

Decay-to-Recovery Behavior and on-off Recovery of Photoluminescence Intensity from Core/Shell Quantum Dots

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Supporting Information

ABSTRACT: We report on the intriguing phenomenon of the evolution of photoluminescence from CdSe core, CdSe/ZnS core/shell, and CdSe/ $Cd_{1-x}Zn_xSe_{1-y}S_y$ core/graded shell green-emitting quantum dots (QDs). The thickness and composition profile of QDs was found to control how the optical characteristics evolve under different light exposure conditions. Unexpectedly, changes of emission intensity (decreasing and increasing) and spectral band position were observed, which can be reversible or irreversible, depending on the QD architecture and exposure conditions. It is revealed that competition between the reversible and irreversible optical changes led to unique decay-to-recovery behavior for the QD emission, metastable bright states of QDs that can be activated and deactivated numerous times, and decoupled optical changes (reversible intensity changes vs irreversible spectral shifts). We suggest that the distinct dynamic response of each QD architecture arises from how the core and shell interact with each other and the influence of environment parameters (i.e.,



oxygen, H₂O, and light). Furthermore, there is a large difference in the decay and recovery rates (seconds vs many minutes) to be considered for dynamic photonic systems. This work offers a general framework for evaluating dynamic photoluminescence properties of QDs where stable or variable/controlled emission is required, in situations where long device lifetimes are highly desirable (e.g., QD displays, LEDs, and lasers), or in the case of exploring dynamic properties for tunable emission patterning. **KEYWORDS:** *quantum dots, dynamic emission, quantum yield, photostability, decay and recovery*

Quantum dots (QDs) have gained significant interest in the area of photonics due to their tunable emission across the visible spectrum, narrow emission bands, and high quantum yields.¹ In addition, these small semiconductor nanoparticles are compatible with many surface functionalization schemes,¹ deposition approaches,^{2,3} and patterning techniques,^{4,5} making them ideal candidates for a variety of technologies including LEDs,^{6,7} solar cells,^{8–11} lasing media,^{2,3} and cell tracking.¹²

The wide range of applications for QDs have, therefore, resulted in intense research examining how the compositional profile (core, core/shell, and core/graded shell) can be used to tune their optical properties in a controllable manner.^{13–17} Typically, the introduction of a protective inorganic shell around a QD core improves their optoelectronic properties, with graded or alloyed core/shell interfaces providing the greatest improvements.^{16,17} QDs are commonly evaluated by considering steady-state characteristics like quantum yield (QY), emission full-width half-maximum (fwhm), photoluminescence (PL) lifetime, and Auger relaxation dynamics.^{13–18} The formation and dynamics of excitons and

multiexcitons have also been shown to depend on the presence (and type) of inorganic shell. $^{19,20}\,$

However, one of the most critically important metrics of evaluation is the stability of emission characteristics like spectral position, fwhm, and intensity since they play such a critical role in device lifetime and scientific investigation. For example, the issue of QD emission stability is very important to consider for characterization techniques like the variable strip length method (for optical gain) and fluorescence lifetime imaging (for cellular and nanoparticle imaging/tracking) where stable emission is required to obtain meaningful results.^{12,21,22} Additionally, QD stability is critically important in photonic systems that need to have a long lifetime under a variety of environmental conditions (QD LEDs, displays, and lasers).^{6,23,24} However, the lack of complete emission stability (i.e., unstable emission) can be valuable for dynamic, light-intensity dependent photonic systems. Indeed, controllably

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quantum dot	composition	absorption peak (nm)	PL peak (nm)	Stokes shift (nm)	fwhm (nm)	quantum yield (%)
core	CdSe	553	560	7	26	3
core/shell	CdSe/ZnS	546	554	8	28	16
core/graded shell	$CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$	492	508	16	33	73

Table 1. Optical Characteristics of Plain CdSe Core, CdSe/ZnS Core/Shell, and CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y Core/Graded Shell QDs in the Solution state

variable emission is actually necessary, as in the case of dynamic photopatterning. 25

Various studies have examined how the emission of QDs evolve in response to chemicals, gaseous environments, polyelectrolyte matrices, substrates, and light exposure.^{26–30} Blue shifting is a very common phenomenon and is caused by an increase of quantum confinement of the exciton due to a reduction of QD size. Typically, size reduction is attributed to chemical or photochemical oxidation and corrosion of the QD surface,³¹⁻³⁴ since it can be significantly reduced by placing QDs in a nitrogen environment or vacuum.³⁴⁻³⁶ Blue shifting of PL can vary from a few nanometers in dark environments (i.e., oxidation), 35 to 15–20 nm under light exposure (i.e., photooxidation). 31,34,35 Changes of QD emission intensity (decreases and increases) have also been observed. In general, intensity is altered by modifying nonradiative trap states, which includes bypassing (via a more efficient recombination pathway), saturating (by ligand, H₂O, or charge carriers), or removing these pathways (shelling, photorestructuring/annealing of the QD surface). The variety of mechanisms that affect emission makes it difficult to evaluate and understand the situation. In general, a PL intensity increase is much more common in the literature than a decrease. For example, increasing intensity upon light exposure has been attributed to photoactivation (in vacuum),³⁵ photoinduced H_2O defect passivation,³¹ increased coordination of ligands with the QD surface via pH changes or light,^{37,38} and photoinduced surface annealing/restructuring.³⁴ On the other hand, the decrease of PL intensity has been credited to the formation of surface quenching states during photooxidation as a result of photobleaching.^{35,36} Interestingly, photobleaching has been shown to still occur in a nitrogen environment, so it has been suggested that the formation of lattice defects in the CdSe/ZnS QD likely leads to nonradiative recombination pathways.³⁹

Additional complexity is introduced due to some of these changes being reversible and others being irreversible. For example, reversible changes to intensity were demonstrated by heat cycling due to photoinduced surface transformation,⁴⁰ pressure cycling due to adsorption/desorption of H₂O,³¹ and light exposure cycling due to light-activated rearrangement of surfactant molecules.³⁸ Additional complications include the variety of rates over which these changes can occur (seconds vs minutes vs hours). For example, studies that utilized PL integration times on the order of 20 s to 2 min might have missed changes occurring within the first seconds of light exposure.^{41,42}

Different studies have presented routes for mediating these changes to emission, typically involving the introduction of an inorganic protective shell around the QD core where the exciton is located.^{34,35,38} For example, previous studies have compared bare CdSe core QDs to CdSe/ZnS core/shell QDs in a variety of environments.³⁵ However, these measurements were performed either under continuous darkness or continuous light exposure without checking for reversibility

and, therefore, did not observe the unique light-mediated on- off (reversible) PL intensity recovery.

