Evidence for the Role of Holes in Blinking: Negative and Oxidized CdSe/CdS Dots

**Wei Qin and Philippe Guyot-Sionnest***

James Franck Institute, 929 E. 57th Street, The University of Chicago, Chicago, Illinois 60637, United States

Upon photoexcitation, colloidal quantum dots exhibit photoluminescence (PL) blinking, impeding applications in single dot imaging[1,2] and quantum information.[3,4] The blinking is typically characterized by a large variation in the time duration of two PL levels (on and off states), which obeys a power-law statistics.[5−7] Some experiments also showed that there are other PL levels in single dots,[8] and several core/shell systems have been reported to suppress blinking,[9−14] but the origin of the power law and the nature of the off-state are still debated.[15−17]

The off state was initially assigned to a charged dot arising from photocharging.[18] However, the PL lifetime of the off-state has been found to be not governed by Auger recombination.[19] Furthermore, the PL of a single negatively charged quantum dot has been directly observed to be larger than that of the off state.[14] The photocharging process can therefore no longer explain the off state. A grey state, brighter than the off state, has also been detected in some types of single CdSe/CdS dots.[20,21] The grey state has also been proposed to be a charged dot, which was considered as a positive charged dot based on the better hole confinement in CdSe/CdS,[20,21] although the sign of the charge (electron or hole) was actually unknown.

In this work, we studied CdSe/CdS nanocrystals with a thin CdS shell (3−5 monolayers), and two different CdSe core diameters: 3 nm (sample I) and 5 nm (sample II). The reduced confinement in the larger cores is known to reduce the Auger rate, allowing for PL detection of the negative trion. We also used ZnO nanocrystals films to allow electron-transfer in order to manipulate the duration time of negatively charged dots. Finally, we studied thick shells/large cores CdSe/CdS (sample III), which are known to exhibit suppressed blinking. Such a system allows multiple electrons charging

ABSTRACT
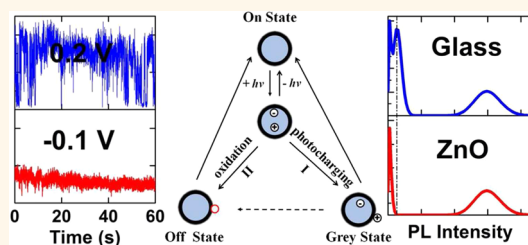
Thin shell CdSe/CdS colloidal quantum dots with a small 3 nm core diameter exhibit typical blinking and a binary PL intensity distribution. Electrochemical charging with one electron suppresses the blinking. With a larger core of 5 nm, the blinking statistics of on and off states is identical to that of a smaller core but the dots also display a grey state with a finite duration time (∼6 ms) on glass. However, the grey state disappears on the electron-accepting ZnO nanocrystals film. In addition, the grey state PL lifetime on glass is similar to the trion lifetime measured from electrochemically charged dots. Therefore, the grey state is assigned to the photocharged negative dots. It is concluded that a grey state is always present as the dots get negatively photocharged even though it might not be observed due to the brightness of the trion and/or the duration time of the negative charge. With thick shell CdSe/CdS dots under electrochemical control, multiple charging, up to four electrons per dot, is observed as sequential changes in the photoluminescence lifetime which can be described by the Nernst equation. The small potential increment confirms the weak electron confinement with the thick CdS shell. Finally, the mechanism of hole-trapping and surface oxidation by the hole is proposed to account for the grey state and off state in the blinking.

by electrochemistry, and the PL lifetime of the different charge states is monitored as a function of the electrochemical potential.

RESULTS AND DISCUSSIONS

Thin Shell CdSe/CdS Quantum Dots. On a glass substrate, all thin shell CdSe/CdS dots blink. However, there are differences based on the core diameters.

The CdSe/CdS dots with a smaller core (sample I) show a PL intensity with the typical bimodal distribution of on and off

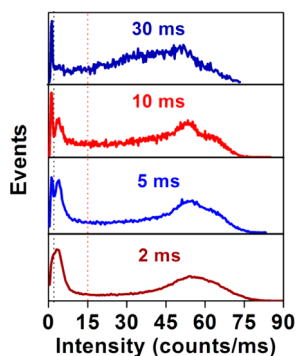* Address correspondence to pgs@uchicago.edu.

Figure 1. Typical PL histograms of a single CdSe/CdS (sample II) dot display the evolution of a grey state with different binning times. The dashed lines are defined as the thresholds at the minimum counts between peaks to separate three different PL intensity levels: on, grey, and off state. Specifically, PL intensity of the off state was the same as the background. The typical PL histograms of a single CdSe/CdS (sample I) are also shown in Supporting Information, Figure S3 with different binning times.
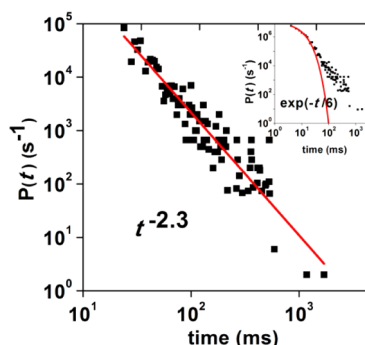

Figure 2. The time distribution statistics for the PL intensity below the red dashed line (Figure 1) with the 2 ms binning time (inset), arising from both the grey and off state. After subtracting an initial exponential component ($\exp(-t/6$ ms), inset) for the grey state, the power-law blinking statistics for off state recovered.

states, where the off state is as dark as the background measured from regions without dots. The time distribution for the off state obeys the power-law statistics with an average exponent of 2.0 ($\pm$0.3), which is consistent for different single dots (Supporting Information, Figure S2). However, similar to previous results,[6] the distribution for the on state shows a cutoff power-law statistics in which both the exponent and cutoff time show a large variation with the choice of the binning time (Supporting Information, Figure S3).

