Probing the structural dependency of photoinduced properties of colloidal quantum dots using metal-oxide photo-active substrates

Kira Patty,¹ Seyed M. Sadeghi,^{1,2,a)} Quinn Campbell,¹ Nathan Hamilton,¹ Robert G. West,¹ and Chuanbin Mao³

¹*Department of Physics, University of Alabama in Huntsville, Huntsville, Alabama 35899, USA*

²*Nano and Micro Device Center, University of Alabama in Huntsville, Huntsville, Alabama 35899, USA*

³*Department of Chemistry and Biochemistry, Stephenson Life Sciences Research Center, University of Oklahoma, Norman, Oklahoma 73019, USA*

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We used photoactive substrates consisting of about 1 nm coating of a metal oxide on glass substrates to investigate the impact of the structures of colloidal quantum dots on their photophysical and photochemical properties. We showed during irradiation these substrates can interact uniquely with such quantum dots, inducing distinct forms of photo-induced processes when they have different cores, shells, or ligands. In particular, our results showed that for certain types of core-shell quantum dot structures an ultrathin layer of a metal oxide can reduce suppression of quantum efficiency of the quantum dots happening when they undergo extensive photo-oxidation. This suggests the possibility of shrinking the sizes of quantum dots without significant enhancement of their non-radiative decay rates. We show that such quantum dots are not influenced significantly by Coulomb blockade or photoionization, while those without a shell can undergo a large amount of photo-induced fluorescence enhancement via such blockade when they are in touch with the metal oxide. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4894445>]

I. INTRODUCTION

Semiconductor colloidal quantum dots (QDs) have a wide appeal for various applications including solar cells, light sources, and optical sensors for biological, chemical, and imaging applications.^{1–5} This appeal is largely due to their high quantum yield and the ability to engineer their electronic and optical properties during synthesis. In addition to the benefits of customization, such colloidal QDs are known to be highly photo-active. In particular, they exhibit an increase in their fluorescence intensity, known as photo-induced fluorescence enhancement (PFE), over a period of continuous irradiation. The primary mechanisms for PFE are passivation of surface defects via adsorption of environmental molecules (e.g., water) and the formation of an electrostatic barrier via electron ejection from a photo-ionized QD, which suppresses the photo-ionization of neighboring QDs (i.e., Coulomb blockade).^{6–10} The type of substrate has been shown to have a significant impact on the QDs.¹¹ The selection of ligand can also have a significant impact on the QDs' photoluminescence. For example, it is known that the use of amine ligands generally results in a significant increase in the QD's quantum yield versus the unligated form; however, amines are known to dissociate more readily than other ligand materials such as trioctylphosphine oxide (TOPO).^{12,13}

Recently, we have shown that nano-scale-thin layers of metal oxides can have significant impact on the photo-induced properties of colloidal QDs.^{14,15} Our results demonstrated that, depending on the types of these oxides and the base-substrates on which they were deposited, such oxides could promote unique sets of photo-induced processes in such QDs.

For example, when about 1 nm of Al oxide is deposited on a Si substrate, it can significantly enhance passivation of the QDs, thereby enhancing the QDs' quantum efficiencies as they are being irradiated.¹⁴ On the other hand, when 1 nm of Cr oxide is deposited on a borosilicate glass base-substrate, it can profoundly accelerate the rate of photo-oxidation of the QDs.¹⁵ We have also shown that when metallic nanoparticles are coated with an ultrathin layer of Cr oxide, the plasmonic enhancement of the energy transfer between CdSe/ZnS QDs can be suppressed with irradiation.¹⁶

These prior results suggest that when a substrate is coated with an ultrathin layer of a specific metal oxide, it can be used as a photo-active substrate to study some of the characteristic features of QDs using the unique photocatalytic effects of the oxide. Utilizing such photo-active substrates (PASs), our objective in this paper is to investigate the impact of the structures of colloidal QDs, including their cores, shells, and ligands, on their photophysical and photochemical properties and the way such QDs interact with the environment (including the PASs) and light. For this, we consider two types of PASs, one consisting of about 1 nm of Al oxide (Al-PAS) and the other 1 nm of Cr oxide (Cr-PAS), both on borosilicate glass base-substrates. In this study, we explore the impact of irradiation on four colloidal QDs with different structures deposited on these substrates and find out how such substrates can be used to study their structural-dependent photo-ionization relaxation, photo-induced passivation and oxidation, and the way Coulomb blockade (photo-ionization) depends on excitation intensity.

