

# Blinking Suppression in CdSe/ZnS Single Quantum Dots by TiO<sub>2</sub> Nanoparticles

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Unique optical properties of semiconductor quantum dots (QDs), such as size-dependent tunable photoluminescence (PL) and broad absorption and narrow emission bands, have attracted much attention for both basic research and device applications.<sup>1–5</sup> With the introduction of colloidal QDs, a strong interface among nanomaterials, biotechnology, and biology has emerged. In particular, QDs have become powerful substitutes for organic dye molecules in the imaging of biomolecules,<sup>6–8</sup> cells,<sup>9–16</sup> tissues,<sup>14</sup> and animal models.<sup>11,16,17</sup> Despite the fact that QDs find enormous applications in bioimaging and device technology, blinking PL is an intrinsic limitation in the advancement of QD technology toward single-molecule biophysical and biochemical investigations<sup>18–23</sup> and single-photon quantum optical devices that require incessant or on-demand single-photon emission. These points underline the importance of developing novel nonblinking QDs or eliminating the undesirable blinking of existing core and core/shell QDs.

Blinking means stochastic fluctuations in the PL intensity of QDs between bright and dark states. Due to the significant impacts of QDs in various fields, blinking suppression and the underlying mechanism of blinking are greatly investigated at theoretical<sup>19,20,24–36</sup> and experimental<sup>21,22,37–62</sup> levels. Blinking originates from Auger annihilation, during which a charge carrier, typically an electron, from bi- or multiexciton state of a QD gets trapped into energy states on the surface or outside and provides net positive charge to the QD. Although a charged QD can continuously absorb excitation light and form a trion state, its radiative relax-

**ABSTRACT** The photoluminescence of semiconductor quantum dots and fluorescence of single molecules intermittently turn ON and OFF, a phenomenon referred to as blinking. In quantum dots, blinking occurs as a result of intermittent Auger ionization, which results in the formation of positively charged quantum dots. Due to strong Coulombic interactions, successive photoactivation of a charged quantum dot results in nonradiative carrier recombination, inducing long-lived OFF states in the intensity trajectories. Blinking is an undesirable property with respect to applications of quantum dots toward single-molecule imaging and single-photon logic devices. Here we report significant blinking suppression for CdSe/ZnS single quantum dots in the presence of TiO<sub>2</sub> nanoparticles. In this work, we continuously recorded photoluminescence intensity trajectories of single quantum dots with and without TiO<sub>2</sub> nanoparticles. Interestingly, the intensity trajectory of a single quantum dot that was covalently tethered on a cover glass and dipped in water resulted in near-complete blinking suppression as soon as a TiO<sub>2</sub> nanoparticle solution was introduced. The blinking suppression was associated with a decrease in the photoluminescence intensity but without considerable changes in the photoluminescence lifetime, indicating that nonradiative carrier recombination in quantum dots was channeled into electron transfer to TiO<sub>2</sub> nanoparticles and back electron transfer to quantum dots. On the basis of these experiments and recent reports on photoinduced electron transfer from quantum dots to TiO<sub>2</sub> nanoparticles, we hypothesize that blinking of a quantum dot can be suppressed by increasing the rate of nonradiative regeneration of its neutral state by interfacing with a well-defined charge carrier trap such as an electron acceptor, which accepts an electron during Auger ionization and neutralizes the charged quantum dot by back electron transfer. Correlation between blinking suppression and electron transfer in a quantum dot–TiO<sub>2</sub> nanoparticle system may have important implications, for the preparation of nonblinking quantum dot for incessant and on-demand light emission, donor–acceptor systems for efficient solar energy harvesting, and hybrid semiconductor materials for quantum optical devices.

**KEYWORDS:** quantum dots · blinking · TiO<sub>2</sub> nanoparticles · electron transfer · photoluminescence · single molecules

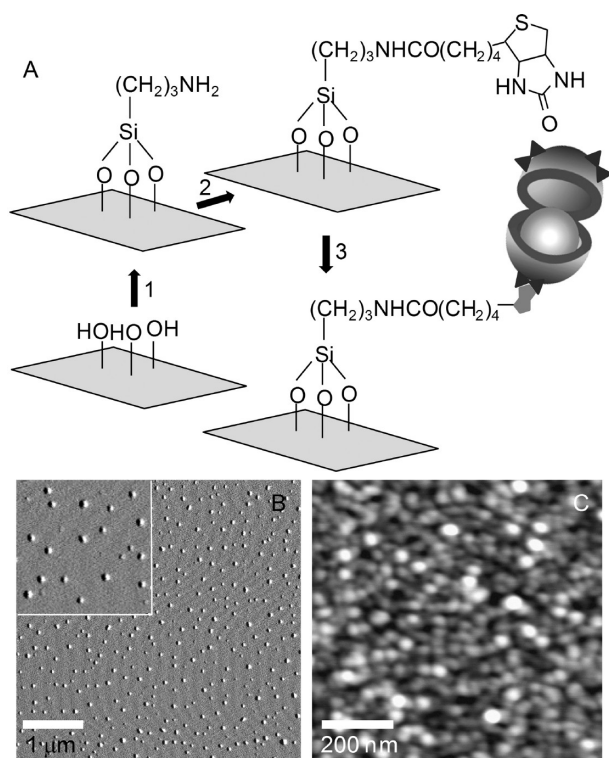
ation will be hindered due to strong Coulomb interactions as well as nonradiative Auger recombination through energy transfer to the excess charge carrier.<sup>18–22,24–28,63,64</sup> As the rate of such nonradiative relaxation is much larger than that of radiative relaxation, QDs continue to stay in the OFF state until neutralized by nonradiative carrier recombination. This simple model based on Auger ionization provides a tangible picture of blinking; however, it is largely inconsistent with the power-law distribution of ON time. Thus, theoretical models involving

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**Figure 1.** (A) Steps involved in the conjugation of QDs to glass surface: (1) 0.5% solution of 3-aminopropyltriethoxy silane in acetone, (2) 10  $\mu\text{M}$  aqueous solution of biotin-3-sulfo NHS ester, and (3) 10 pM aqueous solution of QD605–streptavidin conjugate. (B) AFM image of high-density of QDs tethered on a coverslip; inset shows zoomed-in and scanned AFM image. (C) AFM image of a QD sample overlaid with a thin layer of  $\text{TiO}_2$  NPs.

diffusion-controlled electron transfer from the core to the surface or an outside trap through surrounding medium were applied to understand the power-law distribution of blinking time. In other words, a QD under constant photoactivation shows blinking because it can undergo random processes of ionization and neutralization, such as Auger ionization and transient electron transfer from core to resonant energy states on or near the surface. Strong confinement of charge carriers is the barrier to suppress nonradiative recombination and blinking. This rationale motivated many researchers to investigate blinking suppression by both perturbing the energy states of QDs and introducing ultrafast electron transfer processes. Although a detailed understanding of the blinking mechanism is still challenging, various approaches have been investigated to address and suppress blinking PL of QDs, including the effects of noble metal nanoparticles (NPs)/surfaces,<sup>37–42</sup> temperature,<sup>21</sup> shell thickness of higher band gap materials,<sup>43–47</sup> electron transfer to and from inorganic NPs and organic molecules,<sup>48–51</sup> capping by thiols and polymers,<sup>22,52–55</sup> oxygen depletion,<sup>56</sup> modified synthesis,<sup>52,57,58</sup> and excitation energy and intensity.<sup>21,26,37,59–62</sup> Blinking suppression to varying extents was accomplished by these approaches; however, a complete solution to suppress the blinking of different types of QDs is yet to be identified. As an exception, Wang *et al.* recently accomplished

the synthesis of a completely nonblinking ternary core/shell CdZnSe/ZnSe QD by radially alloying CdZnSe into ZnSe.<sup>57</sup> Despite the above experimental investigations and the discrepancies in the electron transfer model<sup>27,29–31</sup> and power-law statistics,<sup>20,31–36</sup> suppression of blinking is sought after for extended applications of single QDs.

