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X-ray radiation hardness and influence on blinking in Si and CdSe quantum dots

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We study the effect of X-ray irradiation on the photoluminescence (PL) efficiency and intermittency (blinking) of single Si/SiO_2 and CdSe/CdZnS quantum dots (QDs). Our results show that the PL efficiency of Si nanocrystals is not significantly altered up to a cumulative fluence of 10^{20} photons/m^2 (corresponding to ~300 kGy of absorbed dose in SiO_2), while CdSe particles become completely dark already after a 17 times lower fluence. In both types of QDs, the statistical nature of blinking ON- and OFF-times remains unaltered: mono-exponential for Si and power-law for CdSe QDs. However, the evolution of the blinking parameters with absorbed dose depends on the choice of material. On average, both ON- and OFF-time constants do not vary in Si nanocrystals, highlighting their radiation hardness. Instead, the ON-time exponent increases while the OFF-time exponent decreases with the increasing dose for CdSe dots, confirming their efficiency quenching. Ensemble measurements did not show PL spectral changes neither indicated removal of surface ligands in irradiated CdSe dots. Thus, ionization-generated non-radiative centers in the core-shell system modify blinking of CdSe dots and eventually rapidly quench their emission, in contrast to robust Si/SiO_2 nanocrystals. Our study is important for the future use of luminescent QDs in harsh environments, such as space, and the engineering of their blinking properties via ionizing radiation. *Published by AIP Publishing.* https://doi.org/10.1063/1.5053885

Semiconductor nanocrystals (NCs) or quantum dots (QDs) represent a disruptive technology for use in displays,[1] solar concentrators,[2,3] as luminescent bio-labels[4,5] and single-photon sources.[6] This class of nanomaterials can now be fabricated with high throughput techniques based on physical and chemical methods,[7–9] featuring high quantum yields (QY)[10–12] and narrow photoluminescence (PL) linewidths.[13–15] Along with their application on Earth, the benefits of QD-based technologies could potentially be exploited in the space environment as, e.g., in compact spectrometers.[16] However, the presence of ionizing radiation in space, e.g., galactic cosmic radiation, and in other harsh environments can decrease the performance of electronic devices.[17,18] Among the different types of radiation, X-rays emitted from the solar corona[19] can also ionize the exposed material in space and affect the behavior of related instruments.[18,20,21] Hence, it is important to study and understand the effect of X-ray exposure on the optical and electrical performance of semiconductor QDs.

In addition to applied aspects, the ionizing radiation can be used as a tool to improve the fundamental understanding of QD photo-physics derived from single-dot characterization methods. In the last few decades, single-dot studies on NCs have revealed interesting phenomena impossible to observe with ensemble studies, such as narrow homogeneous linewidths,[13–15] spectral diffusion,[22] and PL intermittency under continuous-wave excitation (blinking).[23,24] The universal phenomenon of blinking, characterizing virtually all known types of fluorophores (molecules, proteins, nanowires, etc.),[25] is generally understood as the effect of the NC core charging because of carrier trapping at the interface or in the shell. Consequently, non-radiative Auger recombination controls charge carrier dynamics until charge neutralization, switching back to the ON-state.[24] The modification of charge traps can result in measurable changes in QD PL, helping to elucidate relevant QD charge dynamics. Blinking lowers the efficiency of optoelectronic devices, therefore representing an unwanted process. However, the use of QDs as fluorescent labels could exploit blinking as an additional tuning parameter in the case of multiplex labeling.[26] Eventually, a possibility could be to engineer the blinking frequency of QDs by intentionally introducing additional trap states, for example, by X-ray irradiation.