Our results showed that at low excitation intensity QDs without shells show distinct sensitivities to Cr and Al oxides while being significantly influenced by a Coulomb blockade. This leads to a very large PFE for Al-PAS of approximately

^{a)}Electronic address: seyed.sadeghi@uah.edu

25 times the initial emission intensity. Under these same conditions but on the Cr-PAS, the PFE of such QDs was observed to be only 6 times the initial emission intensity. We also showed that for certain core-shell QDs with ternary cores and ZnS shells, a Coulomb blockade plays a much less significant role. In the high irradiation intensity regime, however, the situation changes drastically. In such a regime, it is well known that strong photo-oxidation reduces the effective core size of QDs, leading to a blue shift in the emission spectra. This process happens with significant reduction of the quantum efficiency of such QDs, as new defects are formed.^{17,18} We showed in this paper that the presence of metal oxides can change this process dramatically. In particular, in QDs without shells such metal oxides can have very subversive effects, leading to a dramatic reduction of the amount of PFE. On the other hand, in the ternary core shell QDs studied in this paper, our results showed photo-oxidation can lead to a strong reduction of the QDs' core sizes without significant enhancement of their non-radiative decay rates. This suggests that, when combined with the structural properties of the QDs, the impact of metal oxides can open a unique opportunity to use photo-oxidation to control the sizes of QDs without significant enhancement of their non-radiative decay.

II. MATERIALS AND METHODS

We acquired four types of CdSe based colloidal QDs. The first type of QD (labeled QD1) is a core only CdSe with an octadecyl amine ligand in toluene from NN Labs, LLC. The second type of QD (QD2) is a core/shell CdSe/ZnS with an octadecyl amine ligand in powder form from Ocean NanoTech, LLC., mixed with toluene for preparation of spin solutions. The third type of QD (QD3) is a core/shell CdS_xSe_{1-x}/ZnS with an oleic acid ligand in toluene obtained from CytoDiagnostics, Inc. The fourth type of QD (QD4) is a core/shell CdSeS/ZnS, COOH functionalized, in toluene obtained from Sigma Aldrich. The emission peaks of QD1, QD2, QD3, and QD4 were measured on borosilicate glass substrates to be about 625, 628, 630, and 666 nm, respectively, for an excitation of 7.3 W/cm² at 488 nm.

Samples were prepared by sputtering of about 1 nm of Al or Cr onto a masked glass substrate. Schott D263M borosilicate glass was selected as the control base-substrate for this study as does not possess optical, physical, or chemical properties that could impact the QD emission.^{19–21} The thickness of these layers was calculated from the calibrated deposition rates of the sputter machine for each metal. The substrates were exposed to air to permit oxidation of the metals. Broadband absorption measurements for the Al-oxide on glass (Al-PAS) and Cr-oxide on glass (Cr-PAS) revealed no significant heat effects or absorption. QDs were applied via spin coating. Stock solutions were diluted with PMMA and toluene to form spin solutions. The concentration of the QD solutions used for spin coating was 12.6×10^{17} QDs/cm³. The spin coating conditions were a 15 s spread at 200 rpm followed by 60 s spinning at 2000 rpm. At this concentration and spin conditions, the QDs are sufficiently dense on the sample as to permit the formation of a Coulomb blockade. The

masked side of the substrate (no metal oxide) acted as the reference. The samples were illuminated with an Ar ion laser (488 nm) perpendicular to their planes soon after the QD spin coating. A microscope objective was used to excite the samples and collect of emission of the QD thin films. A thermoelectrically cooled spectrometer recorded the spectra of the QD fluorescence for analysis. All tests were performed in air.