In this work, single-molecule video microscopy and steady-state and time-resolved spectroscopy were used to understand the blinking behavior of the same single QDs in the presence and absence of  $\text{TiO}_2$  NPs. We selected  $\text{TiO}_2$  NPs because they are traditionally among strong electron acceptors in solar cells.<sup>48,65–70</sup> We demonstrate that the blinking of CdSe/ZnS QDs can be considerably suppressed by adding  $\text{TiO}_2$  NP solutions to single QDs. Isolated QDs were covalently attached on glass coverslips, and we continuously recorded the PL intensity trajectories of the same single QDs first without  $\text{TiO}_2$  NPs and next after adding  $\text{TiO}_2$  NPs. Interestingly, we found that the trajectory of single QDs abruptly changed from continuous blinking into suppressed blinking as soon as  $\text{TiO}_2$  NPs were introduced. This finding calls upon the blinking suppression in QDs in the presence of  $\beta$ -mercaptoethanol, which was reported by Hong and Ha.<sup>22</sup> Unpredictably, the blinking suppression was not associated with any significant changes to the PL lifetime, which indicates that the effect of  $\text{TiO}_2$  NPs should be mostly on detrapping of a charge carrier after Auger ionization but radiative carrier recombination processes. In other words,  $\text{TiO}_2$  NPs contribute mostly to the carrier recombination in a charged QD by accepting a trapped electron from around or the surface state of the QD and bringing about back electron transfer. Thus, the role of  $\text{TiO}_2$  NPs is to suppress blinking by perturbing the probability of a QD to continue in the charged or OFF state.

## EXPERIMENTAL

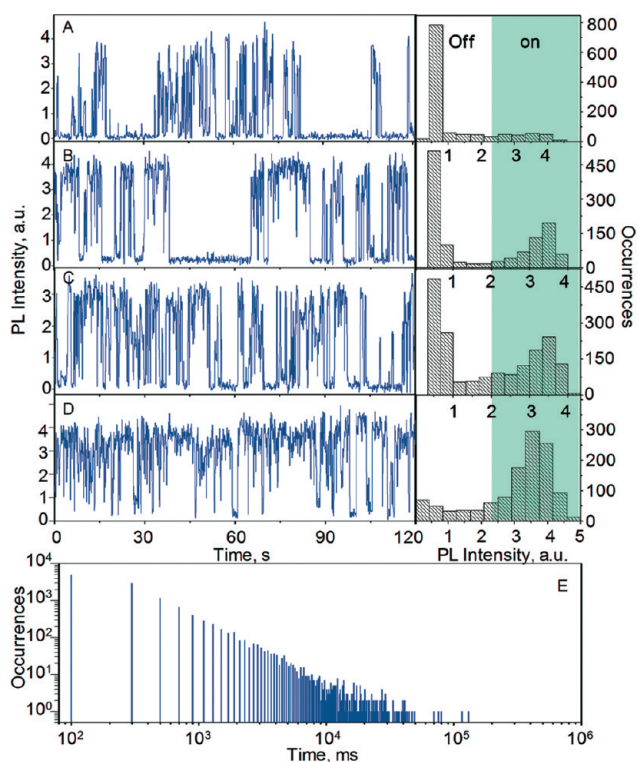
We obtained CdSe/ZnS QDs (PL maximum  $\sim 605$  nm) from Invitrogen Corporation.  $\text{TiO}_2$  NPs were prepared by the hydrolysis of titanium isopropoxide in a mixture of isopropanol and hydrochloric acid. Single-molecule samples were prepared by tethering QDs on a coverslip, as shown in Figure 1. Coverslips were cleaned using nascent chlorine by dipping in a mixture of sodium hypochlorite and hypochloric acid and sonicating for 15 min. The coverslips were then repeatedly washed with deionized water and acetone and subsequently silanized for 30 min at room temperature by dipping in a 0.5% solution of 3-aminopropyltriethoxy silane in acetone. Silanized coverslips were copiously washed with water and acetone, dipped in a 10  $\mu\text{M}$  aqueous solution of biotin 3-sulfo *N*-hydroxysuccinimide ester for 30 min at room temperature, and thoroughly washed with deionized water. During this step, the primary amino group on the silanized glass surface was coupled with NHS ester group

and provided us with biotinylated coverslips. In the successive step, CdSe/ZnS QDs were uniformly tethered on the biotinylated glass plate through biotin–streptavidin linkage by placing a 10 pM solution of QD–streptavidin conjugate on one side of the coverslip for 30 min at room temperature. The density of the QD was controlled by varying the concentration of QD solution. Unbound QDs were removed by washing with deionized water. Finally, QDs were dipped in deionized water, and single-molecule images, PL intensity trajectories, and PL lifetimes were recorded. Figure 1B shows a tapping-mode AFM image of a single QD sample that was prepared by reacting a 0.5 nM QD solution on a biotinylated glass plate. The effect of TiO<sub>2</sub> NPs on the blinking of single QDs was investigated after placing 20 μM aqueous solutions of TiO<sub>2</sub> NPs on single QD samples. In solution, the distances between QDs and TiO<sub>2</sub> NPs are not fixed. Thus, control samples with fixed distance between QDs and TiO<sub>2</sub> NPs were prepared by tethering single QDs on a coverslip followed by overlaying the sample with a thin layer of TiO<sub>2</sub> NPs. Figure 1C shows a tapping-mode AFM image of a single QD sample overlaid with a thin layer of TiO<sub>2</sub> NPs.

Single-molecule experiments were carried out using far-field video microscopy. For PL lifetime measurements of QDs at single-molecule and ensemble levels, samples were excited with 400 nm fs laser pulses from an optical parametric amplifier (OPA). The OPA was pumped by 800 nm pulses (200 kHz) from a regenerative amplifier that was seeded by a mode-locked Ti:sapphire laser (76 MHz). Single-molecule images and trajectories were recorded in an inverted optical microscope (Olympus IX 71) that was equipped with a 60× objective lens (Olympus, NA 0.98). Fluorescence signal collected using the objective lens was filtered through a band-pass filter for QD605, magnified using a 3.3× telescopic lens, and recorded using an image intensifier charge-coupled device assembly (Hamamatsu Photonics). Fluorescence decay profiles were recorded using an assembly of a polychromator and a streakscope (Hamamatsu Photonics). Topography images of single QD and QD–TiO<sub>2</sub> samples were obtained using a MFP-3D AFM (Asylum Research). Tapping-mode AFM images were collected in air, using reflective aluminum-coated ultrasharp (radius of curvature <10 nm) silicon cantilevers (Olympus). The cantilevers were ~160 μm long and had a spring constant of ~42 N/m and a resonance frequency of ~300 kHz.

