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Auger Ionization Beats Photo-Oxidation of Semiconductor Quantum Dots: Extended Stability of Single-Molecule Photoluminescence**

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Abstract: *Despite the bright and tuneable photoluminescence (PL) of semiconductor quantum dots (QDs), the PL instability induced by Auger recombination and oxidation poses a major challenge in single-molecule applications of QDs. The incomplete information about Auger recombination and oxidation is an obstacle in the resolution of this challenge. Here, we report for the first time that Auger-ionized QDs beat self-sensitized oxidation and the non-digitized PL intensity loss. Although high-intensity photoactivation insistently induces PL blinking, the transient escape of QDs into the ultrafast Auger recombination cycle prevents generation of singlet oxygen ($^1O_2$) and preserves the PL intensity. By the detection of the NIR phosphorescence of $^1O_2$ and evaluation of the photostability of single QDs in aerobic, anaerobic, and $^1O_2$ scavenger-enriched environments, we disclose relations of Auger ionization and $^1O_2$-mediated oxidation to the PL stability of single QDs, which will be useful during the formulation of QD-based single-molecule imaging tools and single-photon devices.*

Photo-oxidation of organic dye molecules and inorganic nanoparticles is ubiquitous and is one of the major challenges in the durability of fluorescent labels and photosensitizers. The unparalleled optical properties of QDs present enormous opportunities from biological imaging to single-photon devices.[1] Stable PL is an essential element for such applications. Despite the unique size-dependent tunable and bright PL of QDs, these tiny crystals at single-particle level suffer from unpredictable intensity loss, which is contributed by the digitized (one-step) ON and OFF intermittency, also called blinking, and the digitized or non-digitized (gradual) photo-darkening. Blinking is due to Auger ionization and subsequently the carriers follow non-radiative recombination in the trion state.[2] During such blinking, the OFF states dominate until the ionized QD is neutralized. On the other hand, photo-darkening is the result of irreversible surface oxidation.[2,3] Nonetheless, passivation of non-radiative carrier recombination centers on the surface of QDs by water, dissolved oxygen or a thin layer of oxide is known to enhance the PL quantum efficiency.[4] These contradicting observations of PL enhancement, quenching, and fluctuations of QDs complicate applications that require temporal and spatial precisions, such as single-molecule bioimaging and single-photon light sources.

The PL intensity and blinking of QDs are enhanced or suppressed as functions of the degree of quantum confinement and the relative rates of radiative and non-radiative carrier recombinations. For example, the rates of non-radiative Auger recombinations can be considerably suppressed by either minimizing the overlap between the wave functions of charge carriers in core/shell QDs[5a] or the smoothening of the confinement potentials of charge carriers in alloyed QDs.[5b,c] Further, suppression of blinking and enhancement of PL can be achieved by the chemical passivation of defects or dangling bonds using shells from large band-gap semiconductors[5,6] or molecules such as thiols.[7] Nonetheless, ligand exchange reactions and photoactivation invariably accompany enhancement or suppression of PL intensity and blinking.[8] Further, oxidation is one of the major challenges in the PL stability and the physical structure of QDs, which can be controlled to a greater extent by protection using shells from other semiconductors, silica or polymers.[6,9] Even in the case of core/shell QDs, oxidation of the shells adversely affects the PL. Although the role of $^1O_2$ on the spectral blue-shift of QDs is hypothesized,[3b] relations among photoactivation, Auger ionization, $^1O_2$, and the non-digitized PL intensity loss remain unresolved.

Here, we report the relations of self-sensitized production of $^1O_2$, Auger ionization, and photo-oxidation on the non-digitized PL intensity loss of single CdSe/ZnS QDs. Without Auger ionization or any $^1O_2$ scavenger, the PL intensities of single QDs immersed in aerated solvents and shined with a beam of high-intensity coherent photons (532 nm) monotonously decrease. However, interestingly, the PL intensity is preserved by the transient escape of single QDs from photo-oxidation into the Auger-ionized state. The roles of $^1O_2$ on the oxidation of QDs and the gradual loss of PL intensity are validated by the detection of the phosphorescence of $^1O_2$, and the stabilization of the PL intensity of single QDs under anaerobic conditions and Auger ionization, and in the presence of $^1O_2$ scavengers. Further, from the PL intensities of single QDs as functions of the local concentrations of $^1O_2$ scavengers or sensors and the intensities of excitation light, we derive conditions ideal for exceptionally enhancing the durability of single QDs. Hypothesis of photo-oxidation and ionization, and the corresponding changes in the PL intensity of single QDs are shown in Figure 1.