In this work, we examine how the emission from QDpolymer composite films with different green-emitting QD architectures (core, core/shell, core/graded shell) evolve when in darkness, when exposed to light, and when undergoing light-dark-light cycles. The photoresponsive behavior can be engineered into a QD by ensuring that the CdSe core (where the exciton is located) is exposed to the environment, either upon synthesis or through chemical/physical modification/ degradation of the protective inorganic shell by light, oxygen, and water. We suggest that the competition between reversible and irreversible mechanisms can lead to unique decay-torecovery behavior for intensity, metastable bright states that can be turned on and off many times, and decoupled optical changes (reversible intensity changes vs irreversible spectral shifts). Furthermore, there is a large rate difference between the decay and recovery mechanisms (seconds versus many minutes), suggesting the presence of fast processes (i.e., immediate decay upon light exposure) under certain conditions. The distinct response of each green-emitting QD architecture arises from how the core and shell material interact with each other (crystal lattice mismatches) and the environment.

RESULTS AND DISCUSSION

QD Optical Characteristics. Colloidal green-emitting plain CdSe core QDs were synthesized following a seeded-growth procedure,^{25,43} while the ZnS shell for the CdSe/ZnS core/ shell QDs was synthesized following a procedure reported in literature.^{15,25} Green core/graded shell $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs were synthesized by modifying a reported method.^{44,45} TEM micrographs show an outer diameter of 3.9 ± 0.3 nm (shell thickness ~ 0.5 nm) for the CdSe/ZnS QDs, while the $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs have a diameter of 7.6 \pm 0.5 nm (shell thickness ~ 2.7 nm; Figure S1). The thicker shell for the core/graded shell QD could be synthesized due to the reduced crystal lattice mismatch between the CdSe core and graded composition shell. Core only, core/shell, and core/graded shell QDs were used to examine how the compositional profile affects the general optical characteristics in the solution state (Table 1). Each QD type displays a broadband absorbance down to the UV and narrowband emission in the green region (Figure S2).

In addition, the fwhm of all QD types is narrow, under 35 nm, indicating a relatively homogeneous size distribution. The quantum yield (QY) shows a strong dependence on QD composition profile, with the plain core CdSe QDs having the lowest QY and the core/graded shell CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QDs possessing the highest QY. The significant increase of QY for the core/shell and core/graded shell QDs can be attributed to the passivation of the CdSe core surface states.^{17,18,46,47} In addition, the simple ZnS shell yields less effective surface passivation than the graded shell due to the presence of defect sites that arise from the crystal lattice mismatch (12%) between

CdSe and ZnS.^{17,47} These trends are consistent with previous studies examining how QD shelling can influence the optical characteristics.^{17,47,48}

Emission Evolution: Darkness. In addition to QY, the OD composition profile should also strongly influence the optical stability (intensity and spectral position) of QDs since the environment can lead to changes in the QD surface composition (oxidation, corrosion, etc.). These changes can then affect surface passivation and the relaxation pathways available to the exciton (trap states and nonradiative relaxation pathways). The QD composition profile and shell thickness become particularly important for type-I QD designs since the exciton can be localized to the QD core and, therefore, isolated from the environment. Furthermore, QD composition profile and shell thickness are very important when QDs are deposited into films since the QDs are in close contact with a variety of additional factors (oxygen, moisture, and surrounding materials) that have been shown to cause changes to the spectral position and QY of QDs.^{25,35,36}

To examine how QD composition profile and shell thickness affect PL stability in a dark environment (ambient atmosphere, temperature, pressure), each type of QD (plain core, core/shell, core/graded shell) was deposited into a poly(methyl methacrylate) (PMMA) film. QD-polymer films of thickness 270 nm (\pm 50 nm) were prepared by spin-casting a QD-PMMA mixture at 2500 rpm for 1 min, as outlined previously.²⁵ All QD-polymer films uniformly covered the substrate, exhibiting minimum scattering, and displayed uniform PL emission (Figure S3). The PL intensity and spectral position of QD emission were then monitored while the films were in a dark environment. The composition profile and shell thickness of QDs were found to strongly influence how the intensity and spectral position evolve during this period of darkness (Figure 1). The core CdSe QDs display a large decrease of intensity (a 95% decrease) and a moderate blue shift (5 nm), which results from oxidation and corrosion of the CdSe surface to CdSeO₂ and activates nonradiative surface quenching states (Figure S4).^{35,3}

The core/shell CdSe/ZnS QD undergoes a less pronounced decrease of intensity (a 60% decrease) and a small red-shift ($\Delta\lambda$ \approx 1 nm) over the same period. The reduction of intensity indicates a decreased passivation of the CdSe core by the thin ZnS shell (\sim 0.5 nm). The very small red shift could be due to a reduction of quantum confinement of the CdSe core due to removal of the compressive ZnS shell.49-51 However, in general, the very weak spectral shift indicates quantum confinement of the exciton is not significantly altered, which means the core undergoes minimal physical change in size since the CdSe/ZnS QD is type-I with the exciton confined to the CdSe core. In short, these results show that the CdSe/ZnS QD experiences degradation of the 0.5 nm thick ZnS shell by oxidation and corrosion with little modification to the CdSe core (Figure S4). Modification of the ZnS shell is not surprising since the ZnS shell is the material in direct contact with the environment.

Finally, the core/graded shell CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QD shows no clear change of intensity ($\Delta I < 5\%$) or spectral position ($\Delta \lambda < 1$ nm) over the same period. Although oxidation of the outer graded shell is likely occurring, its effects do not directly affect the CdSe core due to the thickness (2.7 nm) and thermodynamic stability of the graded Cd_{1-x}Zn_xSe_{1-y}S_y shell. Both the thicker shell and thermodynamic stability result from the graded shell composition profile



Figure 1. Evolution of the PL intensity (a) and spectral shift $(\lambda_t - \lambda_0)$ (b) of QD-PMMA films using the CdSe core, CdSe/ZnS core/shell, or CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y core/graded shell QDs under darkness.

imparted during synthesis, which reduces the strain energy from the crystal lattice mismatch between CdSe and ZnS allowing for thicker epitaxial shells to be grown (compared to sharp transition core/shell QDs).^{47,49}

These distinct emission trends clearly show that the composition profile and shell thickness of the QD affect how the optical properties evolve in a dark environment under ambient temperature and gaseous composition. The proposed physical changes underlying these PL trends are shown in Figure S4. The consideration of these trends is important to consider when trying to improve the lifetime of QD devices and systems during storage. The proposed physical mechanisms leading to this distinct behavior are based on the indirect evidence from PL emission. Direct verification of reduced QD size or crystal lattice due to oxidation and corrosion via high-resolution TEM is extremely difficult due to the very small physical changes that are likely occurring (<1 nm change) and because exposure to the e-beam during high resolution TEM could alter the QDs.

