Photoluminescence of Colloidal CdSe/ZnS Quantum Dots: The Critical Effect of Water Molecules

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An investigation of the photoinduced fluorescence enhancement (PFE) behavior of CdSe/ZnS core/shell quantum dots deposited at low densities, under anhydrous and controlled water humidity, under oxygen or argon, is presented. The photoluminescence properties of CdSe/ZnS QDs are highly dependent upon the local gaseous environment. Under anhydrous conditions, under either oxygen or argon, there was no observed PFE, even though there were remarkable differences in the photoluminescence spectra. Under argon, (i) the initial photoluminescence properties are independent of humidity level; however, (ii) the PFE effect observed is highly dependent on the environmental humidity levels. Under oxygen, (i) the initial photoluminescence properties (spectra and yield) are dependent on humidity levels and (ii) the PFE effect observed is highly dependent on the humidity levels. Comparing D_2O versus H_2O humidity level effects on the photoluminescence properties of CdSe/ZnS QDs provides evidence for a water-molecule-stabilized state that facilitates luminescence processes. The products of CdSe/ZnS QDs exposed under a humid oxygen environment were evaluated by X-ray photoelectron spectroscopy. Oxidation of both the CdSe core and the ZnS shell was established. Oxidation of the ZnS shell is suggested to be a result of reaction with peroxide products resulting from the oxygen radical anion. These results highlight the important sensitivity of QDs to water and prove the existence of competing electronic and chemical effects on different time scales.

1. Introduction

Colloidal semiconductor quantum dots (QDs), made of cadmium selenide (CdSe) capped with a thin layer of higher band-gap material, zinc sulphide (ZnS), have received much attention due to their unique optical properties. The photoluminescence (PL) spectra are narrow and centered at a wavelength that is tunable by the QD core diameter, a result of exciton confinement within the QD core.[1] The exact mechanisms controlling the PL yield remain uncertain. Even so, the broad absorption and narrow emission spectra, the high quantum yields, and photostability of CdSe/ZnS core shell QDs have meant that they have been readily adopted by the bioscience community as fluorescence probes for biomolecular and in vivo (i.e., cell biology) analytical applications.[2,3] There are concerns about the use of QDs in this way and these include (i) core degradation and the subsequent release of toxic cadmium ions[4] and (ii) photoinduced biomolecular damage.[5] However, often overlooked is the fact that the PL properties of CdSe/ZnS core shell QDs are not comparable to organic fluorophores. This is exemplified by the photoinduced fluorescence enhancement (PFE)[6] and the fluorescence intermittency (FI) (or blinking)[7−9] of QDs.

The exact mechanism to explain the PFE effect (of CdSe/ZnS core shell QDs) has been difficult to elucidate.[6] This is despite a large number of different studies having been performed where the PL has been investigated, perhaps because

of widely varying conditions. Conditions studied include under different gaseous environments,[7,10] with different capping agents[11] on various substrates,[12,13] and also where the samples of QDs have been prepared as multi- and monolayers.[14,15] Although a consensus on the PFE mechanism has not been reached, suggested mechanisms include (i) passivation of surface states by photoabsorbed molecules,[16−18] (ii) photoinduced surface transformation or photoinduced rearrangement of capping agents on QD surfaces,[6,19] (iii) photoneutralization of local charged centers inside and outside the QDs,[7] and (iv) photoionization of QDs, often termed photoelectrification.[14,20−23]

As well as studies to evaluate the PFE effect, a significant number of studies have been done to try to elucidate the mechanism of fluorescence intermittency (FI), or blinking, of colloidal CdSe/ZnS QDs.[8,12,15] In this case, dispersed samples, rather than monolayers, of CdSe/ZnS QD samples have been evaluated on substrates[7] or in solution.[6] In general, a model where there is (i) a ground state, (ii) a light-emitting state, and (iii) a "dark" trapping state is used to explain the switching "on" and "off" of photoluminescence.[24] More recently, Rosen et al. suggested "the long-lived trap hypothesis" whereby the electron or the hole is trapped in the surrounding matrix, where recombination of the photoexcited hole−electron pair occurs via a radiationless Auger process.[9] This "long-lived trap hypothesis" does not explain the experimentally observed power law distribution of the blinking times observed of CdSe/ZnS QDs, thus further explanations have been proposed, including multiple traps.[25]

The PL yield, spectrum, and lifetime of CdSe/ZnS QDs have been shown to be dependent upon the presence of water molecules (humidity), oxygen (as an electron acceptor and by energy transfer),[15,26] and electron donors or acceptors.[27−30] In

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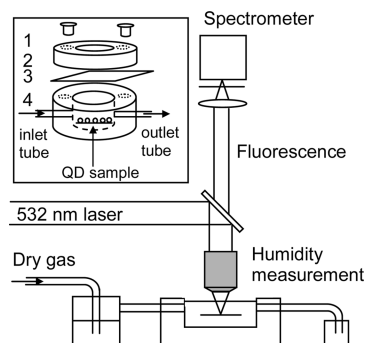‡ University of Sheffield.
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Figure 1. Schematic diagram of the experimental setup used for the PL measurements and for exposure of samples for XPS analysis. The main diagram shows a schematic representation of the chamber holding the QD sample and how this is configured with respect to how argon or oxygen gas is bubbled through H_2O or D_2O, to various depths, prior to introduction via the inlet tube of the chamber. The outlet tube is directly connected to the humidity/temperature meter for humidity measurement. The scheme shows a simplistic representation of the optical setup used for the PL spectral measurements. The inset figure shows details of the chamber consisting of (1) screw-threaded connections used for clamping and (2) a Teflon frame holding a (3) quartz window approximately 8 mm above (4) the Teflon chamber with inlet and outlet channels for the delivery of the various gases at specific humidity levels to the QD sample at the base of the chamber.

addition, it has been suggested that the emission properties of CdSe/ZnS QDs are also influenced by the properties of the substrate[13] as well as the QD density (monolayers or multilayers).[14] Thus, it is possible that the PL of QDs, and the observed effects, namely, PFE and FI, may be controlled or perturbed by the local environment in a predictable way. Currently a comparison of the various different studies done to explain PFE and PI effects is complicated by the fact that different conditions have been used for many of these studies. In this paper, the impact of humidity under either an oxygen or an argon environment on the PFE is carefully evaluated to provide a systematic understanding of the impact of environmental conditions on the PL of CdSe/ZnS QDs.