There are only a few reports available in the literature on the effects of ionizing radiation on QDs. Ensemble absorption studies of $CdSe_{1-x}Te_x$ and $CdS_{1-x}Se_x$ QDs have revealed a blue-shift and the bleaching of confinement-related features after 40 keV X-ray exposure.[27,28] Several weeks/months of post-irradiation storage were required to fully recover the QDs. The irradiation effect was explained by the ionization of the QDs and their subsequent charge-transfer with the host matrix.[27,28] For CdSe-QDs embedded in a dielectric matrix, no PL quenching was observed up to a dose of 3.2 kGy[29] in correlation with the effect of X-rays and electron irradiation on absorption.[28,30] Higher doses were tested on CdTe/CdS-QDs embedded in porous Si, which showed a decrease in the PL intensity starting at ~5 kGy with complete quenching at ~160 kGy (SiO_2).[31] The X-ray

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or e-beam irradiation can also cross-link the ligands on the surface of QDs, resulting in a more rigid shell afterwards.[32,33] However, it is important to note that none of the reported works probes the single-dot properties of NCs following X-ray irradiation nor it compares the performance of completely different material systems under identical irradiation conditions.

Recently, we reported the effect of X-ray exposure on the PL of single Si/SiO_2-QDs and we demonstrated that lifetime, emission energy, and linewidth were surprisingly unaffected up to the high dose of ~65 kGy (SiO_2).[34] Although the preliminary study showed dot-to-dot variations of the blinking ON- and OFF-time constants as a function of X-ray dose, it was limited in terms of the number of samples/dots probed, blinking statistics, and maximum absorbed dose. In this letter, we analyze under identical conditions the irradiation effect for two types of core/shell QDs: CdSe/CdZnS and Si/SiO_2. The former is a model system for semiconductor quantum dots, whose refined wet chemistry synthesis allows us to obtain QY > 80% (reflecting material quality) and narrow emission linewidths.[11,12] The latter represents nanostructures of silicon, the most ubiquitous material in electronics. The fabrication of Si/SiO_2-QDs is still not much refined, with QY~20%–30% and broad linewidths.[35,36] Additionally, a key difference in single-dot blinking between these two material systems is that ON- and OFF-time statistical distributions follow mono-exponential statistics for Si and power-law for CdSe-QDs.[37] Here, we confirm the X-ray radiation hardness of Si-QDs at least up to ~300 kGy of cumulative absorbed dose (limited only by the experiment duration), while CdSe-QDs appear to completely quench already after ~18 kGy (SiO_2). (Note, we refer here to SiO_2 to have comparable X-ray fluence. Indeed, both samples were irradiated side-by-side.) The type of blinking distribution of ON- and OFF-times is unaffected by the irradiation. However, the dependence of the blinking parameters on the absorbed dose is specific to the material: for Si-NCs, both ON- and OFF-time constants do not vary; for CdSe-NCs, the ON-time power law exponent increases, while the OFF-time exponent decreases with the increasing dose, indicating an increase in OFF-time durations with irradiation. Finally, we propose that ionization-induced non-radiative centers in the core-shell system can explain the blinking modification and quenching of CdSe-QDs. By probing the effect of X-ray irradiation at the single-dot level, our work provides insights into the radiation hardness of quantum dots and the possibility of their blinking-engineering.

A detailed experimental description can be found in the supplementary material. Briefly, two samples were tested against X-rays. In the first one, CdSe/CdZnS-QDs (referred to as CdSe-QDs) were chemically synthesized following well-established protocols.[7,9] From TEM analysis (Fig. S1), the core diameter is ~6.2 nm and the shell thickness is ~0.7 nm (i.e., >1 monolayer) on average, though several QDs feature thicker shells (>2 monolayers). The addition of the CdZnS shell increases the QY from 6.6% (core-only) to 35.2% (core-shell) and redshifts the first exciton peak (Fig. S2), in accordance with the previous literature.[38] After synthesis, the particles were dispersed in toluene and spin-coated on a clean Si wafer to obtain an average density of less than one dot per μm^2 to facilitate access by a far-field single-dot technique. Samples with a higher concentration (films) of CdSe-QDs were prepared for ensemble PL spectral and FTIR measurements. In order to verify the stability of the material over time, a control CdSe-QD sample was identically prepared. It was not irradiated and stored in air at room temperature as the irradiated sample. In the second sample, Si/SiO_2-QDs (referred to as Si-QDs) were formed from a low-doped Si wafer by electron-beam lithography, reactive ion etching, and self-limiting oxidation.[39,40] Their QY is ~30% from a previous study,[36] hence similar to the CdSe-QDs used here. The crystallinity and size of both Si[40] and CdSe (Fig. S1) QDs were checked by TEM. A micro-photoluminescence (μPL) setup with an inverted microscope and a cooled electron-multiplying CCD (EMCCD) camera allowed us to perform single-dot measurements. The camera was attached to the exit port of the microscope during intensity/blinking acquisitions or placed after a spectrometer for spectral acquisitions. The samples were excited by a 405-nm diode laser at an excitation power density of ~5–10 W/cm^2. To study blinking, PL image sequences of 10 000 and 20 000 frames were acquired with frame-times of 0.5 and 0.1 s, respectively, for Si and CdSe-QDs (read-out time < 20%). The ON-/OFF-time blinking statistics of single QDs were extracted using custom plugins in ImageJ and MATLAB. To irradiate the samples, we used a tungsten-target X-ray source operating at (130 kV, 300 μA) in the continuous mode. The X-ray emission spectrum of the source has a peak at ~8 keV and a tail up to 130 keV, according to the manufacturer's specifications. The calculated absorbed dose rate was 1.64 Gy/s (SiO_2) for samples placed ~5 cm from the source. By assuming 10 keV photons, the X-ray fluence rate was estimated to be 6.3×10^{14} photons m^{-2} s^{-1}. Blinking traces were acquired for both samples before irradiation and after each irradiation step, while the control CdSe sample was probed after the corresponding irradiated sample using the same measurement conditions.