## RESULTS AND DISCUSSION

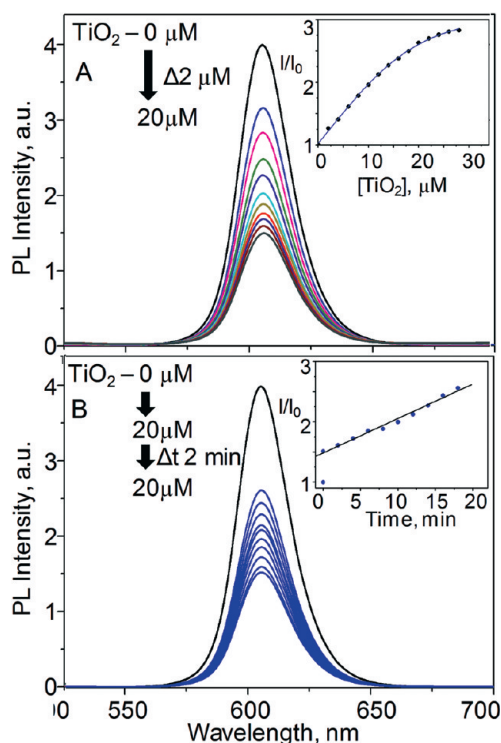
Surface-bound QDs in an aqueous medium showed PL blinking (Figure 2A–D) with OFF periods distributed on a power-law statistics (Figure 2E) over 4 decades of time. Dot-by-dot variations in the blinking statistics are shown in Figure 2 by plotting the PL trajectories (left panel) and intensity histograms (right panels) for four QDs. Histograms in the right panel indi-



**Figure 2.** (A–D) Dot-by-dot variations in the PL intensity trajectories (left panel) and histograms (right panel) of single CdSe/ZnS QDs tethered on glass surface and dipped in water. (E) OFF time distribution for 100 single QDs.

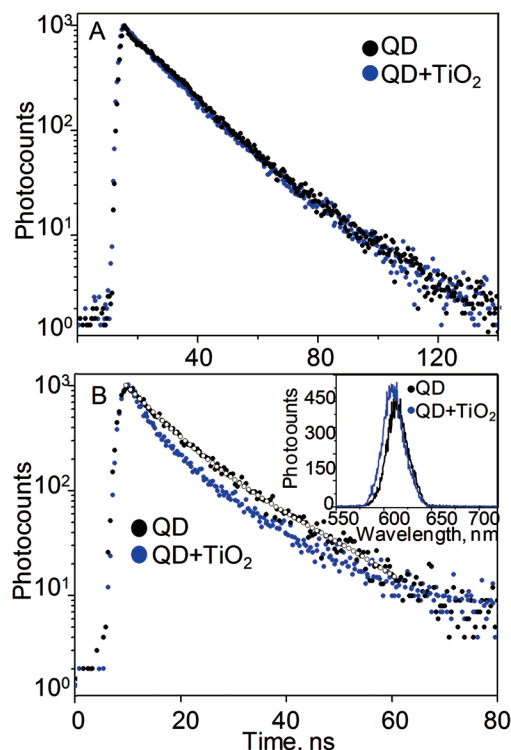
cate the total number of ON (high intensity) and OFF (low intensity) photons for the corresponding trajectory in the left panel. We selected these four trajectories for a simple representation of dot-by-dot variations in the ON and OFF durations (right panel of Figure 2) of single QDs. The variations in the blinking behavior from time-to-time and dot-to-dot arise as a result of stochastic fluctuations in the Auger relaxation processes or transient trapping of charge carriers in the surface traps, as reported previously.<sup>18–22,24–49</sup> The non-exponential distribution of blinking time has been the subject of considerable research at both theoretical and experimental levels. Here, we could map only *four* orders of OFF time distribution, but it can be up to *six*.<sup>18–21,24–32</sup> The power-law behavior in the OFF time distribution can be simply explicated by an exponential distribution in the rate of neutralization of a charged QD by detrapping a charge carrier, usually an electron, from an exponentially distributed trap states.<sup>20,32,33</sup> On the other hand, deviation of ON time distribution from the power-law behavior was investigated by applying dynamic processes to carrier trapping, as reported by Nesbitt and co-workers,<sup>20,26,33,49</sup> Marcus and co-workers,<sup>24,27,29–31</sup> and Tang and co-workers.<sup>34,40,55,60</sup> Recently, deviations of ON/OFF time from power-law statistics are greatly investigated from theoretical and experimental points of view, which contributed considerably to blinking suppression<sup>22,37–47,52–58</sup> and, more importantly, development of completely nonblinking QDs.<sup>57</sup>





**Figure 3.** Fluorescence spectra of QD solutions (1 nM): (A) spectra as a function of increase in the concentration of  $\text{TiO}_2$  NP solution, and (B) spectra recorded at 2 min intervals after the addition of a  $20 \mu\text{M}$   $\text{TiO}_2$  NP solution. Inset of (A): Stern–Volmer plot. Inset of (B): relative PL intensity vs time.

Here we investigated the effect of  $\text{TiO}_2$  NPs on the blinking of single QDs based on a hypothesis that transfer of an electron from an outside/surface trap state to  $\text{TiO}_2$  NP can suppress the blinking by channeling the neutralization of charged QDs through  $\text{TiO}_2$  NPs. In other words, our intention was to suppress blinking by mediating carrier recombination in charged QDs through electron transfer to  $\text{TiO}_2$  NPs and back electron transfer to charged QDs. We found that addition of  $\text{TiO}_2$  NPs to an ensemble solution of QD results in a considerable decrease in the PL intensity. Figure 3A shows the effect of concentration of  $\text{TiO}_2$  NPs on the PL spectrum of a nanomolar aqueous solution of CdSe/ZnS QDs. Initially, a dynamic quenching effect was detected, which gradually changed into deviation from the Stern–Volmer plot (inset of Figure 3A) with increase in the concentration of  $\text{TiO}_2$  NPs. Also, a gradual decrease in the PL intensity of a QD solution was detected with time after the addition of  $20 \mu\text{M}$   $\text{TiO}_2$  NP solution (Figure 3B). However, unexpectedly, we could not find any decrease in the PL lifetime values for QD solutions with either increase in the concentration of  $\text{TiO}_2$  NPs or time under incubation after the addition of  $\text{TiO}_2$  NPs (Figure 4A). On the other hand,  $\text{TiO}_2$  NPs are well-known to quench the excited state of QDs by accepting an electron, thus making QD– $\text{TiO}_2$  systems both promising models of photoinduced electron transfer and ideal candidates for solar cells, as reported by Jin and Lian,<sup>48</sup>



**Figure 4.** PL decay profiles of (A) an aqueous solution of QDs (1 nM) with and without the addition of a  $\text{TiO}_2$  NP solution ( $20 \mu\text{M}$ ) and (B) a single QD before ( $\tau_{\text{av}} = 5.4 \text{ ns}$ ) and after ( $\tau_{\text{av}} = 4.3 \text{ ns}$ ) the addition of a  $\text{TiO}_2$  NP solution ( $20 \mu\text{M}$ ). Inset: PL spectra of a single QD in the presence and absence of  $\text{TiO}_2$  NPs.

Kamat and co-workers,<sup>67–69</sup> and others.<sup>65,66,70</sup> Here, decrease in the PL intensity (Figure 3) without any changes to PL lifetime (Figure 4A) indicates the formation of a ground-state QD– $\text{TiO}_2$  complex and static quenching of the excited state of QDs by  $\text{TiO}_2$ . Figure 4B shows PL decay profiles of single QDs with and without  $\text{TiO}_2$  NPs. Also, the decrease in the PL intensity of QD solutions with time after the addition of  $\text{TiO}_2$  NPs (Figure 3B) indicates that a QD– $\text{TiO}_2$  complex is formed by the gradual association of  $\text{TiO}_2$  NPs on the surface of QDs. Such an association was evidenced by the presence of aggregates in ensemble solution samples. However, AFM images show that single-molecule samples do not form such aggregates because QDs are isolated and tethered on the glass surface. Due to the static quenching of the QD's PL intensity by  $\text{TiO}_2$ , contributions of QD– $\text{TiO}_2$  complexes to the PL spectra and decay profiles should be negligible, which prevented us from evaluating the redistribution in the radiative to nonradiative relaxation rates in QDs. In electron transfer experiments, nonluminescent QD– $\text{TiO}_2$  complexes are studied by transient absorption measurements. For example, Robel *et al.* found that the disruption of an electron–hole pair in CdSe QDs by the transfer of electrons from QDs to  $\text{TiO}_2$  NPs can increase the rate of bleaching recovery or decrease the lifetime.<sup>67</sup> Due to static quenching of the excited state of QDs, QD– $\text{TiO}_2$  complexes are unlikely to be detected in single-

molecule measurements, as well, evidenced by considerable decrease in the number of PL spots after the addition of a TiO<sub>2</sub> NP solution to single QD samples (Figure 5). On the other hand, without TiO<sub>2</sub> NPs, QDs were photostable for over 15 min under  $\sim 200$  W/cm<sup>2</sup> excitation power (532 nm). Thus, the PL signals in single QD experiments should come from QDs that show dynamic or no interactions with TiO<sub>2</sub> NPs. Gradual decrease in the number of fluorescence spots indicates that the dynamic interaction changes into static, probably due to gradual association of TiO<sub>2</sub> NPs on the surface of QDs.