The CdSe/CdS dots with a larger core (sample II) also blink but show a PL intensity histogram that is sensitive to the binning time with a clear trimodal distribution for a 5-10 ms time bin (Figure 1). Therefore, the histogram shows an off state, a grey state and a bright state, respectively, although the grey state is only resolved for a particular choice of binning time. Indeed, the histogram peak for the grey state vanishes when the binning time is increased to 30 ms, leading to the typical bimodal PL intensity distribution. Such a grey state has been previously attributed to the emission from a charged dot.[20,21] This dependence on the binning time indicates that, unlike the off state, the grey state has some defined duration time, shorter than 30 ms. To analyze the time distributions, two thresholds are defined in the histograms to separate the off, grey, and on state (Figure 1). Since there are only two distinct PL peaks with the 2 ms bin time, the duration time below the higher-level threshold arises from both the grey state and off state (Figure 2). The duration time distribution shows an initial single exponential decay with the time constant of 6 ms followed by a power-law statistics with an exponent of 2.3. Performing the same analysis with the 5 ms bin time also leads to an initial exponential decay with a comparable time constant (Supporting Information, Figure S4). However, for long binning time, the exponential decay is not resolved and

only the power-law statistics remains. Therefore, we conclude that the grey state has a duration time of about 6 ms in these CdSe/CdS dots, and this is in line with previous results.[20] By selecting the photons in the intermediate peaks of PL histograms (Supporting Information, Figure S6), the PL lifetime of the grey state is measured to be 0.8 $\pm$ 0.1 ns.

If the duration time of the grey state is shorter than the binning time, the grey state would not be observed as a separate peak in the histogram, such as in sample I (Supporting Information, Figure S3). Furthermore, the blinking statistics of the on state for sample II (Supporting Information, Figure S4) is similar to that of sample I, suggesting that it is independent of the appearance of a grey state. Therefore, we propose that a grey state with a duration time shorter than the minimum binning time might still be present in the blinking of single dots, even though it might not be resolved.

The grey state has been assumed to arise from photocharging of the dots[20] and assumed to be a positive charge.[21] The single dots of CdSe/CdS with a larger core (sample II) were then drop-casted on cross-linked ZnO nanocrystals films on ITO coverslips,[14] the purpose being to facilitate electron transfer from the CdSe/CdS dots. The effect is striking since the dots on ZnO no longer show a grey state, instead displaying the conventional binary PL intensity distribution and statistics for off and on state (Figure 3). The on-time statistics has a typical exponential cutoff at long times which is similar to that of sample I without the appearance of a grey state (Supporting Information, Figure S3).[6,7] The disappearance of the grey state when the sample is in contact with ZnO is explained by its shortened duration time.

Using electrochemistry at a negative potential, it is possible to inject electrons in the dots to directly compare the grey state PL lifetime on glass, and the negative trion lifetime. Using ensemble measurements done on a dilute submonolayer of dots, the PL lifetime
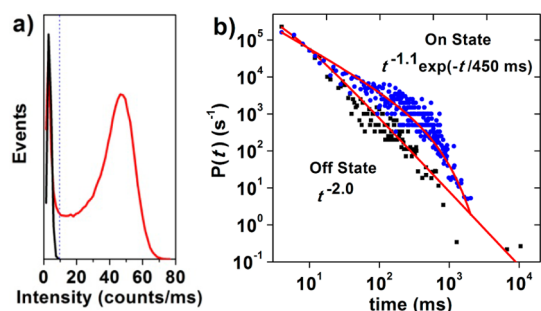
Figure 3. (a) PL histogram for a single CdSe/CdS (sample II) on the ZnO nanocrystals film (red) and the background (black). The dashed line is the threshold to separate the on/off states. (b) Corresponding blinking statistics of off state and on state with the 2 ms binning time.
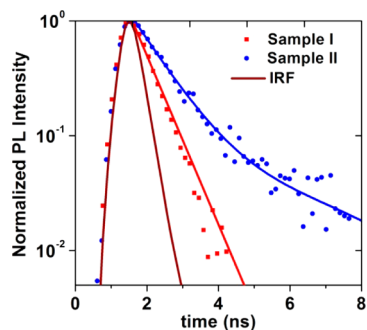

Figure 4. Lifetime traces (data points) for trion decay of both samples from ensemble measurements under electrochemical control with the IRF trace measured from the fast fluorescence decay of 1% picric acid shown on a semilog scale. The corresponding lines of multiexponential fits are also displayed to give the trion lifetime of ∼0.55 ns (sample I) and ∼0.90 ns (sample II).