III. RESULTS

To investigate how Al-PAS and Cr-PAS impact the PFE of these QDs, samples were irradiated at 7.3 W/cm² (low) and 100 W/cm² (high) for an initial period of 25 minutes (min) followed by a 5 min period of no irradiation and a final 5 min irradiation period. Fig. 1 shows how the QDs' peak emission evolves over time for low and high intensity excitation. To facilitate analysis, the emission intensities of each QD type are normalized to the initial intensity, I_0 , of the respective reference measurement on glass (no metal oxide).

FIG. 1. PFE (I/I_0) for the four types of QDs on Al-PAS (blue line 2), Cr-PAS (red line 3) and glass (black line 1) over time. The test specification was an initial 25 min of irradiation followed by 5 min without irradiation and concluded by an additional 5 min of irradiation at either low (7.3 W/cm²) or high (100 W/cm²) intensity. Results for irradiation at 7.3 W/cm² are given for QD1, QD2, QD3, and QD4 in subplots a, b, c, and d, respectively. Results for irradiation at 100 W/cm² are given for QD1, QD2, QD3, and QD4 in subplots e, f, g, and h, respectively.

We start with the low intensity case. As shown in Fig. 1(a), QD1 (no shell) undergoes a significant amount of PFE on Al-PAS (line 2). In contrast, PFE on Cr-PAS only reaches about 6. Additionally, for such QDs, we can see a clear relaxation of the PFE after the 5 min rest period. The magnitude of this relaxation is largest on Al-PAS (line 2). For QDs with ZnS shells (QD2, QD3, and QD4), we see that PFE on both PASs are suppressed compare to that on the glass reference (line 1). Additionally the overall amount of PFE in such samples is significantly smaller than that of QD1. The results shown in Fig. 1 clearly indicate the profound and distinct impact of PASs on the PFE of the different QDs, highlighting the influence of their structures. The behavior of the QDs on such substrates can be further understood by considering the emission enhancement factor, E_{enh} , defined as the ratio of emission intensity of the QDs on PAS to that on glass. As can be seen in Figs. 2(a)–2(d), all QDs except QD1 show suppression of PFE ($E_{enh} < 1$) for excitation at low laser intensity.

FIG. 2. E_{enh} for the four types of QDs on Al-PAS (solid line) and Cr-PAS (dashed line) substrates. All test specifications are the same as in Fig. 1. Results for irradiation at 7.3 W/cm² are given for QD1, QD2, QD3, and QD4 in subplots a, b, c, and d, respectively. Results for irradiation at 100 W/cm² are given for QD1, QD2, QD3, and QD4 in subplots e, f, g, and h, respectively.

At high laser intensity, QD1 and QD2 show characteristic features, including a sharp rise followed by reduction of their emission intensity as irradiation continues (Figs. 1(e) and 1(f)). When metal oxides are present, however, the QDs' emission is suppressed more significantly. In fact while Al oxide leads to maximum enhancement of PFE at low intensity (Fig. 1(a), line 2), it now leads to the largest amount of emission suppression (Fig. 1(e), line 2). In the following section, we demonstrate that one of the reasons behind the sharp rise is the impact of the laser intensity on the Coulomb blockade caused by darkened QDs. Note that for QD1 (CdSe QDs) E_{enh} is essentially flat after the initial decline (Fig. 2(e)). This indicates a similar rate of photo-induced processes in such QDs on glass and on the oxides. For the case of QD2 (CdSe/ZnS QDs), however, the situation is quite different, as E_{enh} continues to decline for QDs on the oxide. The rate of this process is greater for the QDs on Al-PAC (Fig. 2(f), solid line) than those on Cr-PAS (Fig. 2(f), dashed line). This suggests that the metal oxides present different rates of photochemical and photophysical events in QDs with shells, compared to these QDs on the glass substrate.

