SHORT COMMUNICATION

Single-molecule photochemical reactions of Auger-ionized quantum dots

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Abstract

Photoinduced electron transfer in donor-acceptor systems composed of quantum dots (QDs) and electron donors or acceptors is a subject of considerable recent research interest due to the potential applications of such systems in both solar energy harvesting and degradation of organic pollutants. Herein, we employed single-molecule imaging and spectroscopy techniques for the detection of photochemical reactions between 1,4-diaminobutane (DAB) and CdSe/ZnS single QDs. We investigated the reactions by analyzing photoluminescence (PL) intensity and lifetime of QDs at ensemble and single-molecule levels. While DAB was applied to single QDs tethered on a cover slip or QDs dispersed in a solution, PL intensity of QD continuously decreased with a concomitant increase in the PL lifetime. Interestingly, these changes in the PL properties of QD were predominant under high-intensity photoactivation. We hypothesize that the above changes in the PL properties surface due to the transfer of an electron from DAB to Auger-ionized QD followed by elimination of a proton from DAB and the formation of a QD-DAB adduct. Thus, a continuous decrease in the PL intensity of QDs under high-intensity photoactivation is attributed to continuous photochemical reactions of DAB with single QDs and the formation of QD-$(DAB)_n$ adducts. We believe that detection and analysis of such photochemical reactions of single QDs with amines will be of considerable broad interest due to the significant impact of photoinduced electron transfer reactions in energy management and environmental remediation.

Keywords: *quantum dots*; *single-molecule*; *electron transfer*; *Auger ionization*; *CdSe/ZnS*; *photoluminescence*; *photochemical reaction*

Colloidal quantum dots (QDs) show unique optical properties such as broad absorption and narrow emission bands as well as bright, stable, and size-dependent tunable photoluminescence (PL) (1, 2). Also, the large surface area of QDs is promising for the conjugation of various organic and biomolecules (3). The unique optical and structural properties formulate QDs to be ideal donors or acceptors of electrons in the construction of donor-acceptor systems for modern photovoltaic devices (4–14).

Given the significance of QDs in solar energy harvesting, investigation of photoinduced electron transfer in QD-based donor-acceptor systems such as QD-TiO$_2$ (5–9), QD-Indium Tin Oxide (ITO) (10), QD-inorganic complexes (11), QD-C$_{60}$ (12), and QD-polymer (13) is a subject of considerable current research interest. In these

systems, transfer of an electron from a photoactivated QD to the corresponding acceptor results in the formation of charge-separated states. Solar cells based on donor-acceptor systems are designed by directing the charge carrier recombination through an external electrical circuit. Although photoinduced electron transfer processes in QD-based donor-acceptor systems are greatly investigated, photochemical reactions between organic molecules and photoactivated QDs as well as potentials of such reactions for environmental remediation remain mostly unattended.

Recently, Sharma et al. found that *p*-phenylenediamine lowers the PL quantum efficiency of CdSe QD by accepting an electron from it (14). On the other hand, *n*-butylamine is known to passivate surface defects in CdSe QD, suppress non-radiative carrier recombination in the defects, and enhance the PL quantum efficiency of QD (14). Nonetheless, controversies exist in the amine-induced variations of QD's PL quantum efficiency. For example, *n*-butylamine itself at higher concentrations activates non-radiative carrier recombination in CdSe QD and lowers its PL quantum efficiency (15). To-date electron transfer interactions in the above QD-based donor-acceptor systems are found to be reversible by energy wasting back electron transfer. Although reversible electron transfer interactions of QDs with donors or acceptors of electron are greatly investigated, photochemical reactions between hole-acceptors and QDs remain mostly unattended. Importantly, photochemical reactions of highly photostable QDs with dyes, amines, and other organic pollutants would be of great value for environmental waste management. Here we found that photoactivation of CdSe/ZnS QDs in the presence of 1,4-diaminobutane (DAB) results in a gradual but irreversible decrease in the PL intensity of single QDs. This irreversible decrease in the PL intensity is apparent only under high-intensity photoactivation of QDs, which gives us the notion that Auger-ionized QDs accept electrons from DAB molecules and subsequent elimination of a proton from the QD-DAB$^+$ complex results in the formation of a QD-DAB adduct. Thus, we propose that the gradual but irreversible decrease in the PL intensity of single QDs is due to successive photochemical reactions of Auger-ionized QDs with a large number of DAB molecules and the formation of QD-(DAB)$_n$ adducts.