To investigate the effect of TiO<sub>2</sub> NPs on the blinking of single QDs, we recorded and analyzed the PL intensity trajectories of the same single QDs with and without TiO<sub>2</sub> NPs. First we recorded single-molecule videos, and then from the videos, we obtained PL intensity trajectories for long-living single QDs. Despite the fact that a large number of QDs disappeared within minutes after the introduction of TiO<sub>2</sub> NPs, remarkable blinking suppression was detected for live QDs (Figure 6). The arrows in Figure 6 indicate time at which a TiO<sub>2</sub> NP solution was introduced. Thus, the left side of the arrows indicates blinking without TiO<sub>2</sub> NPs, and the right side indicates blinking suppression or modified blinking of QDs due to dynamic electron transfer interactions with TiO<sub>2</sub> NPs. The histograms b and c in Figure 6 show PL intensity distributions of single QDs before and after the addition of TiO<sub>2</sub> NPs, respectively. Considerable increase in the occurrences of ON intensity in Ac–Dc compared to that in Ab–Db shows the effect of TiO<sub>2</sub> NPs on blinking suppression. Note that, to investigate the effect of TiO<sub>2</sub> NP on the blinking of QDs, we continuously recorded the PL intensity trajectories of the same single QDs with and without TiO<sub>2</sub> NPs because ON and OFF times vary from dot to dot irrespective of the presence (Figure 8) or absence (Figure 2) of TiO<sub>2</sub> NPs. In other words, without statistical analysis, blinking suppression need not always be correctly reflected in the intensity trajectories of two separate QDs, one without and the other with TiO<sub>2</sub> NPs. Because the decrease in the PL intensity (Figure 3A) is not correlated with lifetime (Figure 4A), the PL signals of single QDs should come from those QDs for which the radiative rate is not considerably affected. However, irrespective of the extent of blinking suppression by TiO<sub>2</sub> NPs, we found that the PL lifetimes of single QDs were decreased (for less than 10% QDs), increased (for less than 10% QDs), or remained intact (>80%). Figure 4B shows the PL decay profiles of a QD before and after the addition of TiO<sub>2</sub> NPs. All of the decay profiles were fitted to third-order decay kinetics, and average PL lifetimes at ensemble and single-molecule levels were calculated using the equation  $\tau_{av} = (\tau_1\alpha_1 + \tau_2\alpha_2 + \tau_3\alpha_3)/(\alpha_1 + \alpha_2 + \alpha_3)$ , where  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are individual lifetime values and  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are weighted amplitudes. The average PL lifetime of single QDs was decreased from  $\sim 5.5$  ns in the absence to  $\sim 4.5$  ns in the presence of TiO<sub>2</sub> NPs,

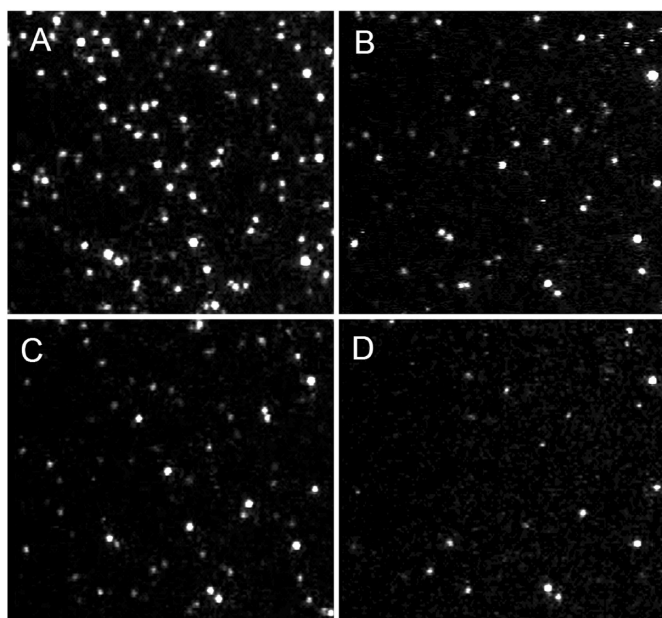
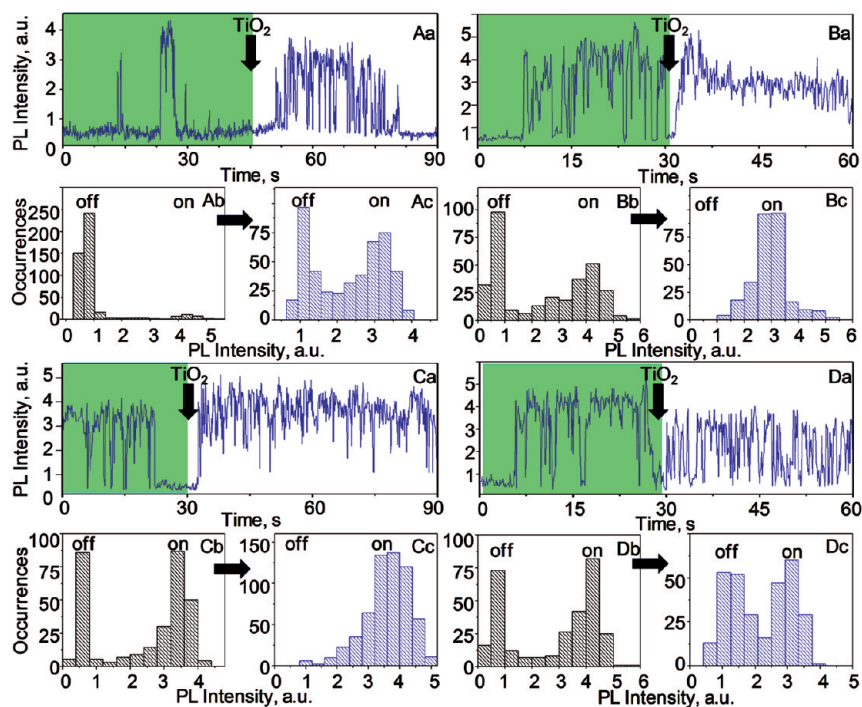


Figure 5. PL images of single QDs tethered on a glass substrate and immersed in water: (A) without TiO<sub>2</sub> NPs, (B) immediately after the addition of a TiO<sub>2</sub> NP solution, (C) 1 min after the addition of TiO<sub>2</sub> NPs, and (D) 2 min after the addition of TiO<sub>2</sub> NPs.

