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# Temporal response analysis of trap states of single CdSe/ZnS quantum dots on a thin metal substrate

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ABSTRACT

To clarify the influence of trap states on the emission dynamics of CdSe/ZnS colloidal quantum dots on metal and glass substrates, we measured the trap state lifetimes of single QDs on different substrates using the photon inter-detection time analysis method. The results indicate that the trap state lifetimes as well as the emission counting rates changed depending on the substrate. Although the reduction in the counting rate can only be understood by the fast energy transfer to the metal substrate, the changes in the trap state lifetime suggest the influence of the substrate on the trap state. Thus, we concluded that the blinking suppression on metal substrate is caused not only by the fast energy transfer, but also by the shortening of recovering time from the trap state.



## 1. Introduction

Semiconductor colloidal quantum dots (QDs), because of their high emission efficiency and wide selectivity of emission wavelength, have long been the materials of choice for composing ultra-small and thin optoelectronic devices such as single-photon sources, light emitting devices, and transistors. These single QDs exhibit blinking behavior caused by quantum mechanical characteristics common to such single nano-emitters [1–5]. Because this behavior is sensitive to the local environment of single nano-emitters, various applications such as sensors have been proposed. However, a significant drawback is that the blinking behavior reduces emission efficiency, which limits their application to optoelectronic devices.

Several methods were proposed to suppress this blinking and to realize blinking-free single-photon sources from single QDs in dielectric media [6–8], in reductant agent solutions [9], on metal films [10–15], and in metal nanoparticles [16–20]. Kanemitsu et al. reported that the blinking was suppressed by the fast energy transfer from QDs to a gold film and emission counting rates from single QDs were increased by plasmonic enhancement effect due to the roughness of the gold surface [12–14]. Although the mechanism of this blinking behavior is still unknown, it has been recently considered that the blinking is caused by ionization of QDs owing to the capture of photoexcited carriers in QDs to trap sites on a substrate [5], and the blinking dynamics should be sensitive to the substrate surface on which QDs are dispersed. Although the influence of the substrate on the emission dynamics of the excited state of single QDs has been previously studied, little emphasis has been placed on the influence of the substrate on the trap state itself.

In this paper, we attempt to clarify the trap state effects on the emission dynamics of the excited state of single QDs on metal and glass substrates using histograms of photon inter-detection times (PIT) [21–23] to directly measure the trap state lifetime and the emission counting rate in the ON state. We found that the lifetime of the trap state is changed depending on the substrates and these affects on the blinking behavior, not only fast energy transfer to Au substrate. These results suggest that, besides the fast energy transfer to an Au thin film, the substrate influence on the trap state must be considered to understand the blinking behavior and emission efficiency of single QDs especially for their application to small-integrated devices on various substrates.

## 2. Experimental

The sample preparation included careful cleaning of glassware and $SiO_2$-glass substrate by sonication in acetone, an alkaline detergent, and ultrapure water. After cleaning the $SiO_2$-glass substrate, Au and Cr layers with thicknesses 50 nm and 5 nm, respectively, were deposited by a helicon sputtering system to create an Au/$SiO_2$-glass substrate. Then, it was coated with a 20-nm $SiO_2$ cover

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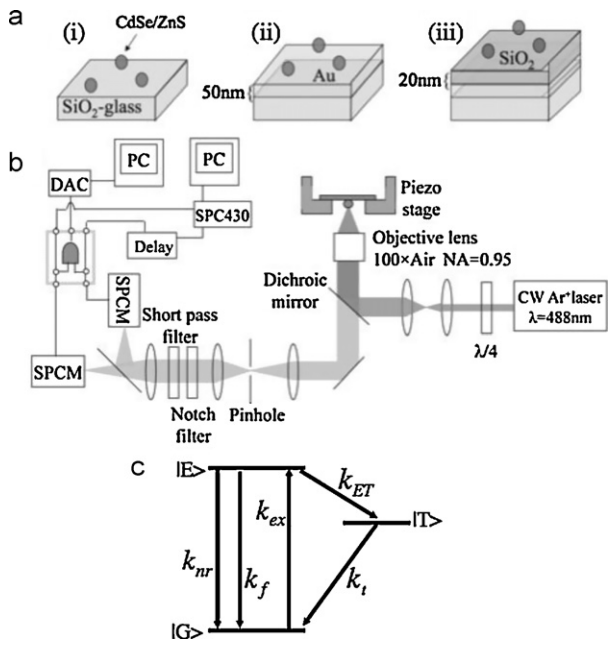