Emission Evolution: Continuous Light Exposure. In the next step, compared to darkness as discussed above, we examined whether continuous light exposure elicits additional mechanisms within the QDs that alter how the emission evolves. This is particularly important to know when developing QD devices and systems that experience constant light excitation and exposure. In this case, the QD-polymer films are continuously exposed to light (24–32 mW, 450–490



Figure 2. Examination of the photoluminescence stability of QD-PMMA films with different types of QD design (CdSe core, CdSe/ZnS core/shell, or CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y core/graded shell). (a) Schematic of the different QDs that were examined. Evolution of (b) PL intensity and (c) spectral shift ($\lambda_t - \lambda_0$) under continuous light exposure (blue light: 450–490 nm, 24–32 mW).

nm) over a period of 45 min, while their PL intensity and spectral position are monitored.

The results indicate that the QD composition profile and shell thickness profoundly impact how the intensity and spectral position of the emission evolves. Furthermore, continuous light exposure can lead to more pronounced shifts compared to when in darkness. For example, the core CdSe QDs undergo a much larger blue shift (16 nm) compared to when in darkness (5 nm), indicating an accelerated oxidation and corrosion of the CdSe core that reduces the diameter and increases quantum confinement. The intensity follows a similar decay rate and magnitude presumably due to a saturation of nonradiative surface quenching states. The decay of PL intensity was corroborated with PL imaging (Figure S5). The decay of PL intensity upon light exposure for plain CdSe core QDs is interesting since some previous studies have shown that CdSe QDs can experience an increase of PL intensity upon light exposure.³¹ This variance could be due to the different environmental and exposure conditions (toluene vs hexane/ H₂O), deposition approach (spin-casting vs Langmuir-Blodgett), film type (QD-polymer vs purely QD), as well as differences in the available QD surface states caused by the different specific CdSe QD synthesis approaches that were used.³¹

Light exposure for the core/shell CdSe/ZnS QDs leads to more pronounced shifts and new behavior, signifying the emergence of photomediated mechanisms. For example, a large continuous spectral blue shift occurs (16 nm) throughout the 45 min of light exposure (instead of a red shift). Furthermore, upon exposure to light, the intensity decreases more rapidly than in the darkness case, and then undergoes a recovery of intensity. The convolution of the competing decay and recovery mechanisms leads to a decay-to-recovery evolution of intensity (Figure 2a,b). Interestingly, the decay occurs much more quickly (seconds-to-minutes) than the recovery step (tens of minutes).

As in the darkness case, the intensity and spectral position of the core/graded shell $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs show minimal change under continuous light exposure (verified with PL imaging in Figure S6). In addition to the thick graded shell QD, thinner graded shell QDs (1 nm shell thickness) were examined to provide a more direct comparison to the CdSe/ ZnS QDs with 0.5 nm shell thickness. The thin graded shell QDs have very different behavior, showing no initial decay step and instead a PL intensity enhancement by a factor of 2-4 over the 45 min light exposure period (32 mW, 450-490 nm). This behavior indicates that a thinner graded shell is not sufficient to completely stabilize the QD against light exposure. However, the thin graded shell appears to prevent decay during initial light exposure, in contrast to the sharp ZnS shell of the CdSe/ ZnS QDs. Therefore, the compositional gradient and thickness of the QD shell has the potential to lead to unique PL intensity behavior upon light exposure.

Continuous exposure experiments of the core, core/shell, and thin core/graded shell QDs in solution show an increase of PL intensity upon light exposure (55%, 16%, and 25% increase, respectively), while the thick core/graded shell QD show minimal change ($\Delta I < 5\%$) (Figure S7a). However, no clear indication of spectral shifting is observed during light exposure for any of the QDs in solution ($\Delta\lambda < 1$ nm) Figure S7b). The absence of PL intensity decay and presence of PL enhancement indicates that it is exposure to the ambient environment and

deposition into a solid film state that leads to the PL decay behavior via a photooxidative effect. Furthermore, the increase of PL intensity with no concurrent spectral (blue) shift indicates that the PL recovery/enhancement mechanism is due to a unique mechanism that does not cause spectral blue shifting. This provides additional evidence that more than one mechanism underlies the evolution of QD PL upon light exposure.

Emission Evolution: Decay-to-Recovery Behavior (CdSe/ZnS QDs). As mentioned, the decay-to-recovery evolution of intensity for the CdSe/ZnS QDs arises from a combination of competing decay and recovery mechanisms. However, there are a variety of mechanisms that lead to decay and recovery (reversible or irreversible) in QDs so additional information is required before a conclusive determination can be made.

Continuous Light Exposure of Different Power. PL intensity recovery only occurs upon light exposure so it is likely that the characteristics of recovery depend on the exposure power. However, it is also possible that light exposure also affects the decay mechanism. Therefore, the relative strength of each effect and its dependence on exposure power needs to be compared. The time-to-recovery is an ideal parameter to consider for this comparison as it represents the time required for the effects of the recovery mechanism to overcome those from the decay mechanism. The results show that the decay-to-recovery behavior is affected by the exposure power, where an increase of exposure power from 3 to 32 mW (450–490 nm) reduces the time required for the CdSe/ZnS QDs to enter the recovery stage ($\tau_{recovery}$) from ~3.5 to 1 min (Figure 3a,b).

This indicates that the recovery mechanism has a stronger dependence on (and is proportional to) the number of incident photons than the decay mechanism since recovery overcomes decay eventually (for the power range examined). Next, the time-to-recovery follows a downward linear relationship with exposure power (Figure 3c).

This suggests that the rate of the recovery is linearly proportional to the number of incident photons, or that the ratio of the rates of the recovery and decay mechanism is linear. Then, the rate of blue shifting increases with higher exposure power (Figure 3d), which shows that photooxidation and corrosion of the CdSe core scales with the number of incident photons. In order for photooxidation and corrosion to reduce the CdSe core size, the ZnS shell must either be removed or significantly degraded during this period. However, removal and degradation of the ZnS shell should reduce surface passivation (and the intensity). Therefore, we can speculate that the blue shifting is a result of the decay mechanism, which means the decay mechanism also is proportional to the exposure power.