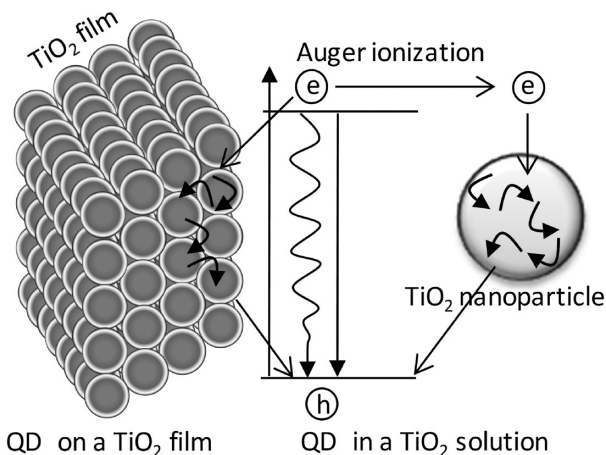
much less than the changes reported for ensemble QD–TiO<sub>2</sub> systems ( $\tau_{av}$  decreased from  $\sim 4$  to  $0.4$  ns<sup>68</sup> or from  $\sim 16$  to  $10$  ns<sup>48</sup>). As the blinking suppression is not associated with considerable decrease in the lifetime values, we assume that the role of TiO<sub>2</sub> NP is mainly to accept an electron trapped in a surface state or an outside state and execute ultrafast back electron transfer to charged QDs. Such channeling of carrier relaxation processes through electron transfer from QDs to TiO<sub>2</sub> NPs and back electron transfer from TiO<sub>2</sub> to charged QDs probably resulted in blinking suppression by shortening OFF periods and increasing the number of ON events. In other words, channeling of carrier recombination through TiO<sub>2</sub> NPs suppresses both nonradiative Auger recombination and the probability for a QD to continue in the charged state.

To address suppressed blinking without considerable decrease of PL lifetime, we contrast the current work with a recent report on electron transfer and PL blinking in a single-molecule QD–TiO<sub>2</sub> system.<sup>48</sup> The major difference between our work and this report is on the nature of single-molecule samples. In the current work, single-molecule samples were prepared by tethering QDs on coverslips followed by immersing in water and adding an aqueous solution of TiO<sub>2</sub> NPs. The samples in ref 48, on the other hand, consist of high-quality TiO<sub>2</sub> thin films on which carboxylic acid functionalized QDs were uniformly deposited by spin-coating. We found that blinking of single QDs can be suppressed by adding colloidal TiO<sub>2</sub> NPs, but without considerable decrease in the PL lifetime. In contrast, for QDs deposited on a high-quality TiO<sub>2</sub> film, the duration of OFF events was increased and the PL lifetime



**Figure 6.** PL intensity trajectories (Aa–Da) and histograms (Ab–Db and Ac–Dc) for four single QDs that are covalently attached to a coverslip, immersed in water, and with and without adding  $\text{TiO}_2$  NPs. Left (highlighted in green) and right in “a” indicate blinking before and after the addition of  $\text{TiO}_2$  NPs, respectively. The histograms b and c illustrate ON and OFF intensity distributions before and after the addition of  $\text{TiO}_2$  NPs, respectively.

was decreased, suggesting that photoactivated QDs relax by direct electron transfer to  $\text{TiO}_2$  film. In such high-quality  $\text{TiO}_2$  films, following electron transfer, the trapped charge carrier can delocalize at greater extent by hopping among  $\text{TiO}_2$  particles. Thus, back electron transfer can be delayed, and charged QD can be left in the dark state for an extended period, which induces long-living OFF states in the PL intensity trajectories. On the other hand, blinking suppression in the current work designates that isolated  $\text{TiO}_2$  NPs prevent extensive delocalization of the trapped charge carrier and facilitates more rapid regeneration of neutral QD by back electron transfer. The two systems are schematically

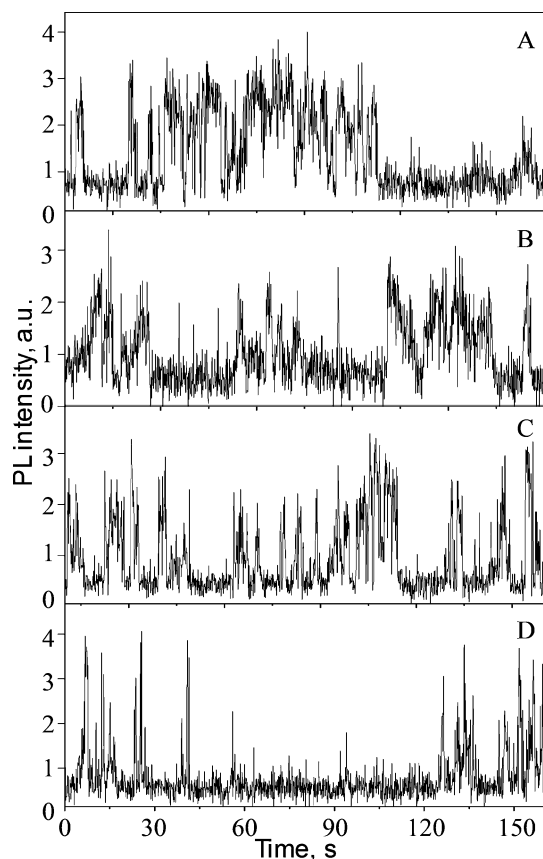


**Figure 7.** Relaxation processes expected in QD- $\text{TiO}_2$  NP systems: (left) QDs deposited on a high-quality  $\text{TiO}_2$  NP film, and (right) QDs immersed in a  $\text{TiO}_2$  NP solution.

presented in Figure 7. On the basis of the difference between the samples in these reports, we assume that the electron transfer interactions between  $\text{TiO}_2$  NPs in solution and QDs tethered on glass surface are rather dynamic in nature. From an electron transfer or solar cell point of view, the long-living dark state of a QD deposited on a high-quality  $\text{TiO}_2$  film is promising for efficient charge separation, whereas colloidal  $\text{TiO}_2$  NPs in the current work are promising to understand the blinking mechanism and suppress undesirable blinking in single QDs. Nevertheless, nonradiative carrier recombination during long-living OFF states can trim down the efficiency of a solar cell.

To understand the role of dynamic interactions on the blinking suppression, we fixed the distance between QDs and  $\text{TiO}_2$  NPs by attaching QDs on a glass surface and overlaying with a thin layer of  $\text{TiO}_2$  NPs. We found that the number of PL spots was considerably reduced in samples overlaid with  $\text{TiO}_2$  NPs. As discussed above and in refs 48 and 67–69, the decrease in the number of PL spots (Figure 5) can be attributed to static quenching of the excited state of QDs. Despite the static quenching, many PL spots were present in single-molecule samples. However, unlike in the case of QD- $\text{TiO}_2$  single-molecule samples in aqueous phase (Figure 6), it was technically difficult to compare the PL intensity trajectory of the same single QDs before and after overlaying with  $\text{TiO}_2$  NPs. Thus, we compared the blinking with and without  $\text{TiO}_2$  NPs for different QDs. We found that the blinking of QDs that are overlaid with  $\text{TiO}_2$  NPs varied from dot to dot (Figure 8), which is

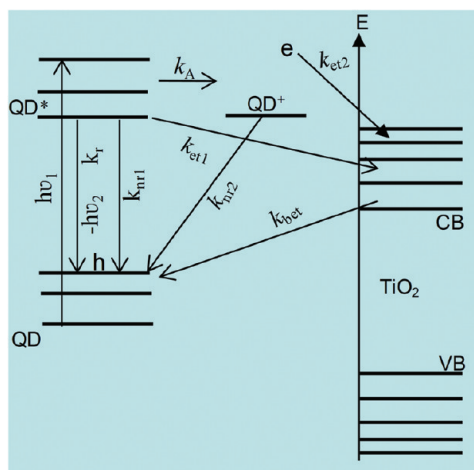




**Figure 8.** Dot-by-dot variations in the PL intensity trajectories of single CdSe/ZnS QDs tethered on a glass surface and overlaid with a thin film of TiO<sub>2</sub> NPs.

probably contributed by difference in the distribution of TiO<sub>2</sub> NPs around QDs. In addition to Figure 8, but without statistical analysis of the blinking trajectories of QDs overlaid by TiO<sub>2</sub> NPs, we consider that electron transfer processes reported in ref 48 are standard for us to compare the blinking suppression of QDs in solution phase.