Figure 1 shows the integrated PL from the same area, where individual Si and CdSe-QDs can be discerned, acquired after different X-ray cumulative absorbed doses.

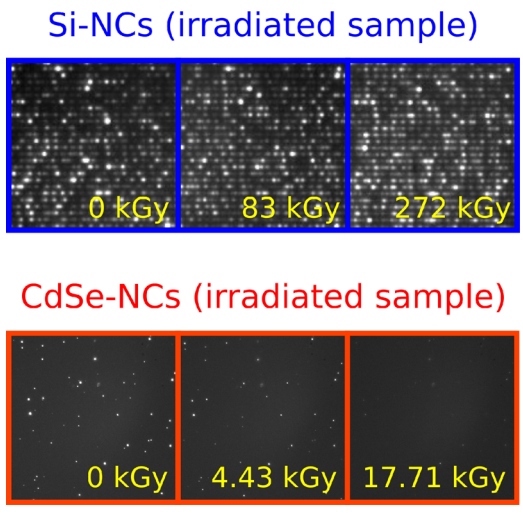

FIG. 1. Integrated PL images showing individual (top) Si and (bottom) CdSe-NCs after different cumulative absorbed doses (yellow text). The doses refer to SiO_2. The widths of the images are 40 μm and 150 μm, respectively, for (top) Si and (bottom) CdSe. The integration time was 5000 s (cumulative) for Si and 10 s for CdSe-QDs.

The images in the upper part of Fig. 1 show that the PL of Si-QDs is intense even at ~270 kGy, thus confirming and extending our previous study, which was limited to 65 kGy.[34] However, if we focus our attention on single luminescent Si-QDs, we can visually notice that different dots vary in luminescence intensity as a result of irradiation. Consequently, the X-ray irradiation is clearly influencing their photophysical properties. On the other hand, the images at the bottom of Fig. 1 demonstrate that the PL of CdSe-QDs is almost completely quenched already after ~18 kGy (SiO_2). Although previous works on matrix-embedded CdSe-NCs showed that these are resistant up to 3.2 kGy,[29] experiments using higher doses have not been reported for these QDs yet. Consequently, the absorption of X-rays in this material system generates additional non-radiative channels in the QDs, and the resulting effect on luminescence increases with the absorbed dose. Additionally, given that the QDs studied in this work are core-shell CdSe/CdZnS in air, i.e., not embedded in a dielectric matrix, the irradiation effect is related only to the QD cores and shells.