of the negative trion is ∼0.9 ns for sample II (Figure 4, and Supporting Information, Figure S7).[14] This is in good agreement with the grey state PL lifetime on glass (Supporting Information, Figure S6) and it supports the assignment of the grey state to the negatively photocharged dot. With the smaller cores (sample I), the negative trion PL lifetime is ∼0.5 ns suggesting that it is half as bright. Such a decrease in brightness of the negative charged dot/grey state is consistent with the nonappearance of the grey state. With pump−probe ensemble measurements, we confirmed that the biexciton lifetime is also twice shorter than for sample II, being 100 and 200 ps, respectively (Supporting Information, Figure S8).[22] The significantly faster biexciton lifetime compared to the negative trion was also reported previously,[13,23,24] suggesting that the Auger recombination of negative trion is less efficient than that of positive trion.[23,24] Finally, using electrochemistry at a positive potential, no change was observed in the blinking behavior on the single CdSe/CdS dot on the ZnO/ITO substrates (Supporting Information, Figure S9), in contrast to one other report.[13]

The assignment of the grey state for thin shell CdSe/CdS dots to negative photocharged dots differs from earlier work[20,21] but is consistent with the recent
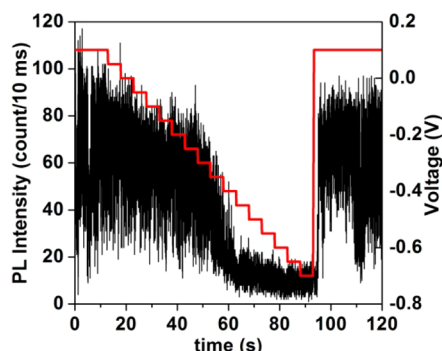

Figure 5. PL trajectory of a single thick shell CdSe/CdS dot, varying applied voltage as shown from 0.10 to −0.70 V in 50 mV steps and back to 0.10 V. Each voltage lasts 5 s.

proposal for thick shell CdSe/CdS.[13] The observation of the grey state in the CdSe systems is then limited by two factors: the generation and stability of the negatively charged dot, determined by the light intensity and the local environment,[23] as shown here by ZnO or the redox potential, and its brightness which is determined by the negative trion lifetime. Negatively photocharged dots may be always present, even though they may be too short-lived or dim to be observed. In general, the electrochemical potential of negative and positive dots should determine their relative stability and, in the case of CdSe, the assignment of the grey state to the negative trion is consistent with the known stability of negatively charged CdSe while positively charged CdSe has not yet been observed.[25]

Thick Shell CdSe/CdS Quantum Dots under Electrochemical Control. Thick shell CdSe/CdS quantum dots (>9 monolayers, sample III) have a largely suppressed Auger recombination rate.[26] This should allow the measurement of PL decay lifetimes of different charged states and help understand the charging process of single dots. With the same instrumental setup as before,[14] the PL of electrochemically charged single CdSe/CdS quantum dots is therefore investigated.

From the PL trace, the PL of the neutral thick shell CdSe/CdS is well above the background and consistent with suppressed blinking.[11,12] Similar to previous results,[14] the PL is quenched and recovers reversibly by adjusting the external voltage (Figure 5). The maximum PL signal begins to diminish as the voltage is below −0.30 V, which suggests that electron injection is initiated at this bias.

The corresponding PL lifetime traces change continuously as the external voltage decreases in 50 mV steps (Figure 6 and Supporting Information, Figure S10). The appearance of a faster decay component in the lifetime traces at low voltage is attributed to the PL from the charged dot.[14] The decay traces at each voltage are fitted with multiexponentials to extract the lifetime constants for the different charged states of the dot. For the voltages above −0.30 V, the lifetime traces can be globally fit by a biexponential decay with
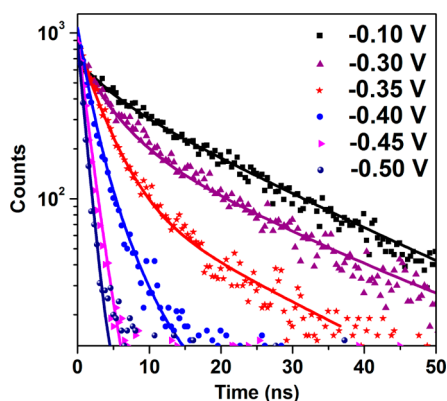
Figure 6. Lifetime decays of a single thick shell CdSe/CdS dot displayed by the data points at different voltages on a semilogarithm scale. The multiexponential fits are presented by the corresponding solid lines. The same data is plotted on a linear scale in Supporting Information, Figure S11 to make the changes of maximum photon counts in the lifetime traces more evident.