Results and discussion

We have investigated photochemical reactions of DAB with QDs at ensemble and single-molecule levels by recording and analyzing PL spectra of QD solutions and PL intensity trajectories of single QDs both in the presence of DAB and under high-intensity photoactivation. Fig. 1A shows the effect of concentration of DAB on the PL spectra of a QD solution. As the concentration
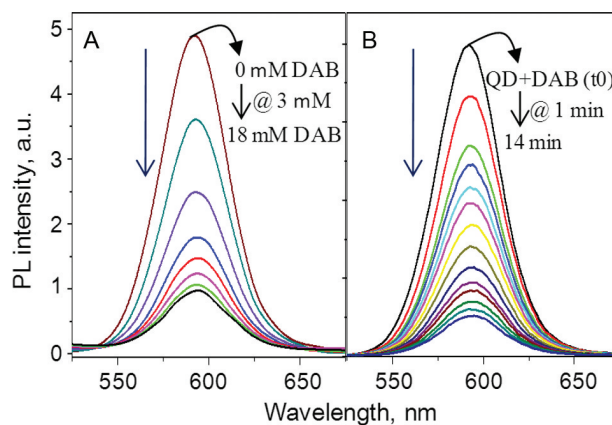

Fig. 1. (A) PL spectra of a 1 µM QD solution in toluene and in the presence or absence of DAB: top to bottom are spectra recorded without adding DAB and with an increase in the concentration of DAB. (B) PL spectra of a 1 µM QD solution in toluene supplemented with 3 mM DAB solution: top to bottom are spectra recorded at 1 min intervals after photoactivation (400 nm).

of DAB was increased, PL intensity of QDs decreased. Also, we have examined temporal changes in the PL intensity of QDs under continuous photoactivation. Fig. 1B shows PL spectra of a QD solution in the presence of DAB and under continuous photoactivation. Here, PL intensity of QDs continuously decreased with time but without any changes in the concentration of DAB.

A decrease in the PL intensity of QDs with an increase in the concentration of DAB (Fig. 1A) and a temporal decrease in the PL intensity of QDs under continuous photoactivation (Fig. 1B) are attributed to photochemical reactions of DAB with QDs and the formation of QD-DAB adducts having lower PL quantum efficiencies than pristine QDs.