**Fig. 1.** (a) Optical setup for the measurements of single QDs on each substrate and (b) schematic diagrams of prepared sample configurations ((i) $SiO_2$-glass, (ii) Au/$SiO_2$-glass, and (iii) $SiO_2$/Au/$SiO_2$-glass substrates). (c) Three-state model of single QDs.

layer to form an $SiO_2$/Au/$SiO_2$-glass substrate. The thickness of the cover layer was referred to Ref. [13], in which when the thickness was around 20 nm, the energy transfer effect and metal quenching effect were balanced, resulting in maximizing the counting rate as well as the blinking suppression. By scanning electron microscopy and atomic force microscopy observations, we confirmed that the Au/$SiO_2$-glass and $SiO_2$/Au/$SiO_2$-glass substrates had a roughness of approximately 3 nm. After preparing three types of substrates shown in Fig. 1(a) ((i) $SiO_2$-glass, (ii) Au/$SiO_2$-glass, and (iii) $SiO_2$/Au/$SiO_2$-glass substrates), a 20 μL sample of commercially available CdSe/ZnS colloidal quantum dots (QDs) dispersed polymer toluene solution was spin coated onto each substrate and dried at room temperature. Confocal microscope observations revealed that the prepared samples contain approximately five QDs in the area of 5 μm × 5 μm.

Fig. 1 shows the schematic of the experimental setup. The sample was mounted on a 3D piezo stage set on a confocal microscope stage (IX-70, Olympus) and a CW $Ar^+$ laser (wavelength = 488 nm, Showa Optronics) was used as an excitation light. This light was introduced into the confocal microscope and focused on the sample by a microscope objective (100×, N.A. = 0.9, focal spot size ~500 nm, excitation power ~300 W/cm$^2$). Emission from the single QDs was collected by the same objective and passed through a notch filter to eliminate the excitation light. This emission was divided into two beams by a 50% beam splitter and detected by two avalanche photodiodes (single photon counting modules (SPCMs), SPCM-AQR-14, EG&G). Time intervals between two adjacent detection pulses from the two SPCMs were recorded using a time interval analyzer (PCI-6602, National Instruments; time resolution: 12.5 ns). The locations of single QDs were confirmed by the fluorescence intensity images by scanning a two-dimensional piezo stage. The focal spot was then moved to specific single QDs and the intervals of detection pulses from the SPCMs were continuously recorded. After recording the interval times, histograms of PIT [21–23] and fluorescence intensity time traces with desired time resolution were constructed by computer. Photon correlation measurements ($g^{(2)}(t)$) were simultaneously measured using a time-correlated single photon counting module (SPC-430, Becker & Hickl). By interpreting these measurements, we discussed the influence of each substrate on the trap state dynamics of single QDs.

To analyze the histogram of inter-detection times of photons emitted from single QDs, we considered the three-state model of single QDs in which transitions occur between the ground state $|G\rangle$, excited state $|E\rangle$, and trap state $|T\rangle$ with the rates of fluorescence $k_f$, nonradiative deactivation $k_{nr}$, transfer from $|E\rangle$ to $|T\rangle$ $k_{ET}$, recover from $|T\rangle$ to $|G\rangle$ $k_t$, and excitation $k_{ex}$ (see Fig. 1(c)). If $k_f + k_{nr} + k_{ET} \gg k_{ex}$ (weak excitation condition) and in the absence of background emission, the histogram of PIT [22,23] can be expressed as

$$d(t) = \frac{I_{on}}{\gamma_2 - \gamma_1}[(-\gamma_1 + k_{off})\exp(-\gamma_1 t) + (\gamma_2 - k_{off})\exp(-\gamma_2 t)] \quad (1)$$

with

$$\gamma_{12} = \frac{1}{2}\left[(k_{on} + k_{off} + I_{on}) \pm \sqrt{(k_{on} + k_{off} + I_{on})^2 - 4k_{off}I_{on}}\right], \quad (2)$$