For a quantitative analysis, the number of bright dots and their average PL integrated intensity are plotted in Fig. 2 against the cumulative absorbed dose and X-ray fluence. In the case of Si, there is no substantial variation in the number of bright particles and the efficiency quenching is only ~25% at 272 kGy. Indeed, a control sample is not required for this material system. Hence, this is a direct observation

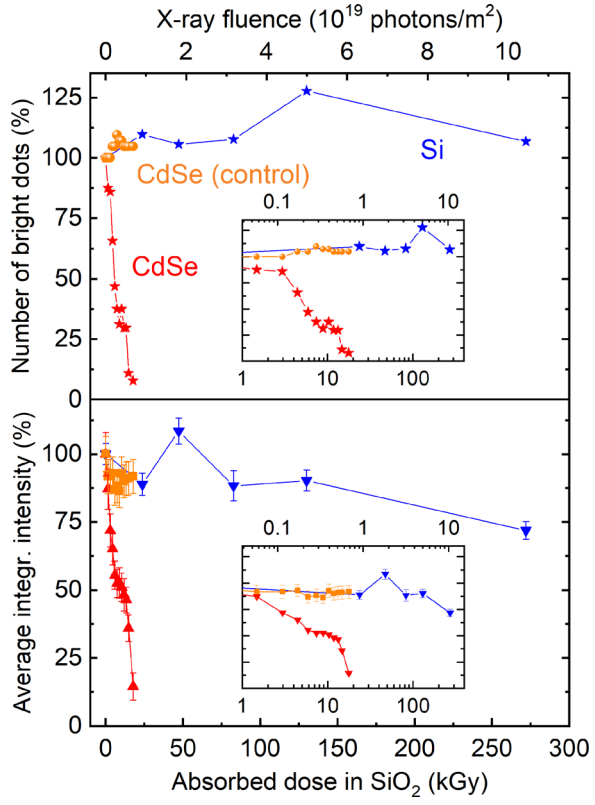

FIG. 2. (Top) Normalized number of bright dots and (bottom) their average PL integrated intensity as a function of cumulative absorbed dose (bottom axis) and X-ray fluence (top axis) for CdSe and (blue) Si-QDs. Insets show data in the semi-log scale for clarity. In all the plots, 100% refers to the initial values. Error bars in the intensity plot show standard deviations of the single-dot intensity statistical distribution. The control non-irradiated CdSe sample data are colored in orange.

of the radiation hardness of Si/SiO_2-QDs, confirming their potential in applications in harsh environments. Conversely, the number of emitting CdSe-QDs strongly decreases, while their intensity vanishes after only ~18 kGy (SiO_2). It is interesting to see that the number of bright CdSe nanocrystals does not change significantly below ~3 kGy (Fig. 2, top, inset), in accordance with previous ensemble studies.[28,29] Instead, a significant drop in PL intensity occurs for higher doses, as observed in CdTe/CdS-QDs.[31] A control non-irradiated sample of CdSe-QDs shows no significant change of PL intensity over time (Fig. 2, orange dots), thus discarding air-induced PL quenching. Given that >200 keV X-rays are required to cause bulk damage in our materials (see Table S1), our X-ray source is not sufficient to generate structural defects in the core-shell structure but can only lead buildup charge by ionization.[18,21] Such a process creates a substantial number of non-radiative channels in CdSe-QDs but not in Si-QDs.

The average PL efficiency and the number of luminescent dots provide important information concerning the radiation hardness of the two types of QDs. Still, both are affected by blinking which should be related to the presence of traps in the proximity of the dot.[24] Blinking characterizes the vast majority of fluorophores,[25] and hence, it does not indicate a particular bad quality of our samples. Therefore, studying the blinking of irradiated QDs may provide additional information concerning the generation of traps in the material. We define as Δt_{ON} (Δt_{OFF}) each time spent in the ON-state (OFF-state), i.e., when the QD is bright (dark). From the literature, the statistics of Δt_{ON} and Δt_{OFF} in Si-QDs exhibit a mono-exponential behavior with respective time constants τ_{ON} and τ_{OFF}.[34,37,41] Hence, properly normalized probability density distributions are $p(\Delta t_{ON}) = \frac{1}{\tau_{ON}} \times e^{-\Delta t_{ON}/\tau_{ON}}$ and $p(\Delta t_{OFF}) = 1/\tau_{OFF} \times e^{-\Delta t_{OFF}/\tau_{OFF}}$. Instead for CdSe-QDs, the blinking statistics feature a power-law behavior (lacking an average), resulting in $p(\Delta t_{ON}) \propto \Delta t_{ON}^{-m_{ON}}$ and $p(\Delta t_{OFF}) \propto \Delta t_{OFF}^{-m_{OFF}}$.[24]