To validate the photochemical reaction of DAB with QDs, we have recorded and analyzed the PL intensity trajectories of single QDs in the presence and absence of DAB and under low- (0.22 kW/cm^2) and high- (2.2 kW/cm^2) intensity photoactivation. Fig. 2 shows PL intensity trajectories of single QDs tethered on a cover slip, immersed in water, and recorded in the presence or absence of DAB. Interestingly, in the presence of DAB and under high-intensity photoactivation, we detected a continuous decrease in the PL intensity of single QDs (Fig. 1B–F). On the other hand, PL intensities of single QDs under high-intensity photoactivation but without DAB remained intact even after several minutes (Fig. 2A). The excitation power density (2.2 kW/cm^2) applied in these experiments was high enough to activate multiple exciton pairs and induce Auger ionization in QDs, which is apparent from intermittent PL blinking of single QDs. Our hypothesis for the gradual decrease in the PL intensity of single QDs in the presence of DAB is
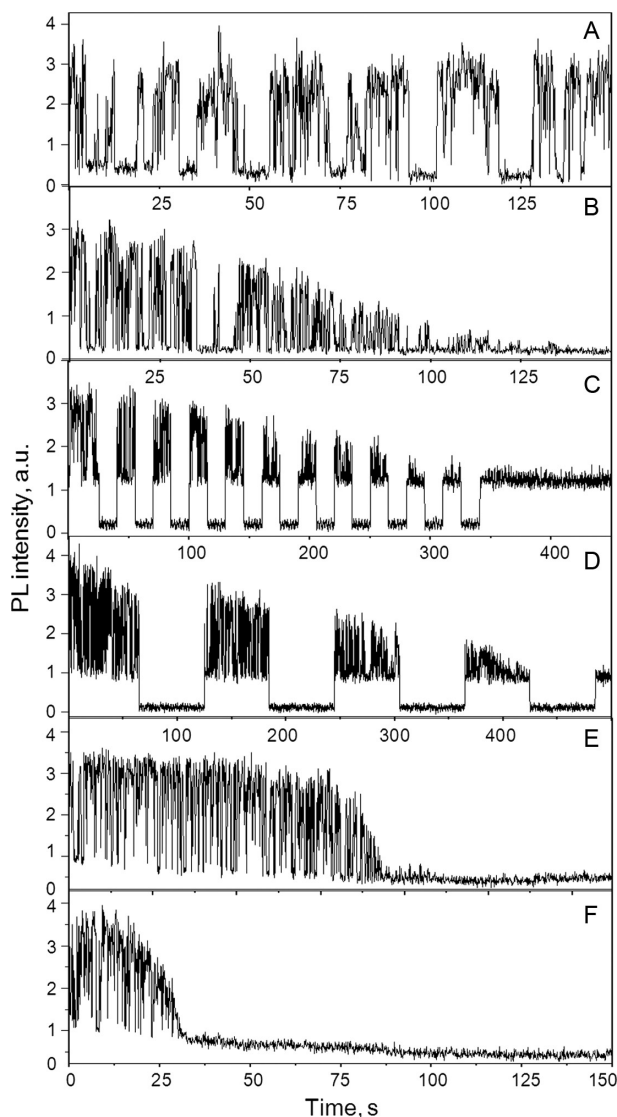
Fig. 2. PL intensity trajectories of single QDs recorded under high-intensity photoactivation (at 532 nm, 2.2 kW/cm^2): (A) without DAB, (B) with 10 μM DAB solution, (C) with 10 μM DAB solution and at 15 s intervals of photoactivation, (D) with 10 μM DAB solution and at 60 s intervals of photoactivation, (E) with 0.1 mM DAB solution, and (F) with 1 mM solution.

that Auger-ionized QDs react with DAB and form QD-DAB adducts having PL quantum efficiencies lower than that of QDs. The reaction of DAB with QD probably took place by the transfer of an electron from DAB to Auger-ionized QD followed by the elimination of a proton from QD-DAB$^+$ adduct. Steps involved in the photochemical reactions of DAB with photoactivated QD is schematically presented in Fig. 3. Under continuous photoactivation, a large number of DAB molecules can be added onto the surface of QDs. Thus, the continuous decrease in the PL intensity can be attributed to the formation of poorly luminescent QD-(DAB)$_n$ adducts.
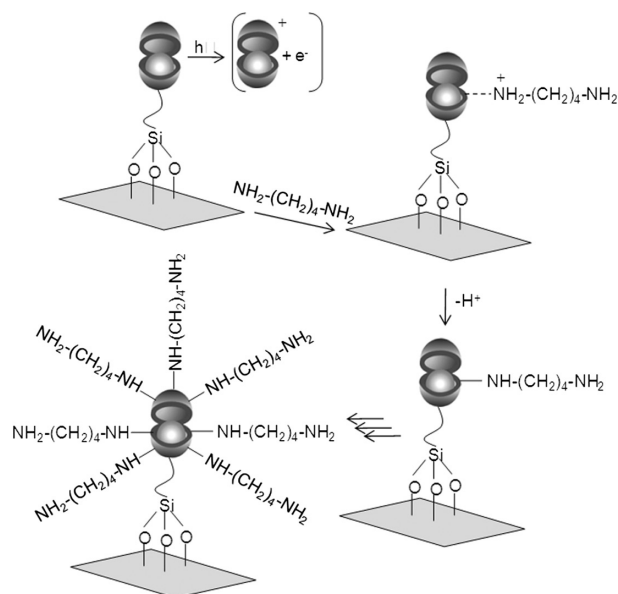

Fig. 3. Schematic presentation of electron transfer from DAB to an Auger-ionized QD and subsequent formation of QD-(DAB)$_n$ adducts.