Figure 7. (a) Component fraction of the different charged states for the same single dot *versus* applied voltage: QD (20 ns), QD$^-$ (4.2 ns), QD^{2-} (2.8 ns), QD^{3-} (1.4 ns), QD^{4-} (0.7 ns). (b) Population of charged states of single thick shell CdSe/CdS dot *versus* voltage, as described by the Nernst equation.

the lifetimes of 20 and 4.2 ns. This is attributed to the negative photocharging of the dot[23] so that it is, for times shorter than the binning time, either neutral or in the -1 charged state. The grey state is not observed, not because the trion PL lifetime is short, but because of a presumably faster electron transfer rate to the substrate than the bin time. As the voltage decreases from -0.30 V, an additional lifetime is added for the PL decay due to the emergence of the -2 charged state. Finally, a set of lifetime constants are extracted to be: $\tau_0 = 20$ ns, $\tau_1 = 4.2$ ns, $\tau_2 = 2.8$ ns, $\tau_3 = 1.4$ ns, $\tau_4 = 0.7$ ns.[27] Here, we attribute the constants to the PL lifetimes of neutral, -1, -2, -3, and -4 charge states. Compared to the typical lifetime of a neutral dot on glass,[11,12] the shorter lifetime of the neutral dot is due to the energy transfer between single dots and ITO substrate,[14] and it is close to the value reported by Galland *et al.*[13]

In our experiment, charged states differing by one charge cannot be separated completely because the thermal energy is not small enough compared to the charging energy. As a result, it is difficult to measure the PL intensity for each charged state at room temperature. However, we can estimate the relationship with the lifetime. Considering that the excitation energy (405 nm laser) is much larger than the band-edge absorption energy of sample III, the absorption cross section for different charged states of a given dot should be identical. Therefore, the PL intensities of the charged states are proportional to their quantum efficiency given by $k_r\tau$, where k_r is the radiative rate and τ is the lifetime. The radiative rate is that of the single $1S_{3/2}$ hole recombining with a 1S electron. Assuming that Coulomb effects do not reorganize the energy levels or change the wavefunctions, the radiative rate, k_r, is then constant for all charged states. In this case, the PL intensity of different charged states is proportional to their lifetime. As for the
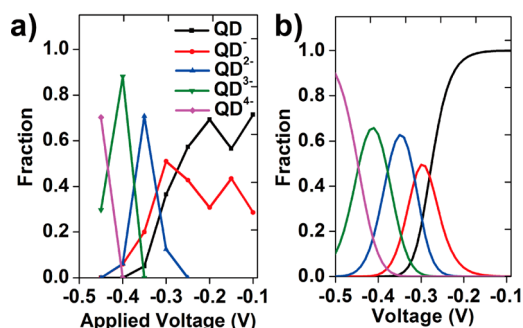
radiative rate ratio of singly charged state to neutral state, it has been previously measured to be about 2.2 ± 0.4,[24] which is consistent with the changes in the degeneracy between bright and dark states for the single exciton. Therefore, the PL intensity ratio of QD, QD$^-$, QD^{2-}, QD^{3-}, and QD^{4-} can be estimated as 1:0.46:0.31:0.15:0.08. The experimental decay curves are now compared to the simulated decay curves at different voltages using the assumption of a constant k_r for the charged states (Supporting Information, Figure S10). The agreement is rather good, including the overall amplitude and the enhanced signal at early time.

The relative fractions of different charged states, calculated from the relative lifetime coefficients (Supporting Information, Table S1, Figure S11),[28] are plotted as a function of voltage (Figure 7a). At equilibrium, the ratios of separate charged states for the same species are given by the Nernst equation,[24,28] and determined by their energy differences. Fitting the lifetime data to the Nernst equation gives 35 and 63 meV for the additional injection energy of the second and third electron, respectively (Figure 7b). The small charging energy, 35 meV, for the thick shell CdSe/CdS dots is actually expected for such large objects.[24] Furthermore, the injection energy of the third electron differs from the charging energy by an additional 28 meV which is the confinement energy between $1S_e$ and $1P_e$. The weak confinement is partially confirmed by intraband spectroscopy on these same samples which shows no absorption peaks above the 0.12 eV (Supporting Information, Figure S12). Therefore, as expected from the small conduction band offset between CdSe and CdS, the electron is very weakly confined in these thick shell CdSe/CdS nanocrystals. Thus, it is worth noting that although blinking is suppressed in large core–shells, it comes at the cost of losing quantum confinement for the electrons. Comparing further Figure 7 panels a and b, the proportion of neutral and singly charged dot deviates evidently from the equilibrium when the voltage is
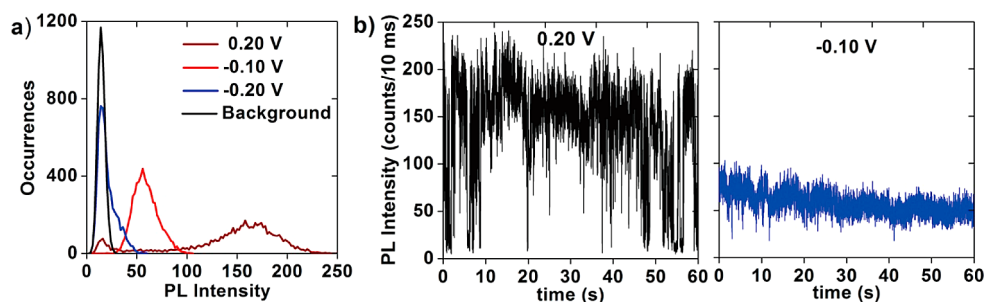
Figure 8. (a) PL histogram of single CdSe/CdS (<6 monolayers) dot at different voltages. (b) Corresponding emission traces at 0.20 V and −0.10 V with 10 ms binning time.