Figure 3 shows τ_{ON} and τ_{OFF} of different single Si/SiO_2-QDs (colour-coded) versus the cumulative absorbed dose. Both ON- and OFF-time distributions retained their mono-exponential character over all the radiation range. Although the time constants vary dot-by-dot, their average values do not show any strong variation up to ~300 kGy. This is reflected in a constant duty cycle (δ_{ON}) (see Fig. S5), which ultimately correlates with their PL efficiency. As a tentative explanation of their hardness, X-ray ionization of SiO_2 could create additional traps which are only weakly involved in the blinking process. From microelectronics[42–45] and blinking[37,41] studies, these traps should be energetically static over time, leading to mono-exponential blinking statistics only when a single trap is resonant.[46] Hence, if additional electron/hole trapping centers are created, they are most likely non-resonant in energy or far in space with respect to the QD electron/hole states in the core.

The blinking behavior under X-ray irradiation of CdSe-QDs is clearly different from the Si counterpart, as shown in Fig. 4 where the ON- (m_{ON}) and OFF- (m_{OFF}) power exponents are plotted against the cumulative absorbed dose. As expected, the average exponents of the control sample (Fig. 4, left part) do not vary considerably. However, for the

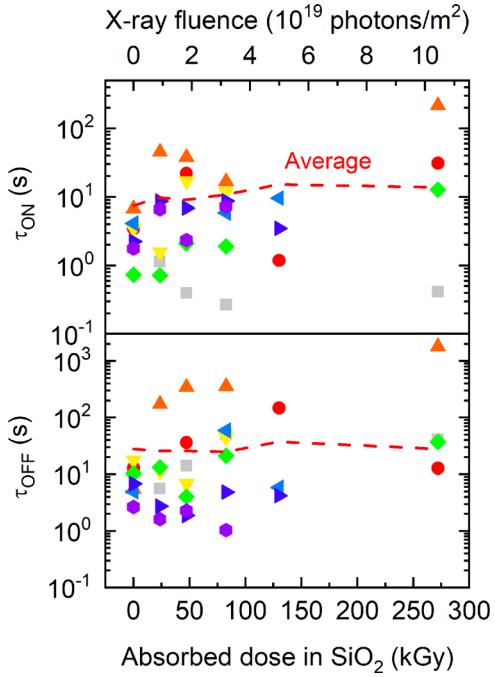

FIG. 3. Blinking ON- (top) and OFF- (bottom) time constants extracted from the blinking traces of single Si/SiO_2-NCs as a function of absorbed dose in SiO_2 (bottom axis) and X-ray fluence (top axis). The red dashed line is the nanocrystal-average.

irradiated QDs, m_{ON} increases and m_{OFF} decreases with dose before complete quenching, which is clearly visible both for individual dots and on average. This proves that all CdSe-QDs stay longer in the OFF-state and shorter in the ON-state upon X-ray irradiation.