The cases of QD3 and QD4 (CdSeS cores) are rather unique, as they exhibit strikingly different characteristic PFE and E_{enh} features than those seen in the cases of QD1 and QD2. To see this effect more clearly, Fig. 3 depicts the ratio of PFE at the high field intensity to that of the low field intensity for each type of QD. These results show a general trend in which the PFE ratio attains its maximum value at early times then decreases. Other than this trend, each of the different QDs shows differences in behavior. Of particular interest is the timing at which the PFE ratio falls below 1 as this indicates significant enhancement of non-radiative decay for the case of the high field intensity at these times. The uniqueness of the results for QD3 and QD4 (Figs. 3(c) and 3(d)) is that when they are on glass this ratio becomes less than one at the early time of irradiation. When they are on

FIG. 3. Ratio of PFE at high (100 W/cm²) intensity to PFE at low (7.3 W/cm²) intensity for the four types of QDs on Al-PAS (blue line 2), Cr-PAS (red line 3) and glass (black line 1) over time.

the oxide, however, they stay consistently above one. Such a process does not happen for QD1 and QD2 (Figs. 3(a) and 3(b)).

As is discussed further in the following section, the importance of such processes is that they happen as the emission peak is blue shifted, indicating shrinkage of the sizes of the QDs, which is a signature of photo-oxidation. Considering that photo-oxidation is known to happen with increase of defect sites and reduction of quantum efficiencies, as seen in the case of QD1 and QD2 (Figs. 1(e) and 1(f)), these results are of considerable interest. These results underline the profound applications of metal oxides to reveal unique structurally dependent photochemical and photophysical properties of QDs.

IV. DISCUSSION

To interpret the results shown in Sec. III, we consider the processes of surface passivation, Coulomb blockade, and photo-oxidation that can occur in our tests in relation to the structural (core/shell arrangement and ligands) differences between the four types of QDs. When such physical processes induce a significant change in the surface characteristics or effective core size of the emissive QDs, the spectral properties over the irradiation period can differ noticeably from the initial properties without these effects.^{22,23}

Multiple pathways have been identified for the passivation of the QDs' surface defects, which are, for some cases, reversible. Surface passivation via the light mediated adsorption of water molecules onto the QD surface is characterized by a spectral blue shift without broadening of the FWHM.^{10,18,24,25} The adsorbed water acts to passivate surface traps on QDs, leading to an increase in the QDs' quantum efficiency.²⁴

Photo-oxidation is an irreversible process which has been shown to provide a short term enhancement of the emission efficiency of densely packed CdSe QDs accompanied by a blue shift in the spectrum; however, photo-oxidation induces new surface defects (i.e., photo-corrosion) that reduce the QDs' emissions over time.^{24,25} Such a blue shift has been attributed to an effective reduction of the core size during oxidation.^{5,22} Photo-oxidation has also been shown to be influenced by the excitation intensity, which impacts when during irradiation the effects of photo-corrosion begin to dominate.¹⁸ On the other hand, much research has been done investigating how the substrate and trapping of photo-ejected electrons influence the formation of the Coulomb blockade and the associated increase in PFE.^{26–30} As a result of photoionization, the QDs are no longer emissive (darkened QDs) and can exert an electrostatic potential on neighboring QDs, suppressing their fast and slow photo-ionization rates.^{31–33}

A. Structural-dependent passivation and photo-oxidation

The results presented in Figs. 1 and 2 showed how the emission peaks of the QDs were influenced by irradiation when they were deposited on Al-PAS and Cr-PAS. The normalized spectra for each type of QD are shown in Fig. 4 for

the case of irradiation at high field intensity, which shows blue shift of the emission peaks. At the low field intensity (not shown), we do not observe any significant spectral changes in the emission of the QDs over the irradiation time. To show the details of such changes, in Fig. 5, we show how the peak wavelength (λ) and FWHM of the QD emission were changed with time. For QD1, the difference between FWHM on the different substrates is noticeably smaller at initial times than at final times (Fig. 5(a)). Note that QD1 represents an extreme case due to its lack of a protective shell. During the first 5 min, the results suggest a reduction of the FWHM. As shown in Fig. 5(e), these processes happen while the emission peaks of the QDs undergo a significant blue shift for which their magnitudes are nearly independent of the type of the substrate. Considering the roll off of emission seen in Fig. 1(e), these events can be associated with the strong photo-oxidation of the QDs.