above −0.30 V, and this is assigned to photocharging (Supporting Information, Figure S13).[23]

Similar experiments were performed on the thin shell CdSe/CdS dots (sample I) (Supporting Information, Figure S14). However, due to the faster PL decay of multicharged states, their lifetime constants could not be extracted beyond the singly charged state. The fast lifetimes are consistent with the smaller core and the greater confinement. This sample has indeed an intraband transition of ~0.2 eV. PL histograms at different voltages showed that the "off" state signal was at the background level (Figure 8a). However, the PL intensity distribution at −0.10 V, at which voltage single electron injection occurs, displays a single intermediate peak between the PL of off state and on state, attributed to much faster flickering between singly charged and neutral dot than the binning time. The PL trace also shows no occurrences of the "off" state at −0.10 V (Figure 8b). Therefore, we conclude that the off state is suppressed by injection of one electron into single colloidal quantum dot with external applied voltage, which is consistent with previous results.[13,14]

Photoluminescence Spectrum of Single CdSe/CdS Dots under Electrochemical Control. The PL spectra of charged dots are presumably indicative of the interaction between the extra electrons and excitons. Photoluminescence spectra of single CdSe/CdS dots are therefore monitored at different potentials. The PL spectrum for the single thin or thick shell CdSe/CdS dots typically exhibits a large full-width of about 50 meV at the half-maximum, due to the coupling with acoustic phonons.[29] For the thin shell CdSe/CdS dots (sample I), there is typically a small red shift of ~10 meV as the voltage decreases (Supporting Information, Figure S15).[30] However, some of the dots show instead an initial blue shift, followed by the red shift of the PL peak when more electrons are injected (Figure 9). For thick shell CdSe/CdS, almost all dots exhibit a small blue shift after charging. These facts suggest that the interactions between the spectator electrons and the generated exciton shift from attractive to repulsive with increased thickness of CdS shell. This trend from red shift to blue shift with electron injection may be due to the increased spatial separation between the electron and hole with increased shell thickness.
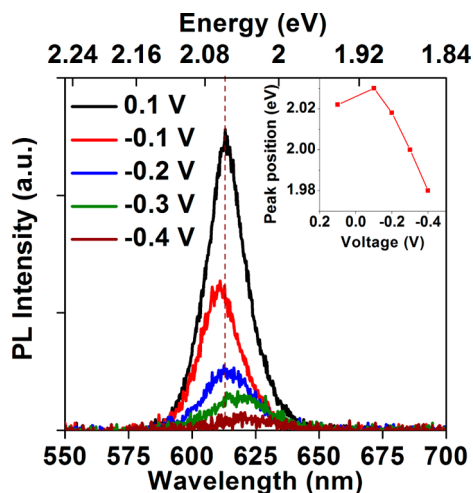

Figure 9. PL spectra of single thin shell CdSe/CdS dot (sample I) with the shift of corresponding peak position (inset) at different voltages.

Such effect is expected with small or negative band offset for the CdSe and CdS conduction band.[31]

Recently, Galland et al. studied single CdSe/CdS quantum dots with thick shells (7−9 monolayers) under electrochemical control.[13] Therefore, it is necessary to clarify the differences between our results and theirs. In agreement with Galland et al., the grey state originates from the negative trion in single thick shell CdSe/CdS dots, and the "off" state in single thin shell CdSe/CdS dots can be suppressed by one electron injection. In this work, however, we demonstrated that the discrete charging process of single dot under electrochemical control could be described by the Nernst equation. In addition, we confirmed that the electron is weakly confined in CdSe/CdS dots. The corresponding voltage separation for the creation of singly charged state and doubly charged state in single dots is about 35 mV in agreement with typical charging energy for these systems.[23] Galland et al. reported instead about ~0.4 V between the two charged states. Such a value, an order of magnitude too large for the charging energy, remains to be explained and it is suspected to arise from a poor connection between the dots they studied and the electrode. Galland et al. also reported that a positive potential would enhance

blinking while a negative potential, still much below electron injection in the nanocrystals, could suppress the blinking, but we did not observe this effect. Prior experiments also did not show a noticeable effect of the potential on blinking until close to the electron injection.[14,32] This leads us to a different interpretation of the off state discussed below.

Phenomenological Model for Blinking. In blinking, the off state has been recently associated to the surface traps which are considered as nonradiative recombination centers, rather than to a charged dot.[19,33] The non-radiative recombination center can be created either by reduction of cations or oxidation of anions among the surface atoms. Electrochemistry has shown that the CdSe dots are stable under reducing but not oxidizing conditions therefore favoring oxidation as the likely origin of the off state.[25,34]