In addition to the blinking suppression by TiO<sub>2</sub> NPs, the PL spectral maximum of QDs fluctuated within 5 nm (inset of Figure 4B), and the average PL intensities of single QDs were increased, decreased, or remained intact (Figure 6). The decrease but not disappearance of the PL intensity of single QDs indicates dynamic interactions between QDs and TiO<sub>2</sub> NPs. We assume that such QDs are equivalent to those contributing to the residual PL intensity in ensemble measurements (Figures 3 and 4A). On the other hand, disappearance (Figure 5) of several single QDs in the presence of TiO<sub>2</sub> NPs should be due to the formation of static complexes. The fluctuations in the spectral maximum and intensity suggest that both charge distribution within a QD and electronic coupling between QDs and TiO<sub>2</sub> NPs fluctuate from time to time for a given QD. Nonetheless, increase in the number of ON and OFF events was detected occasionally (Figure 6D). In other words, for certain QDs, the duration of ON and OFF events was decreased in the presence of TiO<sub>2</sub> NPs. Such blinking with short ON



**Figure 9.** Schematic presentation of photoactivation and relaxation processes in QDs in the presence of TiO<sub>2</sub> NPs.

and OFF durations was associated with a decrease in the average PL intensity (Figure 6D), suggesting that the excited state of QDs is quenched by electron transfer to TiO<sub>2</sub> NPs as well. In other words, we hypothesize that a combination of modified blinking and decrease in the average PL intensity can be complex due to a combined effect of electron transfer from photoexcited QD to TiO<sub>2</sub> NPs, Auger ionization, transfer of a trapped electron to TiO<sub>2</sub> NPs, and back electron transfer. The blinking suppression for most but all QDs was not associated with any changes to the rate of radiative relaxation, indicating that the effect of TiO<sub>2</sub> NPs is on the redistribution of rates among nonradiative processes such as Auger relaxation, transfer of a trapped electron to TiO<sub>2</sub> NPs, and back electron transfer to charged QD. Figure 9 shows our hypothesis about various relaxation processes in QDs in the presence of TiO<sub>2</sub> NPs. The average PL lifetime of QDs in the presence of TiO<sub>2</sub> NPs is given by eq 1.

$$\tau_{\text{av}} = \frac{1}{k_r + k_{\text{nr}1} + k_A + k_{\text{et}1}} \quad (1)$$

where  $k_r$ ,  $k_{\text{nr}1}$ ,  $k_A$ , and  $k_{\text{et}1}$  are the rates of radiative relaxation, nonradiative relaxation, Auger ionization, and electron transfer, respectively. Because the PL lifetimes of most QDs were not affected by TiO<sub>2</sub> NPs, eq 1 can be written as

$$\tau_{\text{av}} = \frac{1}{k_r + k_{\text{nr}1} + k_A} \quad (2)$$

that is, electron transfer from the photoexcited state of QDs is neglected. Thus, in the presence of TiO<sub>2</sub> NPs, the blinking suppression without any decrease in the PL lifetime leaves us with a possibility that  $k_{\text{et}2} + k_{\text{bet}} \gg k_{\text{nr}2}$  (Figure 9), which means blinking can be suppressed by increasing the probabilities for regenerating the excited state of QDs and radiative relaxation. Although nonluminescent QD–TiO<sub>2</sub> complexes are formed in large excess, blinking suppression by TiO<sub>2</sub> NPs suggests

that nonradiative relaxations but not radiative relaxations in QDs can be suppressed by dynamic interactions of TiO<sub>2</sub> NPs with QDs.

## SUMMARY

The central result in the current work is blinking suppression in single CdSe/ZnS QDs by TiO<sub>2</sub> NPs, but without considerable changes to the rate of radiative relaxation. Thus, we hypothesize that blinking suppression occurs due to the suppression of nonradiative relaxation in a trion ( $k_{nr2}$ ) by channeling the neutralization of charged QDs through nonradiative processes such as electron transfer to TiO<sub>2</sub> NPs ( $k_{et2}$ ) and back electron transfer ( $k_{bet}$ ). Fomenko and Nesbitt have recently correlated QD's blinking suppression by propyl gallate ligands with the redistribution in the rates of radiative and nonradiative relaxations and thus disorder in the quantum confinement model.<sup>49</sup> According to previous reports, blinking can be attributed to deviations from the 8-fold degeneracy for the first exciton state in the theoretical model to 5-fold states induced by perturbations from electron–hole exchange interactions, asymmetric crystal structure, and lattice effects.<sup>18–20,49</sup>

Among the five degenerate states, redistribution in the population of dark and bright exciton states by surface trap states, ligands, or unpaired electrons from surface atoms can be correlated with an increase in the radiative rate. Such redistributions in the radiative to nonradiative rates of carrier recombination lead to blinking suppression.<sup>26</sup> On the other hand, Jin and Lian have shown that decrease in the PL lifetime of QDs due to electron transfer to TiO<sub>2</sub> NPs is associated with a decrease in the ON time and an increase in the OFF time.<sup>48</sup> In other words, the present status of blinking suppression shows that redistribution in the rates of radiative to nonradiative relaxations can suppress or support blinking. Because the blinking suppression in the current work is not accompanied by an increase in the radiative rate, we hypothesize that suppression in the nonradiative relaxation in charged QDs by electron transfer to TiO<sub>2</sub> NPs and back electron transfer is critical in the blinking suppression.