Continuous Light Exposure of Pure QD Films Exposed to Water. The surrounding environment of the QD can have a significant impact on the surface of the QD, which directly affects the relaxation pathways available to the QD exciton. Therefore, we cast pure CdSe/ZnS QD films to examine the role of the polymer matrix and examined the PL evolution upon continuous light exposure (450–490 nm). The removal of the protective polymer matrix leads to the emergence of unique PL evolution, specifically the presence of PL enhancement followed by decay (Figure 4a). In this case, the eventual decay indicates that the mechanism causing decay eventually overwhelms (or removes) the PL enhancement mechanism, essentially transforming the CdSe/ZnS QDs into the CdSe



Figure 3. Evolution of the (a) PL intensity for core/shell CdSe/ZnS QD-PMMA films at three different exposure powers (continuous exposure), and (b) a narrowed viewing range of the time-to-recovery for additional exposure powers (dashed lines are guides only). (c) The time-to-recovery of PL intensity versus incident exposure power. (d) Spectral shift ($\lambda_t - \lambda_0$) of the emission peak at three different exposure powers (continuous exposure).

QDs. Soaking the pure CdSe/ZnS QD film in water before light exposure increased the magnitude of PL enhancement compared to the dry state. However, the eventual decay was



Figure 4. Evolution of the (a) PL intensity and (b) spectral shift ($\lambda_t - \lambda_0$) of pure CdSe/ZnS QD films in the dry and wet state upon continuous light exposure (450–490 nm).

not prevented and the intensity eventual returned to a similar dark state as seen with the dry film state.

Both films underwent spectral shifting, with the H_2O soaked QD film showing slightly more blue shifting (Figure 4b). These results clearly show that the polymer matrix does play a role in the PL dynamics of unstable CdSe/ZnS QDs. In this case, removing the protective polymer matrix does not prevent PL recovery but does lead to the emergence of a post-enhancement decay mechanism. Furthermore, H_2O clearly plays a role in the PL enhancement, and possibly the photooxidation (although not as pronounced).

Cyclic Light Exposure (Light Exposure–Darkness– Light Exposure). A variety of mechanisms have been presented in the literature to explain the recovery/enhancement of emission upon light exposure. These include irreversible options like photoinduced surface annealing/ restructuring and photoactivation,^{34,35} which remain upon removal of light. However, reversible mechanisms have also been presented, including photoinduced surface transformation (via heat cycling),⁴⁰ adsorption/desorption of H₂O (via pressure cycling),³¹ and light-activated rearrangement of surfactant molecules in solution (via light exposure cycling of QDs in solution).³⁸ However, so far, reversibility has either required the external modification of the surrounding environment or focused on QDs in solution (neither of which applies to this study). The identification of whether the recovery of PL intensity is irreversible of reversible will help identify the underlying mechanisms behind the PL evolution behavior.

Therefore, the core/shell CdSe/ZnS QD-polymer films (which evolve very differently depending on whether they are in darkness or being exposed to light) were exposed to a cyclic light exposure regime to determine how the recovered PL state responds to a period of darkness (i.e., the removal of electromagnetic energy). A single cycle involves a period of light exposure, followed by a period of darkness, and then a resumption of light exposure. This sequence is designated as an exposure–darkness–exposure cycle. Exposure–darkness–exposure cycling will determine whether the recovered PL state requires continuous light exposure to be maintained (indicating a reversible dynamic process that requires continuous input of energy to occur), or is not affected by the removal of light (indicating an irreversible process).

The results of a single exposure-darkness-exposure cycle are shown in Figure 5a. The QD-polymer film was continuously exposed to light for 10 min (~19 mW, 450-490 nm), during which a continuous recovery of emission occurred as expected. After 10 min of continuous light exposure, the light is removed for 20 min (a 20 min darkness step). Light exposure is then resumed (same intensity and wavelength) and a measurement is collected immediately to determine whether the period of darkness affected the PL recovery. It is clear from Figure 5a (images and spectral intensity data) that removal of light for 20 min leads to a drastic decrease in intensity of the recovered PL state (more than 85% reduction). Subsequent continuous light exposure leads to a gradual increase of PL intensity back to the initial recovered state (larger PL images of the film during this process provided in Figure S8). Repeated exposure-darknessexposure cycles at different times throughout the recovery process lead to a similar response (Figure 5b; a 5 min darkness period).

These results indicate that the PL recovery is a reversible process (or partially reversible). However, the spectral blue shift that occurred during the continuous exposure step does not disappear during a darkness step (it actually continues to a small extent; Figure 5c). This irreversibility indicates that the blue shifting of emission is not directly tied to the PL recovery mechanism but, more likely, to the photooxidative decay process. The independence of PL recovery from spectral blue shifting agrees with the exposure study on QD solutions discussed earlier. The independence of the decay and recovery mechanisms is also supported by the fact that the intensity drop and blue shift that occur after a darkness step appear independent of when the darkness step is initiated over the recovery period (Figure 5d).

The PL intensity drop and blue shift are directly related to the duration of the darkness step, with a longer darkness period leading to s greater intensity drop and blue shift (Figure 6). The PL intensity drop follows an exponential trend (negative time constant; Figure 6c). The blue shift also appears to scale with darkness time, matching closely with the blue shift observed in previous darkness studies (Figure 6d). It is interesting to note that a slight red-shift occurs within the first minute of resuming light exposure after a darkness step (Figure S9), which could be due to an increase in the dielectric constant of the immediate surroundings.^{38,52} Similar exposure–darkness–exposure studies were performed on thin shell core/ graded shell CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QDs. The behavior is similar to the CdSe/ZnS QDs, with the thin shell CdSe/



Figure 5. Examination of the charge-discharge effect observed upon light exposure and removal for a CdSe/ZnS QD-PMMA film. (a) Evolution of PL intensity during an exposure-darkness-exposure trial (darkness period: 20 min) (exposure: 450–490 nm, \approx 19 mW). (b) PL intensity and (c) PL spectral position during exposure-darkness-exposure cycling (5 min darkness periods). (d) Drop of PL intensity and spectral shift after each darkness period.

 $Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs showing a discharge of the PL recovery that scales with time (Figure 6c and Figure S10). However, the amount of PL recovery discharge and degree of blue shifting were less extreme than the CdSe/ZnS QDs, presumably due to the thicker 1 nm graded $Cd_{1-x}Zn_xSe_{1-y}S_y$ shell. An opposite cycling approach can be performed as well (darkness–exposure–darkness cycle), which also leads to jumps of PL intensity and spectral position and corroborates the reversible PL recovery behavior just discussed (Figure S11).