For the case of the other QDs, which are protected by a ZnS shell, we mostly see characteristic features of photo-oxidation, i.e., increase of FWHM and blue shift. These processes occur from the start, although to different degrees.

FIG. 4. Normalized spectra for the four types of QDs at $t=0$ (blue line) and $t=25$ min irradiation (green line) at high intensity (100 W/cm^2). All test specifications are the same as in Fig. 1. Results for QD1, QD2, QD3, and QD4 on Al-PAS are shown in subplots (a)–(d), respectively. Results for the QDs on Cr-PAS are in subplots (e)–(h), respectively.

FIG. 5. FWHM (a)–(d) and peak wavelength (e)–(h) for irradiation at 100 W/cm^2 , for QD1 and QD2 on Al-PAS (blue line 2), Cr-PAS (red line 3), and glass substrate (black line 1). All specifications are the same as Fig. 1.

In the case of QD2, however, the amount of broadening of the FWHM is highest for QDs on Al-PAS (Fig. 5(b), line 2). From the results shown in Fig. 5(b), the magnitude of the wavelength shift of such QDs also happens to be highest. This suggests that when such QDs are on Al-PAS, they exhibit the highest relative rate of oxidation. When these QDs are deposited on Cr-PAS, however, they undergo the least amount of photo-oxidation (Figs. 4(f) and 5(b) line 3). Similar results are seen for the FWHM of QD4 (Fig. 5(d)). Additionally, in QD3 and QD4 (Figs. 5(g) and 5(h)), we observed a large amount of blue shift of about 10 and 6 nm, respectively. Comparing these results with those in Figs. 1(c) and 1(d) under low field intensity (also seen in and Figs. 3(c) and 3(d)), which points to the lack of a strong reduction in the quantum efficiency of such QDs despite strong photo-oxidation. For QD3 on Al-PAS, in particular, the PFE of about 0.5 after 25 min of irradiation at 7.3 W/cm^2 was replaced by 1.2 when the laser intensity becomes 100 W/cm^2 . Such results emphasize the differences in the influence of the Al and Cr PASs. Both materials are widely used in a variety of chemical reactions with and without light-

mediation; however, their respective photo-chemical actions and oxidative strengths differ.^{34–39}

To explore the role of photo-oxidation further, we consider it influences the effective size and non-radiative decay rates of the QDs. The initial QD radii, a_{QD}^0 , were calculated from the measured emission peaks for irradiation at 7.3 W/cm^2 at 488 nm on bare glass substrate using the effective mass approximation reported by Franceschetti for the transition energy, $E_g(\text{eV})$, of a CdSe QD⁴⁰

$$E_g(\text{eV}) = 1.74 + \frac{0.43}{(a_{QD}^0)^2} + \frac{0.44}{a_{QD}^0}. \quad (1)$$

The following equation reported by Chen may then be used to determine the change in CdSe QDs' radii due to photo-oxidation^{16,41}

$$a_{QD} = \frac{(M - m)a_{QD}^0 + m\left(a_{QD}^0 - \frac{\sqrt{6}}{3}d\right)}{M}, \quad (2)$$

$$= a_{QD}^0 - \frac{\text{sqrt}6}{3}d. \quad (3)$$

Here, a_{QD} is the effective QD radius, M is the number of surface atoms, m is the number of oxidized surface atoms, and d is the average diameter of atoms (CdSe) in the QD.

Various studies of the opto-electronic properties of ternary or $\text{CdS}_x\text{Se}_{1-x}$ QDs have shown that the observed emission peak approaches that of CdSe as the amount of S doping decreases (as x decreases).^{42–44} Further, QD4 is identified by the manufacturer as having been annealed. A reported impact of annealing of CdSSe QDs is the reduction of the bandgap energy (emission peak red shift).^{45,46} As the specific synthesis conditions and ratio of S to Se for the commercial QDs used in this research is not known to us, calculations are performed with the above equations (for CdSe) and are approximations.