where $k_{on} = \varphi_{ET}k_{ex}$ and $k_{off} = k_t$ indicate the transition rate between the ON and OFF states, $I_{on} = \phi\varphi_f k_{ex}$ is the photon detection rate when QD is in the ON state, $\varphi_{ET} = k_{ET}/(k_f + k_{nr} + k_{ET})$ is the transfer yield from $|E\rangle$ to $|T\rangle$, $\phi$ denotes the detection efficiency, and $\varphi_f = k_f/(k_f + k_{nr} + k_{ET})$ is the fluorescence quantum yield. Typically, $k_f + k_{nr}$, $k_t$, and $k_{ET}$ are on the order of $10^7$, $10^5$, and $10^6$ [24], and $k_{ex}$ is evaluated to be on the order of $10^5$ s$^{-1}$ from the experimental conditions. If we assume $I_{on} \gg k_{on}$ and $I_{on} \gg k_{off}$, the decay rates $\gamma_1$ and $\gamma_2$ can be approximated as

$$\gamma_1 \approx k_{on} + k_{off} + I_{on} \approx I_{on} \quad (3)$$

and

$$\gamma_2 \approx \frac{k_{off}I_{on}}{k_{on} + k_{off} + I_{on}} \approx k_{off}. \quad (4)$$

From the approximation, Eq. (1) can be simplified as

$$d(t) = I_{on}\ \exp(-I_{on}t) + \frac{k_{off}(k_{on} + k_{off})}{I_{on}}\ \exp(-k_{off}t). \quad (5)$$

By fitting Eq. (5) to the histogram of PIT, we can obtain $I_{on}$ and $k_{off}$ [23].

## 3. Results and discussion

We first performed photon correlation measurements $g^{(2)}(t)$ of QDs on three types of different substrates: (a) $SiO_2$-glass, (b) Au/$SiO_2$-glass, and (c) $SiO_2$/Au/$SiO_2$-glass substrates. Fig. 2 indicates the results for the single QDs on each substrate. From each data set, because $g^{(2)}(0)$ became almost zero for each QD on different substrates, we confirmed that the single QDs on each substrate were observed and that they worked as single-photon sources. By fitting the exponential functions, the decay rates of the excited states were estimated to be about (a) 23 ns, (b) 8 ns, and (c) 14 ns. Depending on the influence of an Au thin film, the decay rates of the excited states increased for the Au/$SiO_2$-glass and $SiO_2$/Au/$SiO_2$-glass substrates. In addition, Fig. 3 shows the time traces of emission counting rates simultaneously obtained from the same single QDs used in Fig. 2. From these results, depending on the Au thin film, we confirmed that the emission counting rates in the ON state were changed ((a) $3.0 \times 10^4$ cps, (b) $1.2 \times 10^4$ cps, and (c) $2.0 \times 10^4$ cps). The ratio of the emission counting rates against the $SiO_2$-glass substrate was estimated to be 1:0.40:0.67 from Fig. 3, which corresponded to the evaluated ratio (1:0.35:0.61) from the decay rates of the excited state in Fig. 2. In addition, the blinking behavior was also suppressed for the Au/$SiO_2$-glass and $SiO_2$/Au/$SiO_2$-glass substrates, while typical blinking behavior was clearly observed on the $SiO_2$-glass substrate. These observations were in good agreement with the previous results reported by Kanemitsu et al. [12–14]. In their papers, the observed blinking behavior was explained by the

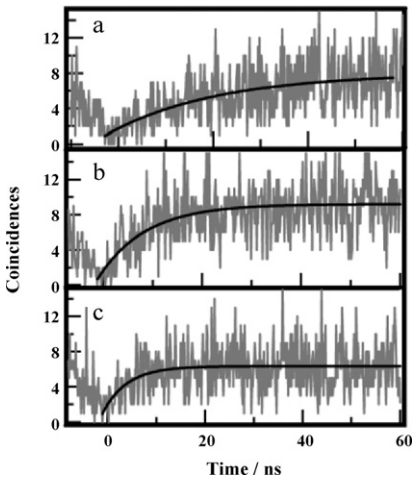


**Fig. 2.** Photon correlation measurements $g^{(2)}(t)$ of single QDs on each substrate: (a) $SiO_2$-glass, (b) Au/$SiO_2$-glass, and (c) $SiO_2$/Au/$SiO_2$-glass. Solid lines were obtained by fitting an exponential function to each histogram.