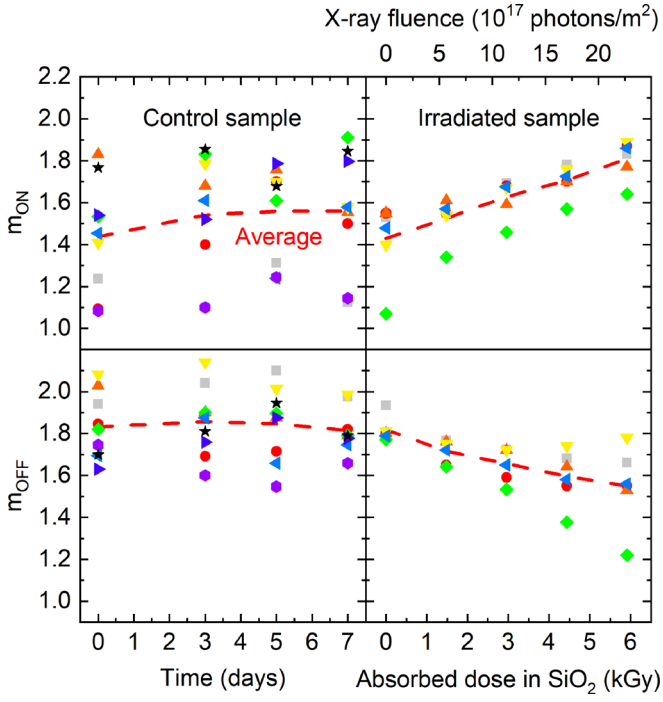

FIG. 4. ON- (top) and OFF- (bottom) power-law exponents extracted from the blinking traces of single CdSe/CdZnS-QDs. Data for control sample (left plots) as a function of time and irradiated sample (right plots) as a function of absorbed dose in SiO_2 (bottom axis) and X-ray fluence (top axis). The statistical average is shown by a red dashed line.

Although the two material samples (Si and CdSe) are synthesized via different methods, they should feature a comparable number of defects or non-radiative centers before X-ray irradiation, given their similar QYs of ~30%. In discussing the possible origin of the dramatic difference between these two materials under X-rays, we first note that Figs. 2–4 compare Si and CdSe-QDs in the same radiation field. One can immediately suggest a higher absorption cross-section of heavy metal-based QDs (3–4 times more electrons per atom) as a reason for these observations. Indeed, our calculations (Fig. S4) indicate an order of magnitude higher absorption cross-section at ~10 keV for CdSe-QDs in relation to those of Si. However, this difference alone clearly fails to explain the effect since we observe a reduction in PL intensity of CdSe nanocrystals of ~25% already at 3–5 kGy, while the same change occurs in Si-QDs only at 272 kGy (see Fig. 2). Therefore, a secondary mechanism must be responsible for the strong X-ray induced degradation in CdSe-QDs. FTIR measurements on ensembles of irradiated CdSe-QDs (Fig. S6) did not indicate removal/decomposition of surface ligands, which are well-known to influence their QY.[12,47] Ensemble PL (Fig. S7) discarded emission from deep traps, which is usually red-shifted and broad.[48,49] The results in Fig. 4 unambiguously prove an increase in OFF-time periods with extended X-ray exposure for CdSe, but not for Si (Fig. 3). Consequently, we connect the change in blinking behavior of CdSe-QDs to an increase in non-radiative traps generated by material ionization, thus creating more channels for the QD to access the OFF-state. These traps seem located in the core-shell system (most likely shell or interface) of CdSe-QDs, not on their surface.

In conclusion, we have studied the effect of X-ray ionizing radiation on the PL intensity and intermittency of single Si/SiO_2 and CdSe/CdZnS QDs. Our results show that the number of luminescent Si-QDs and their intensity remain relatively stable up to ~300 kGy (SiO_2) of cumulative absorbed dose, the maximum level tested so far. Conversely, the PL of CdSe-NCs becomes completely quenched already at ~18 kGy (SiO_2), consistent with previous reports for other Cd-based QDs. Based on our calculations, the effect of X-rays is limited to ionization of the material, excluding any lattice damage. After the exposure to X-rays, in both types of quantum dots, the statistical nature of blinking ON- and OFF-times does not change: it remains mono-exponential for Si and the power-law for CdSe-NCs. Nevertheless, the dependence of the blinking parameters with the increasing absorbed dose depends on the material considered. Both ON- and OFF-characteristic times remain constant on average in Si nanocrystals. On the contrary, the ON-time exponent increases and the OFF-time exponent decreases with the increasing dose for CdSe-QDs, leading to their PL quenching. Removal/decomposition of surface ligands under X-ray irradiation and generation of emissive traps were discarded by ensemble FTIR and PL measurements. Trapped charges resulting from material ionization and responsible for a change in the blinking power exponents of CdSe-QDs must be present in their core-shell system. If we compare the two material systems, Si-QDs seem to be much more stable and resistant against ~10 keV X-ray radiation. Since these X-rays are present in space, e.g., emission from the solar

corona, we have demonstrated that Si-QDs are more promising in their use in space compared to wet-chemistry synthesized heavy metal-based QDs.

See supplementary material for detailed fabrication and experimental procedures, additional data, and discussion.

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