The results from the exposure-darkness-exposure experiments indicate a number of things: First, the recovery of PL intensity and spectral blue shift are not coupled, which means at least two mechanisms are present. Second, the process causing recovery of the PL intensity is (at least partially) reversible since it requires a constant input of electromagnetic energy to be maintained. Third, the mechanism underlying PL intensity recovery may be diffusion-based since it dissipates with time after light is removed. Finally, whatever mechanism underlies the PL intensity recovery process also leads to a small immediate red-shift upon resuming the input of electromagnetic energy (after a darkness period).

Underlying Mechanisms of Dynamic Changes. There are a variety of mechanisms that could be present in each of the QD architectures that could account for the corresponding evolution of PL emission.^{35,38,53} A summary of the evolutionary trends for the core, core/shell, and core/graded shell QD-polymer films under various external factors is provided in Table 2.

As noted previously, direct confirmation of physical (diameter) and material (surface oxidation/corrosion and H_2O passivation) changes to QDs via techniques like highresolution TEM or NMR are very difficult due to the scale of the physical changes (<1 nm), the complexity in identifying different crystal structures over these small scales, the rate of the changes, and the reversibility of some mechanisms. Therefore, the following discussion of mechanisms is based on evidence from the evolution of optical emission under the various external factors, since these characteristics exhibit shifts that can be observed real time, with high accuracy, and require no cleaning steps that could modify the QD-polymer films.

The core/shell CdSe/ZnS QDs are the initial focus since they exhibit the most complex and interesting shifts of intensity and spectral position. To recap, the following phenomena need to be explained. First, continuous light exposure causes a decayto-recovery behavior for intensity (Figure 2b). Second, the decay step is much faster than the recovery step (by an order of magnitude; Figure 2b). Third, the recovery phase occurs earlier for high exposure power (Figure 3c). Fourth, there is a continuous blue shift throughout the decay-to-recovery evolution (most pronounced during the recovery step; Figure 2c). Fifth, the recovery of intensity is semireversible, requiring continuous light input to be maintained (Figure 5a).

Moreover, the blue shift is largely irreversible but the PL intensity recovery process can be "discharged" and "recharged" multiple times (Figure 5c and b, respectively). The "discharge" of recovery upon darkness is proportional to the darkness



Figure 6. Examination of how periods of darkness affect the PL intensity of CdSe/ZnS core/shell QDs exposed to light (exposure: 450–490 nm; QD-PMMA films). (a) PL intensity decay dip and (b) spectral shift for different periods of darkness (10 min into light exposure regime). Magnitude of the (c) PL decay dip and (d) spectral blue shift vs the duration of the darkness step for the core/shell QD and thin core/graded shell QD.

Table 2. Evolution of the Optical Characteristics of the CdSe Core, CdSe/ZnS Core/Shell, and CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y Core/ Graded Shell QD-Polymer Films in a Dark Environment (Top Frame) and under Continuous Light Exposure (Middle Frame; Blue Light: 450-490 nm); PL Evolution of CdSe/ZnS QD-Polymer Film under Cyclic Light Exposure (Exposure–Darkness– Exposure; Bottom Frame)^a

darkness (continuous)								
design com		mposition	intensity	peak po	sition	n proposed mechanism		
core CdSe			decay (↓96%	b) blue shift	(5 nm)	oxidation		
core/shell	core/shell CdSe/ZnS		decay (↓68%) red shift (1 nm)	oxidation		
core/thick grade	core/thick graded shell CdSe/Cd _{1-x'}		stable (±10%	6) stable (± 0)	0.5 nm)	NA		
light exposure (continuous)								
design	design composition		intensity	peak position	Propo	osed mechanism		
core	CdSe	decay (↓98%)	blue shift (16 nm)	oxidation, photoox	idation		
core/shell	CdSe/ZnS	decay-to	o-recovery	blue shift (16 nm)	photooxidation, light-mediated H ₂ O passiv			
core/thin graded s	hell CdSe/Cd _{1-x} Zn _x S	Se _{1-y} S _y enhance	ement (†300%)	red shift (2.5 nm)	light-mediated H ₂ G	D passivation		
core/thick graded	shell CdSe/Cd _{1-x} Zn _x S	$Se_{1-y}S_y$ stable (<u>+</u> 8%)	stable ($\pm 0.5 \text{ nm}$)	NA			
cyclic light exposure (exposure-dark-exposure)								
design	composition	intensity		peak position	proposed mechanism			
core/shell CdSe/ZnS	initial light exposure	recovery	blue shi	ift (varies)	photooxidati passivation	ion, light-mediated H ₂ O		
	darkness step	decay and discharg recovery	e of blue shi	ift (1 nm)	oxidation an mechanisn	d discharge of recovery n		
	subsequent light exposure	recovery	initial r (varie	ed shift (1 nm), blue shi s)	ft photooxidati passivation	ion, light-mediated H ₂ O		
^{<i>a</i>} The proposed me	echanisms causing this b	ehavior are noted	as well.					

period (Figure 6c). Finally, a small red-shift occurs immediately after light exposure during "intensity recharging" (Figure 6b,d). Therefore, mechanisms need to be identified that alter quantum confinement and quantum yield, with one or more mechanisms being semireversible and one or more mechanisms being irreversible.

The core/shell CdSe/ZnS QDs likely have at least two competing mechanisms to explain all the phenomena. The



Figure 7. Schematic outlining the proposed physical evolution of each type of QD (plain CdSe core, CdSe/ZnS core/shell, and CdSe/ $Cd_{1-x}Zn_xSe_{1-y}S_y$ core/graded shell) under light exposure in air over a period of 45 min (organic ligand not shown for clarity).

continuous irreversible blue shift that occurs during light exposure indicates an increase of quantum confinement of the exciton caused by a reduction in size of the CdSe core. Size reduction is typically attributed to an irreversible photooxidation and corrosion of the QD surface, which is reasonable since the QD-polymer film is exposed to an environment with oxygen.³⁵ The rate of spectral blue shifting also slightly increases with exposure power which is expected since photons cause the process to occur.