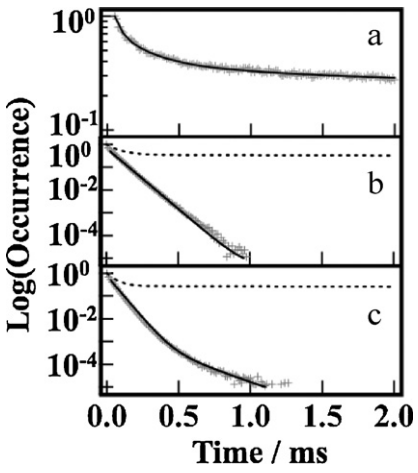


**Fig. 4.** Normalized histograms of photon inter-detection time emitted from single QDs on each substrate: (a) $SiO_2$-glass, (b) Au/$SiO_2$-glass, and (c) $SiO_2$/Au/$SiO_2$-glass substrates. In (a), the range of the vertical axis was changed for the clarification. Solid lines were obtained by fitting a bi-exponential function to each histogram. Broken lines in (b) and (c) indicate the estimated PIT curves by assuming that $k_{off}$ is not changed depending on the substrate and $k_{on}$ is changed proportionally to $I_{on}$.

decreases in the transition probability to the trap states ($\varphi_{ET}$) and the fluorescence quantum yield ($\varphi_f$) caused by the fast energy transfer to the Au film (increase in $k_{nr}$ in Eqs. (1)–(5)). Therefore, because of this fast energy transfer, we considered that the decay rate of the excited state on the Au/$SiO_2$-glass substrate (Fig. 3(b)) increased. Blinking suppression and a decrease in the emission counting rate were observed on the Au/$SiO_2$-glass substrate; the $SiO_2$-glass substrate clearly exhibited opposite behavior (Fig. 3(a)). In addition, because the fast energy transfer to the Au film was slightly suppressed on the $SiO_2$/Au/$SiO_2$-glass substrate (Fig. 3(c)) owing to the 20-nm-$SiO_2$ cover layer and the transition probability to the trap states slightly increased, increase in the emission counting rate with increased fluctuation of the counting rate was observed compared with that of the Au/$SiO_2$-glass substrate. Thus, because the change in the decay rate of the excited state depending on the substrate (Fig. 2) corresponded to the change in the counting rates (Fig. 3), the emission counting rate of single QDs on different substrates could be explained well by the fast energy transfer to the Au thin film. However, because the blinking behavior of the $SiO_2$/Au/$SiO_2$-glass substrate became unclear owing to the increase in fluctuation of the counting rates compared with those of the Au/$SiO_2$-glass and $SiO_2$-glass substrates, it is thought that the duration time of the OFF state (trap state) would also change depending on the substrate. The fast energy transfer alone would not explain this. This suggests the possibility that the trap state lifetime would be varied with the substrates on which single QDs were dispersed.

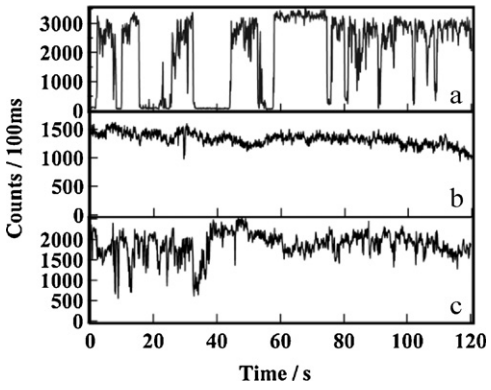


**Fig. 3.** Fluorescence intensity fluctuations of single QDs on different substrates: (a) $SiO_2$-glass, (b) Au/$SiO_2$-glass, and (c) $SiO_2$/Au/$SiO_2$-glass substrates. The excitation intensity was 300 W/cm$^2$.