## REFERENCES AND NOTES

- Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **1996**, *271*, 933–937.
- Dabbousi, B. O.; RodriguezViejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core–Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B* **1997**, *98*, 4109–4117.
- Trindade, T.; O'Brien, P.; Pickett, N. L. Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives. *Chem. Mater.* **2001**, *13*, 3843–3858.
- Biju, V.; Itoh, T.; Anas, A.; Sujith, A.; Ishikawa, M. Semiconductor Quantum Dots and Metal Nanoparticles: Syntheses, Optical Properties, and Biological Applications. *Anal. Bioanal. Chem.* **2008**, *391*, 2469–2495.
- Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. Quantum Dot Bioconjugates for Imaging, Labelling and Sensing. *Nat. Mater.* **2005**, *4*, 435–446.
- Han, M.; Gao, X.; Su, J. Z.; Nie, S. Quantum-Dot-Tagged Microbeads for Multiplexed Optical Coding of Biomolecules. *Nat. Biotechnol.* **2001**, *19*, 621–622.
- Anas, A.; Akita, H.; Harashima, H.; Itoh, T.; Ishikawa, M.; Biju, V. Photosensitized Breakage and Damage of DNA by CdSe–ZnS Quantum Dots. *J. Phys. Chem. B* **2008**, *112*, 10005–10011.
- Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor Nanocrystals as Fluorescent Biological Labels. *Science* **1998**, *281*, 2013–2016.
- Chan, W. C. W.; Nie, S. M. Quantum Dot Bioconjugates for Ultrasensitive Nonisotopic Detection. *Science* **1998**, *281*, 2016–2018.
- Michalet, M.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. Quantum Dots for Live Cells, *In Vivo* Imaging, and Diagnostics. *Science* **2005**, *307*, 538–544.
- Jamieson, T.; Bakhshi, R.; Petrova, D.; Pocock, R.; Imani, M.; Seifalian, A. M. Biological Applications of Quantum Dots. *Biomaterials* **2007**, *28*, 4717–4732.
- Anas, A.; Okuda, T.; Kawashima, N.; Nakayama, K.; Itoh, T.; Ishikawa, M.; Biju, V. Clathrin-Mediated Endocytosis of Quantum Dot–Peptide Conjugates in Living Cells. *ACS Nano* **2009**, *3*, 2419–2429.
- Wu, X. Y.; Liu, H. J.; Liu, J. Q.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N. F.; Peale, F.; Bruchez, M. P. Immunofluorescent Labeling of Cancer Marker Her2 and Other Cellular Targets with Semiconductor Quantum Dots. *Nat. Biotechnol.* **2003**, *21*, 41–46.
- Biju, V.; Itoh, T.; Ishikawa, M. Delivering Quantum Dots to Cells: Bioconjugated Quantum Dots for Targeted and Nonspecific Extracellular and Intracellular Imaging. *Chem. Soc. Rev.* **2010**, DOI: 10.1039/B926512K.
- Biju, V.; Mundayoor, S.; Omkumar, R. V.; Anas, A.; Ishikawa, M. Bioconjugated Quantum Dots for Cancer Research: Present Status, Prospects and Remaining Issues. *Biotechnol. Adv.* **2010**, *28*, 199–213.
- Gao, X. H.; Cui, Y. Y.; Levenson, R. M.; Chung, L. W. K.; Nie, S. M. *In Vivo* Cancer Targeting and Imaging with Semiconductor Quantum Dots. *Nat. Biotechnol.* **2004**, *22*, 969–976.
- Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals. *Nature* **1996**, *383*, 802–804.
- Efros, A. L.; Rosen, M. Random Telegraph Signal in the Photoluminescence Intensity of a Single Quantum Dot. *Phys. Rev. Lett.* **1997**, *78*, 1110–1113.
- Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. Nonexponential “Blinking” Kinetics of Single CdSe Quantum Dots: A Universal Power Law Behavior. *J. Chem. Phys.* **2000**, *112*, 3117–3120.
- Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G. Blinking Statistics in Single Semiconductor Nanocrystal Quantum Dots. *Phys. Rev. B* **2001**, *63*, 205316.
- Hong, S.; Ha, T. Near-Complete Suppression of Quantum Dot Blinking in Ambient Conditions. *J. Am. Chem. Soc.* **2004**, *126*, 1324–1325.
- Kawashima, N.; Nakayama, K.; Itoh, K.; Itoh, T.; Ishikawa, M.; Biju, V. Reversible Dimerization of EGFR Revealed by Single-Molecule Fluorescence Imaging Using Quantum Dots. *Chem.—Eur. J.* **2010**, *16*, 1186–1192.
- Frantsuzov, P. A.; Marcus, R. A. Explanation of Quantum Dot Blinking without the Long-Lived Trap Hypothesis. *Phys. Rev. B* **2005**, *72*, 155321.
- Cragg, G. E.; Efros, A. L. Suppression of Auger Process in Confined Structures. *Nano Lett.* **2010**, *10*, 313–317.