Photo-oxidation and corrosion of the ZnS shell, which occurs before and concurrently with oxidation of the CdSe core, can explain the fast decay of intensity that occurs immediately upon light exposure. Corrosion of the ZnS shell reduces surface passivation of the CdSe core (where the exciton is located), which decreases quantum yield.^{15,17,46} The ZnS shell is in a metastable state before illumination due to the large (12%) crystal lattice mismatch between CdSe and ZnS which causes strain to build up at the CdSe/ZnS interface and within the ZnS shell.^{17,47} Degradation of the ZnS shell during photooxidation leads to the formation of physical defects as the ZnS shell relaxes that act as nonradiative recombination pathways.^{35,36}

This conclusion is supported by the fact that aged CdSe/ZnS QDs (6 months) have a significantly less pronounced initial high quantum yield state and blue-shifted emission peak compared to newly synthesized QDs (Figure S12). The disappearance of the initial metastable high QY state is caused

by slow oxidation and degradation of the ZnS shell while the QDs are stored in solution (air environment). This is bolstered by the fact that aged QDs (with more surface defects) undergo much more recovery upon light exposure, presumably due to there being more defects on the CdSe surface that are temporarily passivated. Decay of QD PL intensity has also been attributed to heating,⁵³ which in this case could occur due to the continuous light exposure. However, this is unlikely since the area of the QD-polymer film exposed to light shows no measurable increase of temperature over a period of 45 min ($\Delta T < 1$ °C; see Experimental Methods).

A number of mechanisms have been presented in the literature to explain the reversible recovery of PL intensity such as photoinduced QD surface transformation (caused by heat cycling),⁴⁰ light-activated rearrangement of surfactant molecules (caused by light exposure cycling),³⁸ and light-mediated adsorption/desorption of H₂O (caused by pressure cycling).³¹ Semireversible intensity recovery attributed to QD surface transformation (CdSe/ZnS QD solutions and films) is unlikely because it requires deliberate heating above room temperature and localized heating of the QD-polymer film was ruled out in this system. Light-activated rearrangement of ligands is also an unlikely mechanism since this effect is observed in core/shell CdSe/ZnS QD solutions where ligand dynamics are not hindered.³⁸

However, the system in this study is a solid QD-polymer film, so the solid polymer matrix surrounding the QDs should

Table 3. General QD Selection and Evaluation Guidelines To Consider When Trying to Identify a QD Architecture That Satisfies Specific Emission Evolution Behavior in Darkness or upon Light Exposure^a

QD selection and evaluation guidelines							
requirements/assumptions	test	data	QD option	example	type		
darkness + air $\rightarrow \Delta l$ or $\Delta \lambda$	darkness test in air	$\Delta l, \Delta \lambda$, rate Δl , rate $\Delta \lambda$	(unstable) core or core/shell	QD air sensor	device		
light exposure $\rightarrow \Delta l$ or $\Delta \lambda$	cyclic light exposure	irreversibility Δl or $\Delta \lambda$	(unstable) core/shell	photoannealing	process		
(irreversible or long-lived)				QD photopatterning	application		
light exposure $\rightarrow \Delta l$ or $\Delta \lambda$ (reversible)	continuous and cyclic light exposure	$\Delta l, \Delta \lambda$, rate Δl , rate $\Delta \lambda$, reversibility	(unstable) core/shell; (unstable) core/thin graded shell	QD photodetector	device		
light exposure $\rightarrow \Delta PL = 0$	continuous light exposure	$\Delta l, \Delta \lambda$, rate Δl , rate $\Delta \lambda$	(stable) core/thick graded shell	variable strip length (VSL)	measurement		
				QD imaging and labeling	application		
				optically pumped QD lasers	device		
darkness $\rightarrow \Delta PL = 0$, light exposure $\rightarrow \Delta PL = 0$	darkness test in air, continuous light exposure	$\Delta l, \Delta \lambda, rate \Delta l, rate \Delta \lambda$	(stable) core/thick graded shell	QD light-emitting diode	device		
				color filters in QD displays	device		

"Examples of common devices/processes/applications/measurements that utilize QD PL emission and specific QD emission evolution behavior are provided for context.

hamper the rearrangement of ligands on, and their diffusion to/ from, the QD surface. Furthermore, if rearrangement of ligands is the underlying reason for the reversible nature of PL recovery, it is reasonable to assume that the matrix would play an important role. However, PL recovery was observed in two different polymers (poly(methyl methacrylate) and polystyrene), which should interact with the QD ligand differently due to the different side groups.

A schematic outlining the physical evolution of each type of QD under light exposure is shown in Figure 7. When the plain CdSe core QD is exposed to light it experiences surface oxidation and degradation which explains the decay of its intensity and blue shift of its emission (Figure 7, row 1). However, it is interesting that the plain CdSe core QDs do not undergo an eventual PL intensity recovery for a number of reasons. First, previous studies have shown that plain CdSe core QDs can undergo PL recovery upon light exposure.³¹ Second, the plain CdSe core QDs do not have a protective ZnS shell so they should also interact with surrounding water and experience the light-H₂O passivation mechanism. In this case, the absence of PL recovery could be due to there being no protective shell, which allows for immediate (and eventually massive) degradation of the CdSe core surface due to photooxidation and corrosion. It seems the damage to the CdSe core overwhelms (or hinders) the light $-H_2O$ passivation mechanism. However, it is possible in this case that PL recovery is occurring but that the oxidation and degradation of the CdSe core is so profound that it overwhelms the PL recovery.

For the CdSe/ZnS core/shell QDs, we suggest that oxidation/degradation of the ZnS shell combined with lightmediated adsorption/desorption of H_2O serves as the mechanism behind PL recovery and its reversible behavior. During QD encapsulation in the polymer matrix (spin-casting), water is likely trapped in the QD-polymer film at the QD surface. When light is incident on the CdSe/ZnS QDs, it leads to oxidation/degradation of the 0.5 nm thick ZnS shell and some degradation of the CdSe core, leading to the initial PL decay behavior and blue shifting (Figure 7, row 2). However, the degradation of the ZnS shell is offset by H_2O mediated passivation (PL recovery behavior). Because light and H_2O are required for the PL recovery to occur, the PL recovery dissipates when light is removed. However, the disappearance of PL is not immediate, which suggests that the underlying recovery mechanism is due to a chemical reaction at the QD surface that continues briefly after the light is removed. PL recovery can be reinitiated upon light exposure because the H_2O surrounding the QD is encased by the surrounding polymer matrix. In fact, it is the degradation of the ZnS shell by the irreversible photooxidation mechanism that allows for the reversible photo-initiated H_2O passivation mechanism to access the QD core/shell interface and core surface.

In the case of the core/thin graded shell CdSe/ Cd_{1-x}Zn_xSe_{1-y}S_y QDs, the graded shell does undergo photooxidation and corrosion upon light exposure. However, the gradient composition of the Cd_{1-x}Zn_xSe_{1-y}S_y shell reduces the radial lattice mismatch between the CdSe core and outer ZnS shell, making the core/graded shell QDs thermodynamically stable even when outer shell surface oxidation occurs. Furthermore, the shell is 1 nm thick, double that of the ZnS shell for the CdSe/ZnS QDs, which prevents the CdSe core from being oxidized and corroded. Therefore, no PL decay is observed and light-mediated adsorption/desorption of H₂O leads to an immediate photoenhancement (Figure 7, row 3).