Figs. 6(a)–6(d) show the change in the effective radius of the QDs for the case of high field intensity calculated from the photoluminescence data. As shown in Fig. 5(a), in the case of QD1, the reduction in effective size is the same on all substrates as can be anticipated from the blue shift seen in Fig. 5(e). For the other QDs, the results show that the type of substrate impacts the reduction in effective size differently. This is most dramatically seen in the case of QD2 where a_{QD} is initially somewhat larger on Al-PAS but quickly shrinks below the values seen for Cr-PAS and glass. Using the measured photoluminescence data underlying Fig. 1, the non-radiative decay rate due to oxidation, $\gamma_{nr}^{ox}(t)$, may be calculated. To do this, we use a simple rate equation for the QDs exciton dynamics as follows:

$$\frac{dn_{ext}(t)}{dt} = k_{exc} - (\gamma_r + \gamma_{nr} + \gamma_{nr}^{ox}(t))n_{exc}. \quad (4)$$

Here, $n_{ext}(t)$ is the exciton population, k_{exc} is the rate of exciton formation, γ_r is the radiative decay rate, and γ_{nr} is the non-radiative decay rate for physical processes other than photo-oxidation. γ_r is taken to be 0.05 ns^{-1} and γ_{nr} taken as 0.1 ns^{-1} , as typically reported by others.^{26,47,48} The results of

FIG. 6. Polynomial fit for the calculated effective radius (a)–(d) and non-radiative decay due to photo-oxidation (e)–(h) for the four types of QDs for the initial 25 min of irradiation at high field intensity (100 W/cm²) on glass (line 1), Al-PAS (line 2), and Cr-PAS (line 3).

this calculation are shown in Figs. 6(e)–6(h). The initial decrease in $\gamma_{\text{nr}}^{\text{ox}}$ is associated with the initial period in which the PFE is seen to increase (Fig. 1). As with the effective core size calculation, the most dramatic difference between substrates in $\gamma_{\text{nr}}^{\text{ox}}$ is seen for QD2. For QD1 there is no significant difference in $\gamma_{\text{nr}}^{\text{ox}}$ on the three substrates; however, like QD2, the oxidation rate on each substrate shows a steady increase after onset. In the cases of QD3 and QD4, the behavior is markedly different. The relative values for $\gamma_{\text{nr}}^{\text{ox}}$ for these ternary QDs are of similar magnitude on the different substrates but the oxidation rates for each substrate are seen to change over the irradiation period; reflected in how lines 1 (glass), 2 (Al-PAS), and 3 (Cr-PAS) cross.

B. Coulomb blockade relaxation

Returning to Fig. 1(a), the relaxation seen for QD1 after the 5 min period without irradiation suggests the possibility that some of the ionized QDs may have been neutralized during this short time; reducing the effects of the Coulomb blockade. As seen in Figs. 1(b)–1(d), such a process was not seen for the other types of QDs, suggesting they are less influenced by this process, leading to a smaller amount of PFE. To investigate this issue further, we studied the emission of QD1 and QD2 on Al-PAS, Cr-PAS, and glass substrates when they underwent 30 min of initial irradiation followed by 2 h without irradiation and an additional 15 min

of irradiation. We consider the intensity of the laser is 7.3 W/cm² to avoid photo-oxidation effects.

As can be seen in Fig. 7(a), the emission of QD1 exhibited a significant amount of relaxation after the 2-hour blocking of irradiation. For the glass substrate (line 1), Al-PAS (line 2), and Cr-PAS (line 3), respectively, this amounts to approximately 49%, 43%, and 46% of the emission of the QDs at the end of the initial 30 min irradiation period. These reductions indicate reversibility as the result of neutralization of the trap sites. In the case of QD2 (Fig. 7(b)), a decrease of approximately 15% was seen on glass (line 1) and about 42% on both Al-PAS and Cr-PAS (lines 2 and 3).