Galland *et al.* proposed a hot-electron trapping mechanism, followed by the nonradiative exciton annihilation at the surface traps, in a process called B-type blinking.[13] This is a surface reduction process. Assigning the blinking to a hot electron trapping/reduction raises several issues. Galland *et al.* considered that electrons in the $1P_e$ state were hot. Yet, we have shown that the $1P_e$ to $1S_e$ separation is small in the thick CdSe/CdS systems due to the vanishing confinement, of the order of the thermal energy. The $1P_e$ electron cannot be considered hot and one should consider higher energy electrons which may be accessible with high-energy photoexcitation or multiexciton recombination.[35] However, the blinking statistics for the off state has been shown to be a universal power-law distribution under different wavelengths and excitation intensities.[35] Furthermore, it was pointed out earlier that the Auger recombination of positive trion might be faster than that of negative trion,[23] and therefore a multiexciton recombination is more likely to excite the hole than the electron. Therefore, the hot-electron mechanism seems to not be directly related to the blinking. In addition, to account for the power-law statistics, there should be many electron trap states randomly distributed in energy. Occupying these surface traps under electrochemical control would require a noticeable current flow and would make it more difficult to inject electrons in the dots. However, cyclic voltametry of thin shell CdSe/CdS ensemble films shows facile electron injection in the quantum states and no large currents associated with surface states.[30,34] Finally, as discussed earlier, we could not modify the blinking statistics of the off state with positive potential. While differences may arise from the dot preparation or the electrochemical setup, the hot-electron trapping model seems inadequate for CdSe, at least until the large density of electron traps is confirmed.

In contrast to electron traps, hole traps are widely expected. Indeed, *ab initio* calculations[36] and positron annihilation spectroscopy[37] on CdSe colloidal nanocrystals
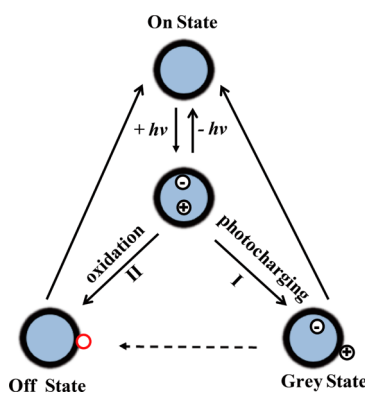

Figure 10. Schematic model for the physical process of the blinking behavior in single colloidal quantum dots. The dashed lines represent the existence of possible transition from the grey state to the off state.

both indicated that hole traps composed the majority of surface traps. This is consistent with the formation of negatively charged dots during photocharging. In addition, the holes in CdSe are very oxidizing, and stable electrochemical hole injection has not yet been observed.[25] Finally, it has been suggested earlier that the Auger process would preferentially generate hot holes rather than hot electrons. Considering these facts, we propose instead that the blinking is related to oxidation by the hole (Figure 10). Upon excitation, the hole may get trapped in a shallow surface state which readily exists in CdSe colloidal quantum dots.[36−38] This leaves a delocalized electron within the core, which is the grey state (Process I). On the other hand, the holes may also oxidize the surface after photoexcitation. Such deep hole traps may be associated with chemical modifications of the surface, such as $S^{2-} + 2 h^+ \rightarrow S$, the formation of disulfide bonds, or higher oxidation states of sulfur.[39] This can produce a quenching center which is not governed by Auger recombination (Process II).[19] Owing to the local inhomogeneous surface, it may be possible to create quenching centers with different energy levels and recovery rates, which would be responsible for the power-law statistics for off-state time distribution. This energy of the oxidation state may drift as the electrostatic environment changes and the state can ultimately be reduced by the environment or by electrons in the dot. Raising the Fermi level to maintain one single electron into the conduction band prevents such oxidation, and suppresses the off state. This cathodic protection mechanism of the surface is also consistent with the observations that adding thiol moiety ligands[40,41] or growing a thick CdS shell for CdSe nanocrystals can help suppress blinking.[11,12]

CONCLUSIONS

The blinking behavior of two samples of CdSe/CdS dots with different core sizes but the same shell thickness was investigated. On bare glass, a grey state is observed only for the CdSe/CdS with the larger core.

The grey state has a finite lifetime instead of a power law as observed by a change in the binning time. This indicates that the appearance of the grey state in histograms is determined by its brightness and duration time. The grey state is "eliminated" by positioning the same CdSe/CdS sample on cross-linked ZnO nanocrystal films to which electrons can transfer. Furthermore, the PL lifetime of the grey state and the negative charged dots are similar. This indicates that the grey state arises from the negatively charged dot.

The stability of the negative charged dots allowed observation of the discrete and multiple charging of single thick shell CdSe/CdS dots by electrochemical control. The lifetime of the different charged states was measured, and a Nernst equation was used to extract the charging energy for each electron injection. The voltage separation for each electron injection was very small, confirming the largely reduced electron

confinement in thick shell CdSe/CdS dots. At potentials where the dot should be neutral, both neutral and photocharged dots are observed from the lifetime measurements. For single thin shell CdSe/CdS dots (sample I) placed on ITO/ZnO to reduce nonradiative energy transfer and under electrochemical control, the off state is suppressed in the negatively charged state, albeit with a reduced emission intensity due to the short-lived trion.

Considering the strongly oxidizing potential of holes in CdSe/CdS, and the fact that cathodic potentials eliminate the off state, hole-trapping and surface oxidation by the hole are proposed to account for the grey state and off state, respectively. Charging studies on single dots supply useful information to unveil the puzzle of blinking behavior, which will be beneficial to the development of nonblinking colloidal quantum dots in the future.