26. Peterson, J. J.; Nesbitt, D. J. Modified Power Law Behavior in Quantum Dot Blinking: A Novel Role for Biexcitons and Auger Ionization. *Nano Lett.* **2009**, *9*, 338–345.
27. Tang, J.; Marcus, R. A. Mechanisms of Fluorescence Blinking in Semiconductor Nanocrystal Quantum Dots. *J. Chem. Phys.* **2005**, *123*, 054704.
28. Neuhauser, R. G.; Shimizu, K. T.; Woo, W. K.; Empedocles, S. A.; Bawendi, M. G. Correlation between Fluorescence Intermittency and Spectral Diffusion in Single Semiconductor Quantum Dots. *Phys. Rev. Lett.* **2000**, *85*, 3301–3304.
29. Tang, J.; Marcus, R. A. Diffusion-Controlled Electron Transfer Processes and Power-Law Statistics of Fluorescence Intermittency of Nanoparticles. *Phys. Rev. Lett.* **2005**, *95*, 107401.
30. Pelton, M.; Smith, G.; Scherer, N. F.; Marcus, R. A. Evidence for a Diffusion-Controlled Mechanism for Fluorescence Blinking of Colloidal Quantum Dots. *Proc. Natl Acad. Sci. U.S.A.* **2007**, *104*, 14249–14254.
31. Frantsuzov, P.; Kuno, M.; Janko, B.; Marcus, R. A. Universal Emission Intermittency in Quantum Dots, Nanorods and Nanowires. *Nat. Phys.* **2008**, *4*, 519–522.
32. Verberk, R.; van Oijen, A. M.; Orrit, M. Simple Model for the Power-Law Blinking of Single Semiconductor Nanocrystals. *Phys. Rev. B* **2002**, *66*, 233202.
33. Kuno, M.; Fromm, D. P.; Johnson, S. T.; Gallagher, A.; Nesbitt, D. J. Modeling Distributed Kinetics in Isolated Semiconductor Quantum Dots. *Phys. Rev. B* **2003**, *67*, 125304.
34. Tang, J.; Lee, D. H.; Yeh, Y. C.; Yuan, C. T. Short-Time Power-Law Blinking Statistics of Single Quantum Dots and a Test of the Diffusion-Controlled Electron Transfer Model. *J. Chem. Phys.* **2009**, *131*, 064506.
35. Sher, P. H.; Smith, J. M.; Dalgarno, P. A.; Warburton, R. J.; Chen, X.; Dobson, P. J.; Daniels, S. M.; Pickett, N. L.; O'Brien, P. Power Law Carrier Dynamics in Semiconductor Nanocrystals at Nanosecond Timescales. *Appl. Phys. Lett.* **2008**, *92*, 101111.
36. Frantsuzov, P. A.; Volkan-Kacso, S.; Janko, B. Model of Fluorescence Intermittency of Single Colloidal Semiconductor Quantum Dots Using Multiple Recombination Centers. *Phys. Rev. Lett.* **2009**, *103*, 207402.
37. Shimizu, K. T.; Woo, W. K.; Fisher, B. R.; Eisler, H. J.; Bawendi, M. G. Surface-Enhanced Emission from Single Semiconductor Nanocrystals. *Phys. Rev. Lett.* **2002**, *89*, 117401.
38. Ito, Y.; Matsuda, K.; Kanemitsu, Y. Mechanism of Photoluminescence Enhancement in Single Semiconductor Nanocrystals on Metal Surfaces. *Phys. Rev. B* **2007**, *75*, 033309.
39. Fu, Y.; Zhang, J.; Lakowicz, J. R. Suppressed Blinking in Single Quantum Dots (QDs) Immobilized Near Silver Island Films (SIFs). *Chem. Phys. Lett.* **2007**, *447*, 96–100.
40. Yuan, C. T.; Yu, P.; Tang, J. Blinking Suppression of Colloidal CdSe/ZnS Quantum Dots by Coupling to Silver Nanoprisms. *Appl. Phys. Lett.* **2009**, *94*, 243108.
41. Masuo, S.; Naiki, H.; Machida, S.; Itaya, A. Photon Statistics in Enhanced Fluorescence from a Single CdSe/ZnS Quantum Dot in the Vicinity of Silver Nanoparticles. *Appl. Phys. Lett.* **2009**, *94*, 193106.
42. Matsumoto, Y.; Kanemoto, R.; Itoh, T.; Nakanishi, S.; Ishikawa, M.; Biju, V. Photoluminescence Quenching and Intensity Fluctuations of CdSe–ZnS Quantum Dots on an Ag Nanoparticle Film. *J. Phys. Chem. C* **2008**, *112*, 1345–1350.
43. Heyes, C. D.; Kobitski, A. Y.; Breus, V. V.; Nienhaus, G. U. Effect of the Shell on the Blinking Statistics of Core–Shell Quantum Dots: A Single-Particle Fluorescence Study. *Phys. Rev. B* **2007**, *75*, 125431.
44. Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. “Giant” Multishell CdSe Nanocrystal Quantum Dots with Suppressed Blinking. *J. Am. Chem. Soc.* **2008**, *130*, 5025–5027.
45. Mahler, B.; Spinicelli, P.; Buil, S.; Quelin, X.; Hermier, J. P.; Dubertret, B. Towards Non-Blinking Colloidal Quantum Dots. *Nat. Mater.* **2008**, *7*, 659–664.
46. Spinicelli, P.; Buil, S.; Quelin, X.; Mahler, B.; Dubertret, B.; Hermier, J. P. Bright and Grey States in CdSe–CdS Nanocrystals Exhibiting Strongly Reduced Blinking. *Phys. Rev. Lett.* **2009**, *102*, 136801.
47. Garcia-Santamaria, F.; Chen, Y. F.; Vela, J.; Schaller, R. D.; Hollingsworth, J. A.; Klimov, V. I. Suppressed Auger Recombination in “Giant” Nanocrystals Boosts Optical Gain. *Nano Lett.* **2009**, *9*, 3482–3488.
48. Jin, S. Y.; Lian, T. Q. Electron Transfer Dynamics from Single CdSe/ZnS Quantum Dots to TiO<sub>2</sub> Nanoparticles. *Nano Lett.* **2009**, *9*, 2448–2454.
49. Fomenko, V.; Nesbitt, D. J. Solution Control of Radiative and Nonradiative Lifetimes: A Novel Contribution to Quantum Dot Blinking Suppression. *Nano Lett.* **2008**, *8*, 287–293.
50. Cui, S. C.; Tachikawa, T.; Fujitsuka, M.; Majima, T. Interfacial Electron Transfer Dynamics in a Single CdTe Quantum Dot–Pyromellitimide Conjugate. *J. Phys. Chem. C* **2008**, *112*, 19625–19634.
51. Cui, S. C.; Tachikawa, T.; Fujitsuka, M.; Majima, T. Solvent-Polarity Dependence of Electron-Transfer Kinetics in a CdSe/ZnS Quantum Dot–Pyromellitimide Conjugate. *J. Phys. Chem. C* **2010**, *114*, 1217–1225.
52. He, H.; Qian, H. F.; Dong, C. Q.; Wang, K. L.; Ren, J. C. Single Nonblinking CdTe Quantum Dots Synthesized in Aqueous Thiopropionic Acid. *Angew. Chem., Int. Ed.* **2006**, *45*, 7588–7591.
53. Heuff, R. F.; Marrocco, M.; Cramb, D. T. Saturation of Two-Photon Excitation Provides Insight into the Effects of a Quantum Dot Blinking Suppressant: A Fluorescence Correlation Spectroscopy Study. *J. Phys. Chem. C* **2007**, *111*, 18942–18949.
54. Antelman, J.; Ebenstein, Y.; Dertinger, T.; Michalet, X.; Weiss, S. Suppression of Quantum Dot Blinking in DTT-Doped Polymer Films. *J. Phys. Chem. C* **2009**, *113*, 11541–11545.
55. Ko, H. C.; Yuan, C. T.; Lin, S. H.; Tang, J. Blinking Suppression of Single Quantum Dots in Agarose Gel. *Appl. Phys. Lett.* **2010**, *96*, 012104.
56. Koberling, F.; Mews, A.; Basche, T. Oxygen-Induced Blinking of Single CdSe Nanocrystals. *Adv. Mater.* **2001**, *13*, 672–676.
57. Wang, X.; Ren, X.; Kahen, K.; Hahn, M. A.; Rajeswaran, M.; Maccagnano-Zacher, S.; Silcox, J.; Cragg, G. E.; Efron, A. L.; Krauss, T. D. Non-Blinking Semiconductor Nanocrystals. *Nature* **2009**, *459*, 686–689.
58. Biju, V.; Makita, Y.; Nagase, T.; Yamaoka, Y.; Yokoyama, H.; Baba, Y.; Ishikawa, M. Subsecond Luminescence Intensity Fluctuations of Single CdSe Quantum Dots. *J. Phys. Chem. B* **2005**, *109*, 14350–14355.
59. Knappenberger, K. L.; Wong, D. B.; Romanyuk, Y. E.; Leone, S. R. Excitation Wavelength Dependence of Fluorescence Intermittency in CdSe/ZnS Core/Shell Quantum Dots. *Nano Lett.* **2007**, *7*, 3869–3874.
60. Lee, D. H.; Yuan, C. T.; Tachiya, M.; Tang, J. Influence of Bin Time and Excitation Intensity on Fluorescence Lifetime Distribution and Blinking Statistics of Single Quantum Dots. *Appl. Phys. Lett.* **2009**, *95*, 163101.
61. Crouch, C. H.; Mohr, R.; Emmons, T.; Wang, S. Y.; Drndic, M. Excitation Energy Dependence of Fluorescence Intermittency in CdSe/ZnS Core–Shell Nanocrystals. *J. Phys. Chem. C* **2009**, *113*, 12059–12066.
62. Goushi, K.; Yamada, T.; Otomo, A. Excitation Intensity Dependence of Power-Law Blinking Statistics in Nanocrystal Quantum Dots. *J. Phys. Chem. C* **2009**, *113*, 20161–20168.
63. Kharchenko, V. A.; Rosen, M. Theory of Linear and Nonlinear Optical Properties of Semiconductor Nanocrystals: Auger Relaxation Processes in Semiconductor Nanocrystals and Quantum Wells. *J. Lumin.* **1996**, *70*, 158–169.
64. Chepic, D. I.; Efron, A. L.; Ekimov, A. I.; Ivanov, M. G.;

- Kharchenko, V. A.; Kudriavtsev, I. A.; Yazeva, T. V. Auger Ionization of Semiconductor Quantum Drops in a Glass Matrix. *J. Lumin.* **1990**, *47*, 113–127.
65. Zaban, A.; Micic, O. I.; Gregg, B. A.; Nozik, A. J. Photosensitization of Nanoporous TiO<sub>2</sub> Electrodes with InP Quantum Dots. *Langmuir* **1998**, *14*, 3153–3156.
66. Plass, R.; Pelet, S.; Krueger, J.; Gratzel, M.; Bach, U. Quantum Dot Sensitization of Organic–Inorganic Hybrid Solar Cells. *J. Phys. Chem. B* **2002**, *106*, 7578–7580.
67. Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO<sub>2</sub> Films. *J. Am. Chem. Soc.* **2006**, *128*, 2385–2393.
68. Kongkanand, A.; Tvrđy, K.; Takechi, K.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Tuning Photoresponse through Size and Shape Control of CdSe–TiO<sub>2</sub> Architecture. *J. Am. Chem. Soc.* **2008**, *130*, 4007–4015.
69. Chakrapani, V.; Tvrđy, K.; Kamat, P. V. Modulation of Electron Injection in CdSe–TiO<sub>2</sub> System through Medium Alkalinity. *J. Am. Chem. Soc.* **2010**, *132*, 1228–1229.
70. Mora-Sero, I.; Gimenez, S.; Fabregat-Santiago, F.; Gomez, R.; Shen, Q.; Toyoda, T.; Bisquert, J. Recombination in Quantum Dot Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, *42*, 1848–1857.