These results refer to different degrees of surface passivation via absorption of environmental molecules (e.g., water) and Coulomb blockade effects. The initial 30 min of irradiation of QD1 on Al-PAS resulted in a PFE of about 17 while on glass the PFE was ~ 7 . This suggests that despite the fact they have similar relaxation, Al oxide provides a higher degree of enhancement via surface passivation.¹⁴ Additionally, the PFE is seen to flatten on glass and Cr-PAS starting at approximately 20 min of irradiation. On Al-PAS, however, it instead continues to increase rapidly with time during the first 30 min of irradiation. This suggests that the efficiency of PFE on glass and Cr-PAS reaches its upper limit (saturation) well before that on Al-PAS. In contrast, the results in Fig. 7(b) for QD2, which has a ZnS shell, show a smaller relaxation on glass (line 1) than on Al-PAS (line 2) and Cr-PAS (line 3). This may suggest that, for such QDs, the time required for neutralization of defect sites on glass is longer than those on the photo-active substrates, leading to a more persistent Coulomb blockade.

Note that the results for QD2 in Fig. 7(b) seem quite compatible with those presented in Fig. 1(b). For the case of QD1, however, we observe some discrepancies between the

FIG. 7. PFE (I/I_0) for QD1 and QD2 on Al-PAS (blue line 2), Cr-PAS (red line 3) and glass (black line 1) substrates over time with a long relaxation period. The test specification was an initial 30 min of irradiation followed by 2 h without irradiation and concluded by an additional 15 min at low (7.3 W/cm²) intensity.

results presented in Fig. 7(a) and Fig. 1(a), although their trends are consistent. We associate these with the fact that in the case of QD2 the ZnS shells protect the CdSe cores and, therefore, they are less influenced by the environment, e.g., relative humidity of the air. For the case of QD1, however, the lack of a shell makes the QDs more sensitive to the environment.

C. Impact of laser intensity and photo-oxidation on Coulomb blockade

The results shown in Fig. 1 indicate that when the laser intensity is increased, the rate of PFE becomes higher for the first couples of minutes of irradiation. This phenomenon can be partially explained considering the impact of the laser intensity on the Coulomb blockade. To see this, note that a QD is influenced by slow (Γ_{si}) and fast (Γ_{fi}) photoionization rates. While the later can lead to its rapid blinking, the former causes its persistent darkening. Following Ref. 7, we consider a blocking factor, α_I , to represent the number of QDs whose ionization is suppressed by the darkening of the ionized QD.^{6,7} We consider α_I depends on the irradiation intensity (I). When such intensity is low, α_I is considered equal to 5.⁶ As I increases, however, one expects that this number decreases. Under these conditions, the fast photo-ionization rates in such QDs become⁶

$$\Gamma_{fi}(I) = \Gamma_{fi}^0(1 - \alpha_I \Phi_d(I)), \quad (5)$$

and the slow rate

$$\Gamma_{si}(I) = \Gamma_{si}^0(1 - \alpha_I \Phi_d(I)). \quad (6)$$

In these equations, Γ_{fi}^0 and Γ_{si}^0 are the initial values of the fast and slow ionization rates before the Coulomb blockade happens (t_0). $\Phi_d(I)$ is the fraction of the excited electrons in a QD that are in the deep trap state with a long neutralization time. Following a rate equation argument for the darkened QD we have^{6,7}

$$\frac{d\Phi_d(I)}{dt} = \frac{\delta_I(1 - \alpha_I \Phi_d)}{1 + \beta_I + \eta_I(1 - \alpha_I \Phi_d)}. \quad (7)$$

Here,

$$\beta_I = \frac{(\gamma_r + \gamma_n(t))}{k_{exc}(I)} \quad (8)$$

and $\eta_I = \Gamma_{fi}^0/k_{exc}(I)$, and $\delta_I = \Gamma_{si}^0/k_{exc}(I)$, wherein $k_{exc}(I) = \sigma_{abs}I/(\hbar\omega)$ is the excitation rate, and γ_r, γ_n are the radiative and non-radiative decay rates of the QDs, respectively.