At the ensemble level, the PL intensity of QDs decreases with time under photoactivation (Figure 2A), which is similar to the photobleaching property of organic fluorophores. However, unlike the digitized photo-darkening of organic single molecules, the PL intensities of single QDs immersed in water or DMSO (Figure 2B) gradually decrease and hit the background level sooner or later. The speed of such non-digitized loss of PL intensity, which is due to photo-oxidation, increases with increase in the intensity of the excitation light. For example a QD excited with a 500 W cm^{-2} (532 nm) laser beam (Figure 2B, red trajectory) darkens twice as fast as a QD excited with a 250 W cm^{-2} laser (Figure 2B, blue

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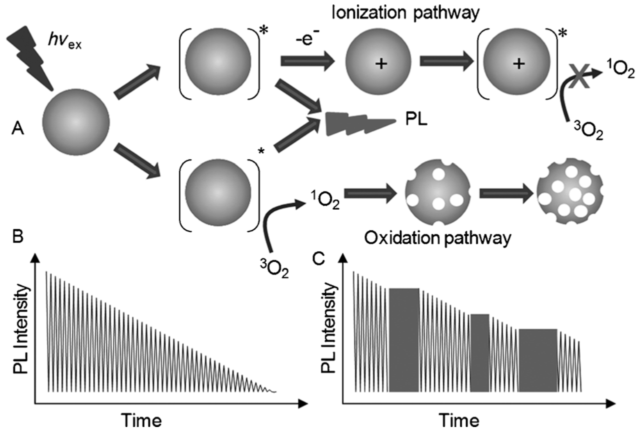

Figure 1. A) Scheme of photo-oxidation and ionization of QDs. B,C) Simulated PL intensity trajectories of single QDs: B) under continuous oxidation and C) under intermittent Auger ionization and oxidation.

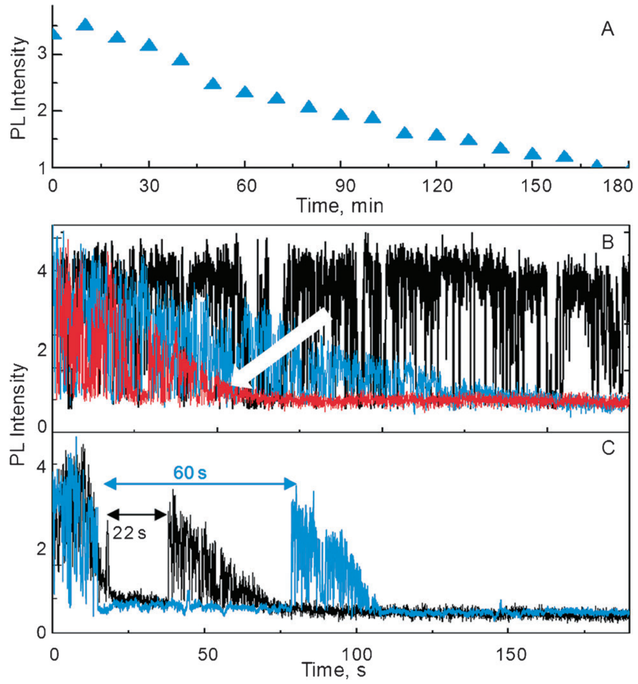

Figure 2. A) PL intensity–time trajectory of a CdSe/ZnS QD solution (20 nm) under photoactivation at 532 nm (with an intensity of 5 $\mathrm{W\,cm^{-2}}$). B) PL intensity trajectories of three single QDs tethered on glass cover slips and illuminated with a 532 nm laser beam: under illumination of laser light with an intensity of 500 $\mathrm{W\,cm^{-2}}$ in air (black), immersed in DMSO and under illumination of laser light with an intensity of 250 $\mathrm{W\,cm^{-2}}$ (blue), and immersed in DMSO and under illumination of laser light with an intensity of 500 $\mathrm{W\,cm^{-2}}$ (red). C) PL intensity trajectories of two QDs tethered on a cover slip, immersed in DMSO, and under illumination of laser light with an intensity of 500 $\mathrm{W\,cm^{-2}}$. The arrows in (C) indicate near-complete recovery of PL intensity after Auger-ionized OFF periods.