The stable optical properties of the core/thick graded shell $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs support the outlined mechanisms for the core CdSe and core/shell CdSe/ZnS QDs. As with the thin shell version, upon light exposure the core/thick graded shell $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs likely undergo some degree of surface oxidation and degradation (Figure 7, row 4). However, the graded shell is very thick (2.7 nm), which effectively isolates the CdSe core from any changes on the shell surface, preventing blue shifting, PL decay, and PL recovery.

General QD selection and evaluation guidelines have been developed based on these findings that outline the experimental tests that should be employed to test whether a specific QD architecture meets the requirements or assumptions of the device/process/application/measurement for which the QDs are being considered with overall spectral behaviors summarized in Table 3.

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CONCLUSIONS

The evolution of PL from core, core/shell, and core/graded shell green-emitting QDs in QD-polymer films was examined under different light exposure conditions in environments commonly experienced by QD systems. It was shown that the compositional profile/shell thickness of QDs (core, core/shell, core/graded shell) significantly affects how the optical characteristics evolve, with very distinct changes occurring for different QD types. For example, decreasing, increasing, and stable intensity were all observed, which could be reversible or irreversible depending on QD type. In addition, spectral blue shifting was observed in some instances and not in others.

The distinct response of each type of QD arises from how the core (and shell) material interacts with oxygen, H₂O, and light. For a core CdSe QD, the material confining the exciton is in immediate contact with its surroundings, and thus responds quickly and strongly to external stimuli. However, thin shell QDs (including core/shell CdSe/ZnS QD and thin graded shell $CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y$ QD) have an inorganic barrier that can (initially) isolate the core from the environment but that can eventually degrade leading to competing physical mechanisms and interesting optical behavior. Finally, a thick graded shell in core/graded shell CdSe/Cd1-xZnxSe1-ySy QD provides exceptional protection for the CdSe core, due to the shell thickness and thermodynamic considerations, which leads to very stable optical properties. These results clearly demonstrate the importance of proper compositional design for the QD depending on the requirements of the stable or dynamic photonic system.

These experiments form one of the first comprehensive studies on how QD architecture relates to emission evolution under various external influences, and they provide evidence of the chemical and physical changes underlying this evolution. For example, we are able to dispel the common notion that depositing an inorganic shell on a core QD (to make a core/ shell QD) ensures strong isolation from the environment. These results provide significant insight into the various mechanisms at play in QDs of different compositional profile under the conditions often experienced by QD photonic systems. Furthermore, it was demonstrated that both reversible and irreversible mechanisms can be active within a QD at the same time, which can lead to a decoupling of optical properties that might not be anticipated (reversible intensity changes versus irreversible spectral shifts). This work may serve as a general framework for evaluating quantum dots in future studies, as well as help identify the appropriate QD composition profile for a specific application.

We suggest these results (and the strategies to obtain them) are significant because they are relevant to the majority of scientific studies and technological applications that make use of the emission from QDs. Furthermore, these results are critical to consider when making assumptions about the stability of QD emission (spectral position, fwhm, and intensity). This includes characterization techniques where stable emission is required to obtain meaningful results (for example, the variable strip length method or fluorescence lifetime imaging), and photonic systems where long lifetimes are desired (e.g., QD displays, LEDs, and lasers). Finally, scenarios exist where unstable emission is desired (or required) for the device to function (for example, sensors for light, oxygen, water).

Future studies should examine how to tune the decay-torecovery behavior of intensity in core/shell QDs by controlling the relevant strength of the decay and recovery mechanisms. This could include changing shell thickness or interfacial defect concentration. Furthermore, investigations into QDs with lower (red-emitting) and higher (blue-emitting) bandgaps should be conducted to see if similar relationships exist.

EXPERIMENTAL METHODS

Chemicals and Materials. Cadmium oxide, tri-*n*-octylphosphine (TOP, 90%), and selenium powder, were obtained from Sigma-Aldrich. 1-Tetradecylphosphonic acid (TDPA, 98%), tri-*n*-octylphosphine oxide (TOPO, 90%), diethylzinc (15 wt % in hexane), and hexane were obtained from Alfa Aesar. 1-Octadecene (ODE, 90%), hexadecylamine (HDA, 90%), butylamine (BA, 98%), oleic acid (OA, 97%), and bis(trimethylsilyl) sulfide (95%) were obtained from TCI. Poly(methyl methacrylate) (PMMA; MW = 120000) was obtained from Sigma-Aldrich. Toluene was obtained from BDH Chemicals. All chemicals were used as received.

Synthesis, Unstable Green CdSe QDs, and CdSe/ZnS QDs. Green-emitting CdSe QDs were synthesized following a literature procedure.^{25,43} Initially, 50 mg of CdO, 300 mg of TDPA, and 4 g of TOPO were inserted into a three-neck flask. The mixture was heated to 120 °C and degassed for 1 h. Subsequently, the temperature was increased to 290 °C under Argon. After the solution became clear and transparent, 1 mL of 1 M Se/TBP solution was quickly injected in order to initiate nucleation and growth. CdSe QDs were grown at 290 °C for 10 s. The heating mantle was then removed to stop the reaction. Afterward, once the temperature reached 70 °C, 5 mL of hexane was added to the solution.

The ZnS shell for the unstable CdSe/ZnS core/shell QDs was synthesized following a procedure reported in literature.^{15,25} Initially, 2 g of TOPO and 1 g of hexadecylamine (HDA) were inserted into a three-neck flask and degassed at 120 °C for 1 h. Afterward, 5 mL of plain CdSe core QDs were added and the temperature was increased to 220 °C under argon. Following this, precursor solution (0.15 mL of diethylzinc and 0.05 mL of bis(trimethylsilyl) sulfide in 1 mL of trioctylphosphine) was injected dropwise to the vigorously stirring reaction mixture. The reaction proceeded for 30 min to grow the ZnS shell. The heating mantle was then removed to stop reaction. A total of 5 mL of hexane was added to the solution once the temperature reached 70 °C.