Using these equations, we can find out how PFE depends on the laser intensity (I). For this, note that, according to the results shown in Fig. 1, PFE is the ratio of emission of QDs at any given time ($P(t)$) to that at the initial time of irradiation ($P(t_0)$)

$$\Theta_I(t) = \frac{P(t)}{P(t_0)} = \frac{1 - \Phi_d(I)}{1 - \zeta_I \Phi_d(I)}. \quad (9)$$

Here, $\zeta = \alpha_I \eta_I(1 + \beta_I + \eta_I)$.

FIG. 8. Impact of the laser intensity on PFE. The solid line presents PFE when $I = 0.05 \text{ W/cm}^2$ and $\alpha_I = 5$, dotted line when $I = 1 \text{ W/cm}^2$ and $\alpha_I = 5$, and the dashed line the case when $I = 1 \text{ W/cm}^2$ and $\alpha_I = 3$.

To carry out our simulation, we consider the radiative (γ_r) and non-radiative (γ_{nr}) decay rates of the QDs are, respectively, 0.05 and 0.1 ns^{-1} . Additionally, it is assumed $\Gamma_{fi}^0 = 0.2 \text{ ns}^{-1}$ and $\Gamma_{si}^0 = 2 \times 10^{-6} k_{exc} \text{ ns}^{-1}$.⁴⁹ α_I , on the other hand, is considered a variable parameter. The results presented in Fig. 8 show that when the applied laser field is weak (0.05 W/cm^2) and, therefore, $\alpha_I = 5$ PFE happens gradually (solid line). This process happens faster (dotted and dashed lines) as the intensity of the laser increases by 20 times. These results do not show the roll-off seen in Fig. 1, since we have not included γ_{nr}^{ox} . Once this rate is included, with time the total non-radiative decay of the QDs increases, reducing β_I and QD emission.

Note that these simulation results show how, in general terms, the excitation intensity influences formation of the Coulomb blockade. The role played by α_I in this process can be seen in Eqs. (5)–(7). If $\alpha_I = 0$ (no Coulomb blocking), the slow and fast ionization rates of the QDs have their highest values (Γ_{si}^0 and Γ_{fi}^0). When α_I becomes non-zero, these rates reduce, making the QDs brighter. For low field intensities, Maenosono, *et al.*^{6,7} showed that $\alpha_I = 5$. However, since the number of the QDs excited by the laser increases as the laser intensity increases, the darkened QDs may not be far from each other. Therefore, the number of the QDs with suppressed photo-ionization in the vicinity of a darkened QD can reduce, requiring α_I becomes less than 5. To distinguish the two major impacts of intense field intensities, in Fig. 8 we consider $\alpha_I = 5$, which is unrealistic for 100 W/cm^2 , to show how higher field intensities increase the rate of PFE. We also chose $\alpha_I = 3$ to demonstrate how reduction of α_I reduces the overall efficiency of PFE. These considerations are applicable to each type of QDs wherein Coulomb blockade plays a role in its PFE. However, the results in Figs. 1 and 2 suggest these considerations apply more vividly to the case of QD1.

V. CONCLUSION

In conclusion, we investigated how the structure-dependent features of four different types of colloidal QDs

can influence their photophysical and photochemical properties using photoactive substrates consisting of ~ 1 nm of Al oxide or Cr oxide. We demonstrated that the COOH functionalized core/shell QDs were largely insensitive to enhancement processes (Coulomb blockade and surface passivation) while the amine ligated CdSe and CdSe/ZnS QDs were greatly influenced by these processes. Results for the high field intensity case were indicative of photo-oxidation and also revealed distinct spectral characteristics based on the type of QD and photoactive substrate. Collectively, our results show the ability of photoactive substrates to interact uniquely with the QDs reveals their photophysical and photochemical properties.

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