma_i t), \tag{2}$$

where i=on or off and $a=\sqrt{t_{c,i}/\pi}/2$. $\Gamma_i \propto 1/\tau_i$ with τ_{on} and τ_{off} being the diffusion correlation times for the bright state $|B\rangle$ and dark state $|D\rangle$, respectively. Dependences of blinking behaviors on various parameters, such as excitation intensity, temperature, and size of the QD, were verified using the DCET model.[17] Here, we will only concentrate on investigating the modifications and control of the PL intensity and blinking statistics with nearby high-reflective mirror and the underlying physical mechanism.

We first analyzed the blinking data for the QD without the mirror for on and off probability distributions using Eq. (2). For short on or off times, the power-law distribution dominates to give the power-law exponent m. In longer on or off times, the spectral diffusion starts to take effect and the on or off probability distributions bend according to the exponential function. The power-law exponents for the on- and off-time probability distributions are obtained by fitting to Eq. (2) with m=1.4(2) and m=1.5(3), respectively, which are consistent with the theoretical predictions of the DCET model.[17] Since the determined Γ_{off} value (0.01 s^{-1}) is much smaller than the Γ_{on} value (1.0 s^{-1}), a much smaller bending for the off-time distribution was observed, as expected from the DCET model.

Next, we investigated the effects of the mirror on the dynamic behaviors of the QD. As shown in Fig. 4, when the mirror moves toward the QD, the bending (therefore Γ_{on}) in the on-time probability function changes significantly at its long-time tail of the distribution [Fig. 4(a)], while Γ_{off} changes only slightly with the same changes in dot-mirror distance [Fig. 4(b)]. This insensitive dependence of Γ_{off} on dot-mirror distance is similar to the result without the mirror and is consistent with the earlier observations that the off-time events are independent of the excitation intensity, temperature, and size.[15,17] To make the comparison, the m value was fixed in fitting the data for each dot-mirror distance and the Γ_{on} and Γ_{off} values for each distance are then obtained by fitting the measured on- and off-time distribution curves, respectively. The curves with black squares in both Figs. 4(a) and 4(b) are the same as the curves measured without the mirror. When the Γ_{on} values are plotted as a function of the dot-mirror distance, a clear oscillatory behavior appears, as shown in the inset of Fig. 4(a). The period of this oscillation coincides exactly with the interference fringe of the PL intensity shown in Fig. 2(b).

These results indicate that along with the PL intensity, the bright state transition can also be modified by changing the local PMD at the QD. The underlying mechanism of the modified blinking statistics can be explained by using the DCET model. In the blinking processes, the transition between states B (excited state) and D (dark state) occurs at the crossing point of Q (reaction coordinate) of the two parabolic energy curves.[17] The time intervals between the blinking events are determined by the diffusion along the reaction coordinate with a sink at Q. According to the DCET model, these transitions are assisted by the phonons.[17] The changes

in the energy positions of the PL spectra with mirror distance occur when the photoexcited QD charge carriers can only make transitions back and forth to the nearby trap states via phonon states. In our experiment, the Stokes and anti-Stokes shifts from the single-QD emission near the mirror indicate the perturbative electron-phonon interaction. When there is a spectral shift, the transition energy of the QD changes as a function of time. The total shift of peak emission from node to antinode is ~115 meV (resulting from the random spectral diffusion). This shows that the electrons and the LO phonons are coupled, which can form strong mixed electron-phonon mode continuum,[18] and the cavity effect on this coupling was previously investigated.[19] Depending on the altered local PMD due to the mirror, the electronic coupling between the excited states of the QD and the trap levels via phonons will be modified, which results in the change in the diffusion correlation time and therefore modified blinking behavior, as observed in our experiment with changing dot-mirror distance. The value of the PL intensity has been modified by a factor of 3 [Fig. 2(b)] and the value of the diffusion correlation on time has been changed by a factor of 2 [inset of Fig. 4(a)], which can be very useful in certain applications.

Emissions from both charged (D^* to D) and neutral (B to G) excitons in individual QD have been observed with spectral shifts.[8] We have also detected the spectral shifts toward blue as well as red sides (with 57.5 meV shifts) by changing the mirror distance when compared to the free space emission. The modified PMD at the QD due to the mirror influences the interband recombination time (enhanced PL intensity), which can also cause Stark shifts of both neutral and charged excitons (but these shifts do no need to be identical).

In summary, by changing the dot-mirror distance, the PL intensity [Fig. 2(b)] and the blinking statistics [Figs. 3 and 4(a)] have been significantly modified and controlled. Photon correlation experiment[4] is underway, and we expect to be able to control the photon statistical properties of the light emitted by the single-QD with a mirror or a better designed optical microcavity. With the external control of the intermittency from a single-QD, we are able to better understand the underlying physics of the blinking phenomenon and hope to ultimately control it for practical applications, such as single-photon source, optoelectronic devices, and biomedical imaging. Also, this work demonstrated a solid-state system for studying cavity-QED effects using single-QD.

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