trajectory). Additional PL intensity trajectories recorded under different excitation laser intensities (125 to 500 $\mathrm{W\,cm^{-2}}$) are provided in Figure S1 (see the Supporting Information). On the other hand, single QDs at the glass–air interface show prolonged stability (Figure 2B, black trajectory). We hypothesize that an increase in the density of non-radiative carrier recombination centers, which are the oxidized sites, with time under photoactivation contributes to the non-digitized loss of PL intensity. In other words, unlike organic single molecules, single QDs traverse a series of oxidized forms with low PL quantum efficiencies.

Interestingly, single-molecule data (Figure 2C) suggest the suppression of both the rates of oxidation and the loss of PL intensity during the Auger-ionized periods. Despite the monotonous decrease of PL intensity during the ON state (Figure 2B and C), the intensity after prolonged Auger-ionized OFF periods recovers to the same level as that before the OFF periods (Figure 2C). We identified this unique behavior for less than 90% of the QDs with long-living OFF states and less than 80% of the ON/OFF events. Note, the OFF periods originate from Auger ionization,[2] during which the relaxation of a photoactivated QD (trion) is dominated by the ultrafast (ca. $10^{12}\,\mathrm{s^{-1}}$) Auger recombination. In other words, QDs overcome photo-oxidation during the OFF periods by shifting the energy transfer pathway from oxygen ($^3O_2$) to the excess charge carrier. As the rates of Auger recombination are much higher than that of interband relaxation ($10^{8-11}\,\mathrm{s^{-1}}$) and energy transfer ($<10^{9}\,\mathrm{s^{-1}}$) to $^3O_2$, QDs entering into Auger-ionized OFF periods are incompetent for producing $^1O_2$ until they are neutralized. Thus, a QD with multiple or long-living Auger-ionized OFF periods not only escapes from oxidation but also retains its PL for longer periods (Figure 2C). Nonetheless, the total number of photons emitted is inversely related to the intensity of excitation light and the concentration of $^1O_2$, which is discussed below.

To understand the relations among Auger ionization, oxidation and the non-digitized PL intensity loss in single QDs, we investigate $^1O_2$ production by photoactivated QDs. Here, a 20 nm QD solution in D_2O was photoactivated at 532 nm, and the decay profiles of $^1O_2$ phosphorescence were recorded in the 1230 to 1330 nm window. The NIR spectrum reconstituted from the decay profiles shows characteristic phosphorescence band (ca. 1270 nm) of $^1O_2$ (Figure 3B). This phosphorescence disappeared upon saturation of the solution with N_2 gas and reappeared upon aeration. The production of $^1O_2$ is further examined using a singlet oxygen sensor green (SOSG) dye. Here, a QD solution (20 nm) was supplemented with an aqueous solution (10 μm) of SOSG. In this sample, QDs were selectively photoactivated at 532 nm, where SOSG is non-resonant. Interestingly, a yellow fluorescence appeared in the solution and was enormously enhanced with time under photoactivation (Figure 3A and C). The yellow fluorescence, as spectrally resolved (Figure 3C), is a combination of the intense green fluorescence of photouncaged SOSG and the red PL of QDs. The new fluorescence band at about 545 nm is red-shifted from the characteristic weak fluorescence band of pristine SOSG (Figure 3D). The 545 nm emission is contributed by the fluorescein part of SOSG, which is non-fluorescent in SOSG as a result of caging by intramolecular electron transfer with anthracene. However, $^1O_2$ produced by QDs uncages the fluorescence by converting anthracene into its 9,10-endoperoxide and thus, blocking the intramolecular electron transfer.[10a] The characteristic phosphorescence of