Synthesis, Stable Green Core/Graded Shell CdSe/ Cd_{1-x}Zn_xSe_{1-y}S_y QDs. Stable green core/graded shell CdSe/ $Cd_{1-x}Zn_xSe_{1-y}S_y$ QDs were synthesized by modifying a reported method.^{44,45} Briefly, 0.2 mmol of CdO, 4 mmol of Zn(acetate)₂, 5 mL of oleic acid, and 15 mL of 1-octadecene were inserted into a three-neck flask and degassed at 150 °C for 1 h. The reaction was heated to 300 °C under argon. For the thick shell QDs, at the elevated temperature (300 °C), 1 mmol of Se, and 4 mmol of S in 2 mL of TOP were rapidly injected into the reaction vessel. The reaction was allowed to proceed at 300 °C for 10 min and then the reaction was stopped by removing the heating mantle. A total of 5 mL of hexane was added to the solution once the temperature reached 70 $^\circ$ C. The thin shell graded shell QDs were synthesized with a slightly shorter reaction time and reactant ratio. A ligand exchange with hexadecylamine was performed to ensure adequate solubility of QDs in PMMA.

Sample Preparation. QD-polymer films of thickness 270 nm (\pm 50 nm) (as evaluated by ellipsometry) were prepared by spin-casting a QD-polymer mixture at 2500 rpm for 1 min, as outlined previously.²⁵ Films had a QD-loading of approximately 1% (volume fraction) which was estimated via fitting of refractive indices derived from ellipsometry data with the Bruggeman model.⁵⁴ The QD-polymer mixture was made by mixing equal volumes of QD (toluene) solution with a 10–12% PMMA (toluene) solution, which was then vortexed. Films were deposited on silicon with a \approx 290 nm surface layer of SiO₂.

Characterization. QD extinction spectra were collected using a Shimadzu UV–vis-2450 spectrometer with D2 and tungsten lamps provided a wavelength range of 300–1100 nm. The spectra were corrected against the solvent background using the same quartz cuvette. Photoluminescence of QDs in solution were performed using a Shimadzu RF-5301PC spectrofluorophotometer with a spectral range of 400–750 nm (1 nm intervals). For the evolution of QD PL in solution, the QD solutions were typically diluted 300–500 times with toluene. The diluted QD solution was then stored under dark for an hour to allow for colloidal stabilization of the QD solution, which provides more reliable data sets. Measurements were conducted over an hour using an excitation wavelength of 440 nm. Three measurements were performed for each QD solution and then averaged.

The photoluminescence evolution studies of QD-polymer films were carried out by examining spectra of the QD-polymer films from hyperspectral datacubes that were collected using a CytoViva Hyperspectral scanning system with a diffraction grating spectrophotometer (spectral range: 400-1000 nm). The evolution of photoluminescence (PL) intensity the various QD types was examined under continuous light exposure (450-490 nm) over a period of 45 min. A 10× objective (NA: 0.30) was used during scanning. All power values are the power measured at 470 nm (center wavelength of the 450-490 nm blue filter bandwidth). The photoluminescence filter cube had optical excitation from a blue bandpass filter (450-490 nm) with a dichroic mirror that reflects optical wavelengths below 495 nm and with a long-pass emission filter that passes optical wavelengths above 500 nm. A 0.25 s exposure time (per line) was used for most scans, with the early dynamics collected by treating a line of a hyperspectral data cube as a point in time (approximately 650 points per line were averaged). Hyperspectral scanning was performed using the same blue excitation bandpass filter (450-490 nm) used for light exposure. The light source was a 120 W Hg vapor short arc lamp with controllable power output (X-cite series, 120Q, Lumen Dynamics). Note, a Savitzky-Golay filter was applied in some instances to reduce high frequency noise.

All continuous PL evolution studies of the QD films used an average of 3 trials that were averaged. Each data point was itself an average of more than 600 spectra obtained from a hyperspectral scan (CytoViva Hyperspectral scanning system). For the PL evolution studies of QD-polymer films in darkness, each data point (at each time step) were collected from a region of the film that had not yet been exposed to light. This approach helped minimize "contaminating" the darkness study by previous light exposure. For each trial of the continuous light exposure evolution study of QD-polymer films, a single region of the film was examined throughout the entire exposure period (typically 45 min). For the thin shell core/graded shell QDs, the more prominent of two PL peaks was tracked since the smaller PL peak was considered to be due to a slightly smaller contamination QD distribution that arose during QD shelling. The continuous light exposure evolution study of QD-polymer films focused on a single region of the film throughout the entire exposure period (typically 45 min). The light exposure– darkness–light exposure experiment was performed by also examining a specific region of the QD-polymer film throughout the trial. The darkness step was performed by closing the shutter on the microscope, which allowed the sample to remain in the same spot after the measurement resumed. All evolution studies were performed under ambient temperature, pressure, and atmosphere unless otherwise specified. For the examination of pure QD films exposed to water, the QD films were soaked in H_2O for 10 min then examined immediately.

Photoluminescence, dark field, and bright field images were collected with a cooled Dagexcel-M Digital Firewire camera and $10 \times$ objective (NA: 0.30), as outlined previously. All photoluminescence imaging was performed using the same blue excitation filter cube from the hyperspectral scans, and the same Hg vapor short arc lamp light source.

The size of the quantum dots was determined using transmission electron microscopy (TEM). The QDs were dispersed in chloroform and hexane, dropped onto a TEM grid, and then examined with a JEOL 100 CX-ll TEM using an accelerating voltage of 100 keV. Approximately 150 particles were examined and averaged to determine the total outer diameter of the QDs. UV–vis spectroscopy was used to measure the 1s absorption peak in order to estimate the diameter of the core via known size-absorption relationships.⁵⁵ The shell thickness was calculated from half the difference between these values.

The thickness of QD-polymer films was determined by spectroscopic ellipsometry (Woollam, model M2000). A wavelength range of 245–1000 nm and a rotating compensator configuration were used. Film thickness was obtained by applying a Cauchy model to the near-transparent wavelength region of a QD-polymer film's optical spectrum, as outlined previously.²⁵

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.7b00173.

TEM of core/shell and thin and thick core/graded shell QDs; UV-vis absorbance, and photoluminescence of core CdSe QD, CdSe/ZnS core/shell QD, and CdSe/ $Cd_{1-x}Zn_xSe_{1-y}S_y$ core/graded shell QDs; Optical imaging of QD-PMMÁ films; Proposed physical evolution of each type of QD; Time evolved PL imaging of an unstable core CdSe and stable CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y core/ graded shell QD-PMMA; Evolution of the PL intensity and PL peak position of each QD solution; PL imaging of an unstable CdSe/ZnS core/shell QD-PMMA film under an exposure-darkness-exposure light cycle; Spectral red-shift data of CdSe/ZnS QDs; Affect of darkness on the PL intensity of thin shell CdSe/ Cd_{1-x}Zn_xSe_{1-y}S_y core/graded shell QDs; Evolution of PL intensity and spectral position for a QD-PMMA film during a darkness-exposure-darkness and a continuous exposure trial (PDF).

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Notes

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