METHODS

All chemical reagents were purchased from Sigma-Aldrich without further purification. The CdSe cores with different sizes were synthesized according to literature methods.[42] In the synthesis of thin CdS shells for sample I and II, CdSe nanocrystals (~0.1 mmol) were precipitated once by adding ethanol to the raw solution and dissolved in 3 mL of ODE with 1.5 g of octadecylamine. Under vacuum, the solution was degassed under 100 °C for 20 min. Refilled with argon, the sample was sustained at 220 °C under which sulfur (0.1 M) and cadmium 2,2-dimethylbutyrate (0.1 M) in ODE were added alternatively into the reaction solution within 1 h. After the reaction, the solution was cooled to room temperature. This method typically grew about a 3–5 monolayers of CdS shells on the CdSe cores. As for the growth of thick CdS shells, the SILAR technique was used as reported previously.[11]

In the single dot measurements, the setup for confocal microscope and the methods to prepare ZnO nanocrystals films were the same as before.[14] For the electrochemical measurements, the single thin shell CdSe/CdS dots were drop-cast on the ZnO/ITO substrates to alleviate the energy transfer between single dots and ITO. However, the thick shell CdSe/CdS dots were directly deposited on the ITO surface without a ZnO spacer, in order to observe the grey state and decrease the background PL from ZnO nanocrystals. In this case, the thick CdS shell alone can help prevent the PL quenching of the single dots from energy transfer, due to the nature of near-field effect.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Absorption and PL spectra for three types of CdSe/CdS samples, blinking traces and statistics, lifetime traces for ensembles under electrochemistry, decay curves for biexciton recombination, intraband absorption spectrum, PL spectra for single dots under electrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. 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.
2. Dahan, M.; Levi, S.; Luccardini, C.; Rostaing, P.; Riveau, B.; Triller, A. Diffusion Dynamics of Glycine Receptors Revealed by Single-Quantum Dot Tracking. *Science* **2003**, *302*, 442–445.
3. Lodahl, P.; van Driel, A. F.; Nikolaev, I. S.; Irman, A.; Overgaag, K.; Vanmaekelbergh, D.; Vos, W. L. Controlling the Dynamics of Spontaneous Emission from Quantum Dots by Photonic Crystals. *Nature* **2004**, *430*, 654–657.
4. Hennessy, K.; Badolato, A.; Winger, M.; Gerace, D.; Atature, M.; Gulde, S.; Falt, S.; Hu, E. L.; Imamoglu, A. Quantum Nature of a Strongly Coupled Single Quantum Dot–cavity System. *Nature* **2007**, *445*, 896–899.
5. Margolin, G.; Protasenko, V.; Kuno, M.; Barkai, E. *Power-Law Blinking Quantum Dots: Stochastic and Physical Models*; John Wiley & Sons, Inc: New York, 2005; pp 327–356.
6. Crouch, C. H.; Sauter, O.; Wu, X.; Purcell, R.; Querner, C.; Drndic, M.; Pelton, M. Facts and Artifacts in the Blinking Statistics of Semiconductor Nanocrystals. *Nano Lett.* **2010**, *10*, 1692–1698.
7. 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.
8. Zhang, K.; Chang, H.; Fu, A.; Alivisatos, A. P.; Yang, H. Continuous Distribution of Emission States from Single CdSe/ZnS Quantum Dots. *Nano Lett.* **2006**, *6*, 843–847.
9. Hohng, S.; Ha, T. Near-Complete Suppression of Quantum Dot Blinking in Ambient Conditions. *J. Am. Chem. Soc.* **2004**, *126*, 1324–1325.
10. 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.
11. 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*, 5026–5027.
12. 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.
13. Galland, C.; Ghosh, Y.; Steinbruck, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I; Htoon, H. Two Types of Luminescence Blinking Revealed by Spectroelectrochemistry of Single Quantum Dots. *Nature* **2011**, *479*, 203–207.
14. Qin, W.; Shah, R. A.; Guyot-Sionnest, P. CdSeS/ZnS Alloyed Nanocrystal Lifetime and Blinking Studies under Electrochemical Control. *ACS Nano* **2012**, *6*, 912–918.

15. Verberk, R.; Van Oijen, A. M.; Orrit, M. Simple Model for the Power-Law Blinking of Single Semiconductor Nanocrystals. *Phys. Rev. B* **2002**, *66*, 2332021–2332024.

16. Tang, J.; Marcus, R. A. Diffusion-controlled Electron Transfer Processes and Power-Law Statistics of Fluorescence Intermittency of Nanoparticles. *Phys. Rev. Lett.* **2005**, *95*, 1–4.

17. Frantsuzov, P. A.; Volkan-Kacso, S.; Janko, B. Model of Fluorescence Intermittency of Single Colllodial Semiconductor Quantum Dots Using Multiple Recombination Centers. *Phys. Rev. Lett.* **2009**, *103*, 207402.

18. Efros, A. L.; Rosen, M. Random Telegraph Signal in the Photoluminescence Intensity of a Single Quantum Dot. *Phys. Rev. Lett.* **1997**, *78*, 1110–1113.