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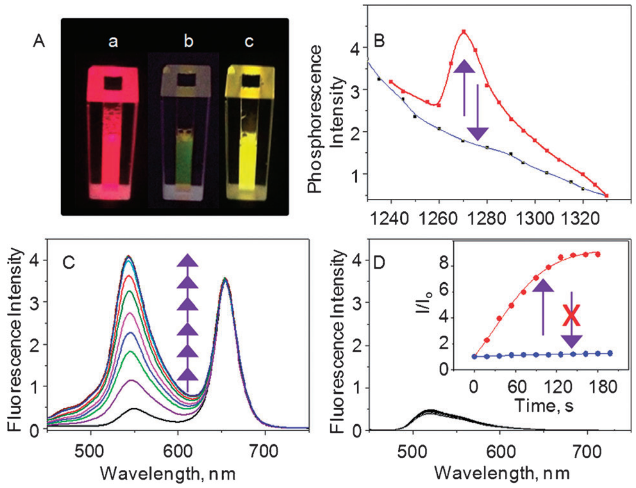

Figure 3. A) Digital images of solutions of a) QD (20 nM), b) SOSG (10 μM) and c) a mixture of QD and SOSG photoactivated for 10 minutes at 532 nm. B) NIR phosphorescence spectra of $^1O_2$ generated in a QD solution under aerated (red) and N_2-saturated (blue) conditions. C) Normalized fluorescence spectra of a mixture of QD (20 nM) and SOSG (10 μM) solutions under photoactivation (30 s intervals) at 532 nm. D) Fluorescence spectra of SOSG photoactivated in the absence of QD. Inset: kinetic traces (at 545 nm) of $^1O_2$-mediated photouncaging of SOSG: with (red) and without (blue) QDs.

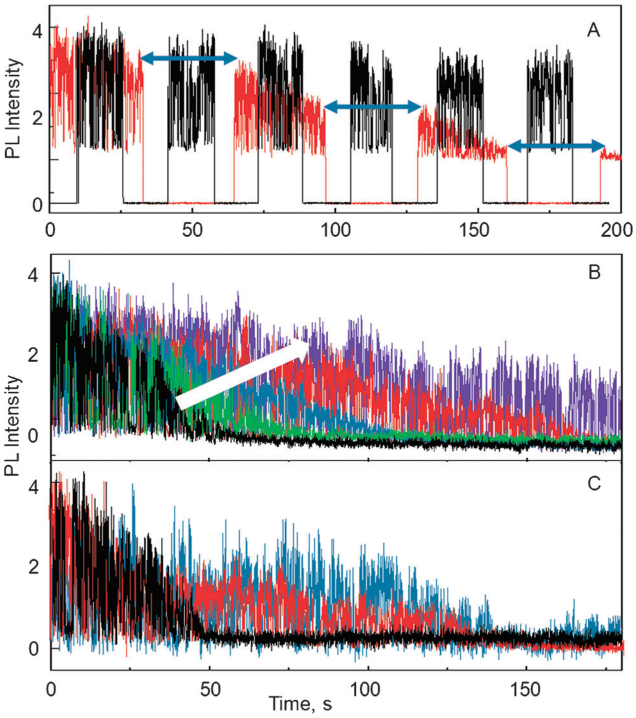

Figure 4. A) PL intensity trajectories of single QDs: A) under laser ON and OFF periods without (red) and with (black) 100 μM DAB. B) Under continuous photoactivation without (black) and with DAB: 0.1 (green), 1 (blue), 10 (red), and 100 μM (purple) DAB; and C) under continuous photoactivation—in air-saturated DMSO (black), with 100 μM DAB added at 25 s (red), and in N_2-saturated DMSO (blue). The excitation light source is a laser operating at 532 nm (with an intensity of 500 W cm^{-2}).

$^1O_2$ and the uncaged fluorescence of SOSG verify not only the production of $^1O_2$ but also the cumulative effect of $^1O_2$ on the oxidation of molecules proximal to QDs. Despite the low (ca. 5 %) quantum efficiency of $^1O_2$ production by QDs,[10b] oxide centers are incessantly speckled on QDs by the cumulative effect of $^1O_2$, which induce the non-digitized PL intensity loss in single QDs.