To discuss these behaviors on different substrates from the trap state perspective, we performed PIT analysis of the same data in Figs. 2 and 3. Fig. 4 shows the histograms of inter-detection times of photons emitted from the single QDs on three different substrates: (a) $SiO_2$-glass, (b) Au/$SiO_2$-glass, and (c) $SiO_2$/Au/$SiO_2$-glass substrates. The results indicated that the decay rates of the fast decay components corresponding to the emission counting rates changed depending on the substrates ($\gamma_1$ = (a) $2.9 \times 10^4$ s$^{-1}$, (b) $1.2 \times 10^4$ s$^{-1}$, and (c) $1.7 \times 10^4$ s$^{-1}$). The ratio of these decay rates of single QDs on different substrates was 1:0.41:0.59 and this ratio agreed well with those from Figs. 2 and 3. Therefore, the difference in the emission counting rates depending on the substrate could be explained by the fast energy transfer to the Au thin film. However, we found that the slow decay components corresponding to the trap state lifetime also changed on each substrate. On the $SiO_2$-glass substrate (Fig. 4(a)), fast and slow decay components were clearly observed, whereas on the Au/$SiO_2$-glass substrate (Fig. 4(b)), only the fast decay component was observed, while the slow decay component became invisible. Furthermore, in Fig. 4(c), because of the decrease in the energy transfer rate owing to the insertion of a 20-nm-$SiO_2$ cover layer between the QDs and the Au thin film, the increase in the decay rate of the fast decay component related to the counting rate and the slow decay component related to the recovering time from the trap state appeared with a different decay rate of $\gamma_2 = 5.3 \times 10^3$ s$^{-1}$ compared with that of the $SiO_2$-glass substrate ($\gamma_2 = 3.1 \times 10^1$ s$^{-1}$).

If there is no change in the recovering time from the trap state $k_{off}$ and if transition rate to the trap state $k_{on}$ is changed proportionally to the photon detection rate $I_{on}$, the PIT decay curves could be estimated from Eq. (5), which are shown as broken curves in Fig. 4(b) and (c). These curves are obviously different from the experimental results. The observed recovering times from the trap state on the Au/$SiO_2$-glass and $SiO_2$/Au/$SiO_2$-glass substrates are faster than that on the $SiO_2$-glass substrate. Thus, we concluded that the blinking suppression of the single QDs interacted with the Au thin film is caused not only by the fast energy transfer but also by the shortening of recovering time from the trap state. The possible origin of this change in the recovering time of the trap state depending on the substrate were conjectured as the changes in the energetic and spatial distributions of the trap state, the influence of electron transfer from the substrate, and so on. However, because even the detailed

mechanism of the blinking behavior has been still under investigation [5], the origin of the substrate dependence of the trap states recovery rate is also unclear at the present stage. If we will investigate the trap state analysis against various types of substrates, these measurements would give the detailed information of the blinking behaviors.

## 4. Conclusion

We measured the trap state dynamics of single CdSe/ZnS QDs on three different substrates: $SiO_2$-glass, Au/$SiO_2$-glass, and $SiO_2$/Au/$SiO_2$-glass substrates. From the results, we found that the trap states changed depending on the substrates and these affect on the emission efficiency of single QDs, not only fast energy transfer to the Au substrate. From PIT analysis method, the decay component corresponding to the trap state clearly appeared on the $SiO_2$-glass substrate, while the decay component corresponding to the trap state became almost invisible on the Au/$SiO_2$-glass substrate. This result was in good agreement with the blinking-free behavior of single QDs on the Au/$SiO_2$-glass substrate in the intensity time traces. In addition, especially on introducing an $SiO_2$ thin cover layer as in the $SiO_2$/Au/$SiO_2$-glass substrate, the behavior changes to the intermediate state compared with that of the $SiO_2$-glass and Au/$SiO_2$-glass substrates. From this analysis, we confirmed that not only the blinking suppression due to the energy transfer to a Au thin film, but also the trap state is also changed depending on the surface condition of the substrates. These results suggest that the substrate influence on the trap state in addition to the fast energy transfer to the Au thin film play an important role in the blinking suppression. When considering the applications to ultra-small optoelectronic devices composed of QDs on metal, glass, polymer, and semiconductor substrates, the influence of the substrate on the trap states must be considered to improve emission efficiency.

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