19. Rosen, S.; Schwartz, O.; Oron, D. Transient Fluorescence of the Off State in Blinking CdSe/CdS/ZnS Semiconductor Nanocrystals Is Not Governed by Auger Recombination. *Phys. Rev. Lett.* **2010**, *104*, 157404.

20. Gomez, D. E.; van Embden, J.; Mulvaney, P.; Fernee, M. J.; Rubinsztein-Dunlop, H. Exciton-Trion Transitions in Single CdSe-CdS Core-Shell Nanocrystals. *ACS Nano* **2009**, *3*, 2281–2287.

21. 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.

22. Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots. *Science* **2000**, *287*, 1011–1013.

23. Galland, C.; Ghosh, Y.; Steinbruck, A.; Hollingsworth, J. A.; Htoon, H.; Klimov, V. I. Lifetime Blinking in Nonblinking Nanocrystal Quantum Dots. *Nat. Commun* **2012**, *3*, 908.

24. Jha, P. P.; Guyot-Sionnest, P. Trion Decay in Colloidal Quantum Dots. *ACS Nano* **2009**, *3*, 1011–1015.

25. Wang, C.; Shim, M.; Guyot-Sionnest, P. Electrochromic Nanocrystal Quantum Dots. *Science* **2001**, *291*, 2390–2392.

26. Garcia-Santamaria, F.; Chen, Y.; Vela, J.; Schaller, R. D.; Hollingsworth, J. A.; Klimov, V. I. Suppressed Auger Recombination in "Giant" Nanocrystals Boosts Optical Gain Performance. *Nano Lett.* **2009**, *9*, 3482–3488.

27. Assuming classical n_e electrons and n_h holes in the single dot, the number of distinct (e, e, h) sets is $n_h n_e (n_e - 1)$, therefore the Auger rate for $n_e e^- + 1 h^+ \rightarrow (n_e - 1)e^-$ scales as $n_e(n_e - 1)$. The PL lifetime of the different charged states follows approximately this superlinear trend with n_e.

28. The calculation of component fraction of different charged states and use of the Nernst equation are described in the Supporting Information.

29. Mittleman, M. D.; Schoenlein, R. W.; Shiang, J. J.; Colvin, V. L.; Alivisatos, A. P.; Shank, C. V. Quantum Size Dependence of Femtosecond Electronic Dephasing and Vibrational Dynamics in CdSe Nanocrystals. *Phys. Rev. B* **1994**, *49*, 14435–14447.

30. Jha, P. P.; Guyot-Sionnest, P. Photoluminescence Switching of Charged Quantum Dot Films. *J. Phys. Chem. C* **2007**, *111*, 15440–15445.

31. Piryatinski, A.; Ivanov, S. A.; Tretiak, S.; Klimov, V. I. Effect of Quantum and Dielectric Confinement on the Exciton-Exciton Interaction Energy in Type II Core/Shell Semiconductor Nanocrystals. *Nano Lett.* **2006**, *7*, 108–115.

32. Jha, P. P.; Guyot-Sionnest, P. Electrochemical Switching of the Photoluminescence of Single Quantum Dots. *J. Phys. Chem. C* **2010**, *114*, 21138–21141.

33. Zhao, J.; Nair, G.; Fisher, B. R.; Bawendi, M. G. Challenge to the Charging Model of Semiconductor–Nanocrystal Fluorescence Intermittency from Off-State Quantum Yields and Multiexciton Blinking. *Phys. Rev. Lett.* **2010**, *104*, 157403.

34. Yu, D.; Wang, C.; Guyot-Sionnest, P. *n*-Type Conducting CdSe Nanocrystal Solids. *Science* **2003**, *300*, 1277–1280.

35. 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.

36. Puzder, A.; Williamson, A. J.; Gygi, F.; Galli, G. Self-healing of CdSe Nanocrystals: First-Pprinciples Calculations. *Phys. Rev. Lett.* **2004**, *92*, 217401.

37. Eijt, S. W. H.; van Veen, A.; Schut, H.; Mijnarends, P. E.; Denison, A. B.; Barbiellini, B.; Bansil, A. Study of Colloidal Quantum-Dot Surfaces Using an Innovative Thin-film Positron 2D-ACAR Method. *Nat. Mater.* **2006**, *5*, 23–26.

38. Jones, M.; Lo, S. S.; Scholes, G. D. Quantitative Modeling of the Role of Surface Traps in CdSe/CdS/ZnS Nanocrystal Photoluminescence Decay Dynamics. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 3011–3016.

39. Considering the potential to inject one electron into the conduction band and the band gap, the estimated potential of the hole in CdSe core is above $+1.5$ V (*versus* Ag). The redox potentials of sulfur are $E_0(S|S^-)) = -0.48$ V, $E_0(S|S_2^{2-})) = -0.43$ V, respectively, both of which are much lower than the potential of the hole.

40. 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.

41. Hohng, S.; Ha, T. Near-Complete Suppression of Quantum Dot Blinking in Ambient Conditions. *J. Am. Chem. Soc.* **2004**, *126*, 1324–1325.

42. Liu, H.; Pourret, A.; Guyot-Sionnest, P. Mott and Efros–Shklovskii Variable Range Hopping in CdSe Quantum Dots Films. *ACS Nano* **2010**, *4*, 5211–5216.