The above hypothesis was investigated by intermittent photoactivation of single QDs in the presence of DAB and under high excitation intensity (2.2 kW/cm^2). Fig. 2C and D shows PL intensity trajectories of single QDs excited at 15 s and 60 s laser 'on'/'off' intervals. We found that the PL intensities of single QDs remained essentially unaffected before and after each laser 'off' period, which indicates that the reaction of DAB with QD should be absolutely photoinduced. In other words, DAB does not react with QDs in the dark. Our hypothesis was further investigated by photoactivating single QDs in the presence of DAB but under low excitation intensity (0.22 kW/cm^2), which is insufficient to activate multiple excitons and induce Auger ionization. Under these conditions, we found that PL intensities of single QDs remained essentially intact even after 10 min. The relation between the concentration of DAB and PL intensities of single QDs is shown in Fig. 2B, E, and F. Here, as the concentration of a DAB solution in a single QD sample was increased (10 μM for Fig. 2B, 100 μM for Fig. 2E, and 1 mM for Fig. 2F), the rate at which PL intensities of single QDs decreased was also increased. These results and the gradual decrease in the PL intensity of single QDs support our hypothesis that Auger-ionized QDs react with DAB.

The photochemical reaction between QD and DAB was further investigated by recording and analyzing PL decay profiles of QD solutions. Fig. 4 shows PL decay profiles of a QD solution recorded at 2 min intervals in the presence of DAB and under high-intensity (2.2kW/cm^2) photoactivation. Auger ionization of QDs under such high-intensity photoactivation is apparent
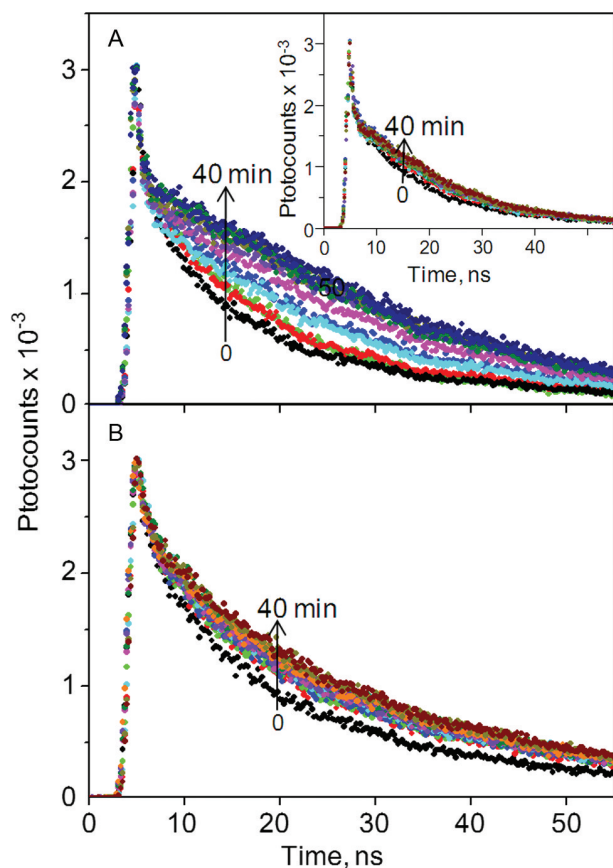
Fig. 4. PL decay profiles of QD solutions: (A) decays recorded at 2 min intervals in the presence of DAB and under high-intensity (2.2 kW/cm^2) photoactivation, and (B) decays recorded at 2 min intervals in the presence of DAB and under low-intensity (0.22 kW/cm^2) photoactivation. Inset of A: decays recorded at 2 min intervals without DAB and under high-intensity photoactivation.