To derive relations among photoactivation, Auger ionization, and the non-digitized PL intensity loss, we continuously recorded the PL intensity trajectories of single QDs with intermittent laser ON and OFF periods. Interestingly, after each laser OFF period, the PL intensity recovers to the same level as that before the laser was turned OFF (Figure 4 A, red trace), which is independent of the laser ON/OFF durations (see Figure S2). The recovery of PL intensity after each laser OFF period, which is comparable to the recovery of PL intensity after each Auger-ionized period (Figure 2 C), rules out oxidation of QDs in the ground state. In other words, the non-digitized PL intensity loss and oxidation of QDs are excited-state processes. When compared with the ultrafast relaxations in a trion, the excited state of a non-ionized QD is sufficiently long ($\lambda_{av} = 22$ ns) for both sensitizing $^3O_2$ into $^1O_2$ and reacting with $^1O_2$. Thus, among the various ground and excited states of QD or Auger-ionized QD, only the excited state of non-ionized QD is responsible for $^1O_2$ production, oxidation, and the non-digitized PL intensity loss.

Scavengers of $^1O_2$ play a crucial role on the stability of fluorophores and biomolecules in single-molecule experiments. To validate the relation between non-digitized PL intensity loss and oxidation of QDs by $^1O_2$, we examined the effect of $^1O_2$ scavengers such as 1,4-diaminobutane (DAB), triethylamine (TEA), and *N*,*N*-dimethylaniline (DMA) on the PL intensity of single QDs. Interestingly, the durability of single QDs is increased by a factor of 10 with an increase in the concentration of the scavenger up to 100 μM (Figure 4 A,B). Here, $^1O_2$ produced by QDs reacts with the scavenger, which is similar to the reaction between SOSG and $^1O_2$, and thus, retards the oxidation of the QDs. The average durations of photo-oxidation of single QDs as functions of the concentration of DAB and the power of the excitation light are summarized in Figure S3. The role of $^1O_2$ scavengers on the PL intensity of single QDs is further investigated by the addition of DAB (100 μM) to a single QD sample at 25 s after the beginning of photoactivation. As expected, the speed of non-digitized PL intensity loss is retarded immediately after the addition of DAB (Figure 4 C, red trajectory). On the other hand, under similar conditions, the PL intensity of a QD without any $^1O_2$ scavenger hits the background in less than 60 s (Figure 4 B,C; black trajectories). Nonetheless, protic scavengers such as DAB at concentrations (above 100 μM) higher than that required for $^1O_2$ scavenging react with QDs and lower the PL intensity (Figure S4, Supporting Information). However, aprotic scavengers such as DMA and TEA stabilize the PL of QDs irrespective of their concentration. The difference between protic and aprotic scavengers on the stability of the PL of QDs needs further attention.

We further characterize the relations of Auger ionization and $^1O_2$ production with the non-digitized PL intensity loss of QDs by recording and analyzing the PL intensity trajectories

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of single QDs immersed in air- or N$_2$- saturated solvents (black and blue trajectories in Figure 4C). The PL intensity of a QD in air-saturated DMSO hits the background within a short time, which is as low as 20 s (50 s on average) under illumination at 532 nm (500 W cm^{-2}); whereas, the durability of single QDs extends by a factor of five in N$_2$-saturated solvents. These observations confirm the roles of oxygen and $^1O_2$ on the non-digitized PL intensity loss of single QDs.

To summarize, we have demonstrated for the first time that the non-digitized PL intensity loss of single QDs immersed in aerated solvents, which is due to oxidation by self-sensitized $^1O_2$, is absent during the Auger-ionized OFF periods. In other words, irrespective of the Auger-ionized durations, the PL intensity of a QD after each intrinsic OFF period recovers to the same level as that before Auger ionization. This PL recovery upon charge recombination is comparable to that after each laser OFF period during the stimulated laser ON/OFF cycles. We provide information about not only the roles of $^1O_2$ on the gradual oxidation and the non-digitized PL intensity loss of single QDs but also the intrinsic stability of QDs by escape from oxidation into the Auger-ionized (trion) state. Direct observation of the escape of Auger-ionized QDs from photo-oxidation is expected to have an impact on the preparation of durable QDs for applications such single-molecule bioimaging and single-photon devices.

Keywords: Auger ionization · photochemistry · quantum dots · single-molecule studies · singlet oxygen

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