from evolution of a fast component in the decay profiles (Fig. 4A and inset). Interestingly, we detected a gradual increase (from 5.9 ns to 9.8 ns, 66%) in the PL lifetime of QDs with time under photoactivation (Fig. 4A). On the other hand, PL lifetime of a QD solution was increased by only <20% when photoactivated without the addition of DAB (inset of Fig. 4A). The spontaneous increase in the PL lifetime of QDs is associated with an increase in the PL quantum efficiency, which originates from an increase in the contribution of radiative carrier recombination in the surface states (16, 17). However, an increase in the PL lifetime of QDs under high-intensity photoactivation in the presence of DAB is associated with a gradual but irreversible decrease in PL intensity. Because amines are known to passivate surface defects in QDs, we attribute the changes in the PL properties of QDs to surface passivation of QDs by photoinduced electron transfer reaction with DAB and the formation of QD-(DAB)$_n$ adducts. The contribution of DAB to an increase

in the PL lifetime of QDs was further investigated by recording and analyzing PL decays of QDs under low-intensity photoactivation. Fig. 4B shows PL decay profiles of a QD solution recorded at 2 min intervals in the presence of DAB and under low (0.22 kW/cm^2) excitation intensity, which is insufficient to activate multi-exciton pairs and induce Auger ionization. Therefore, photochemical reactions of DAB with QD takes place only under high-intensity photoactivation. In other words, the decrease in the PL intensity of QDs with time under photoactivation in the presence of DAB can be attributed to photoinduced electron transfer reactions between Auger-ionized QD and DAB and subsequent formation of poorly luminescent QD-(DAB)$_n$ adducts.

In short, single-molecule photochemical reactions of an aliphatic amine on the surface of quantum dots were detected by analyzing photoluminescence intensity trajectories and lifetimes of quantum dots at ensemble and single particle levels. As QDs were photoactivated in the presence of DAB, we found continuous decrease in the photoluminescence intensity of quantum dots and concomitant increase in their photoluminescence lifetime values. These changes in the luminescence properties were apparent only under high-intensity photoactivation of quantum dots, during which Auger ionization is operational. Thus, the changes in the luminescence properties of single quantum dots are attributed to photoinduced electron transfer reaction of amine with Auger-ionized quantum dots and the formation of quantum dot-amine adducts. Such photochemical reactions of organic molecules on the surface of quantum dots and other nanoparticles would be of great value for energy management and environment remediation.

Experimental procedure

CdSe/ZnS (PL maximum ~600/655 nm) QDs were obtained from Invitrogen Corporation (Japan) and DAB from Sigma Aldrich (Japan). Single-molecule samples were prepared by tethering QDs on cover slips. The procedure for preparation of single-molecule samples is reported elsewhere (9). In short, cover slips were cleaned by dipping in a nascent chlorine solution and silanized using a 0.5% solution of 3-aminopropyltriethoxysilane in acetone. Silanized cover slips were copiously washed with water and acetone, and biotinylated by dipping in a 10 μM aqueous solution of biotin 3-sulfo-*N*-hydroxysuccinimide ester (Sigma Aldrich, Japan) for 30 min. Biotinylated cover slips were copiously washed with deionized water and successively, CdSe/ZnS QDs were uniformly tethered on the cover slips by placing a 10 pM solution of QD655-streptavidin conjugate on one side of the cover slip. After incubation for 30 min at room temperature, unbound QDs were removed by washing with deionized water. Finally, QDs were dipped in deionized water and recorded single-molecule images,

PL intensity trajectories, and PL lifetimes. Single-molecule experiments were carried out in an inverted optical microscope (Olympus IX 70) equipped with a 60 × objective lens (Olympus, NA 0.98). Fluorescence signals collected using the objective lens were filtered through a 620 nm long pass filter, magnified using a 2.5 × telescopic lens, and recorded using an image intensifier, charge-coupled device assembly (Hamamatsu Photonics, Japan). For PL lifetime measurements, 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). Fluorescence decay profiles were recorded using an assembly of a polychromater and a streak-scope (Hamamatsu photonics, Japan).

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Conflict of interest and funding

There is no conflict of interest in the present study for any of the authors.

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