2. Experimental Methods

CdSe/ZnS QDs were obtained in toluene solution from Evident Technologies and were stored under dry argon. The peak emission is at 610 nm, corresponding to an average diameter of the CdSe core of ∼5 nm. For ensemble illumination measurements, the CdSe/ZnS QDs were dissolved at a concentration of 2 μM in dry toluene (Analar grade) and quickly dropcast (5 μL) onto a precleaned microscope slide. The resulting dry spot of CdSe/ZnS QDs has a radius of 4.0 ± 0.5 mm. Within 60s of drop-casting the samples, they were sealed in a specially fabricated flow chamber made of Teflon with a 1 mm thick glass (optical borosilicate, UQG Optics) window, shown in Figure 1, which was flushed with either argon or oxygen (BOC, 99.998% minimum purity) in the dark for at least 50 min before each measurement. The flow gas humidity was measured with an Omega RS-232 HH310 Series humidity temperature meter (error ± 0.03 mol/m³), which is based upon a semiconductor and polymer capacitive sensor. Oxygen or argon was humidified by bubbling the dry gas flow through water (Millipore) or deuterated water (99.999%, Aldrich) at various depths in a bubbler. The samples were exposed to the gas (dry or of various humidities) for a minimum of 50 min in the specially made chamber in the dark prior to exposure to the excitation laser (532 nm, V5 Verdi, Coherent Inc.) via a ×50 objective lens (NA = 0.55, Nikon) with a spot size ∼0.6 μm

waist (assuming diffraction limited). The dropcast QD samples on glass were illuminated with 532 nm light (4.1−7.3 kW/m²) under (i) an argon or (ii) an oxygen environment under a range of different humidity values. The QD photoluminescence was collected through the same lens used for excitation and imaged off a 2″ visible beamsplitter (Newport) and 570 nm long-pass filter (E570lP, Chroma) onto a spectrograph (Acton Scientific, SpectraPro 2300i spectrograph with a 300 g/mm = 500 nm grating) and a CCD camera (Acton Scientific, PIXIS 1024 CCD). We separately confirmed that this detection system remains entirely within the linear sensitivity regime and is well below saturation in all of the measurements. The camera was coupled to a computer and in-house software was used to collect QD photoluminescence data at regular time intervals. The first PL spectrum taken (i.e., $t = 0$) is the moment the sample is first illuminated with the 532 nm laser light, and the laser is left illuminated throughout the experiment with repeated spectra (integration time = 5 s) obtained during the continued illumination.

The QD samples for XPS analysis were prepared by dropcasting a thin film of QDs onto a precleaned microscope slide (as previously) and flushing the chamber cell (Figure 1) with high humidity (1.47 mol/m³) oxygen. The laser (532 nm, 23mW, ∼1 mm diameter spot size) was scanned across the sample, with a park time of 18 min per point. The illuminated QDs were then redissolved in dry toluene, dropcast onto a specially pressed aluminum receptacle (∼2.9 mm dia, 0.9 mm high, 0.5 mm thick, assuming a cylindrical shape with an average volume of 5.9 mm³, 99.999% purity aluminum foil (Sigma-Aldrich)) and stored under a dry argon atmosphere until later XPS analysis. The total quantity of illuminated QDs was ∼100 μg. The aluminum foil receptacles were precleaned by sonication for 20 min each in acetone, then methanol, dried under nitrogen flow, followed by a rinse with acetonitrile to remove any residue, and dried under nitrogen flow (all solvents used were dry and highest purity). X-ray photoelectron spectra were acquired on a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Ltd., Manchester). All samples were run as insulators, requiring use of the electron flood gun. The X-ray source was a monochromated Al source operated with an X-ray emission current of 10 mA and an anode high throughput (acceleration voltage) of 15 kV. Survey scans were acquired with a pass energy of 160 eV and a step size of 1.0 eV, whereas high-resolution spectra were collected at a pass energy of 20 eV and a step size of 0.1 eV. All spectra were charge-corrected to saturated hydrocarbon at 285.0 eV. XPS data were corrected for transmission using the NPL system. Calculation of the transmission function for each operating mode and pass energy allowed the use of a theoretical Scofield relative sensitivity factor library to generate quantitative data.

3. Results and Discussion

3.1. Photoluminescence of CdSe/ZnS QDs Dispersed on a Glass Surface under Gaseous Conditions. *3.1.1. PL Properties under Dry Argon or Dry Oxygen.* The PL spectra of dropcast CdSe/ZnS QDs excited with 532 nm light under a dry argon and dry oxygen environment (time = 0) are shown in Figure 2a. The emission yield for both samples is similar (relative quantum yield for dry argon vs dry oxygen is 1:1.2); the key difference is that the PL spectrum of the QD sample obtained under a dry oxygen environment is slightly broader and shifted to the red with respect to that of a similar QD sample under a dry argon environment (Figure 2a). The spectral red shift (at time = 0) for QDs under an oxygen environment is
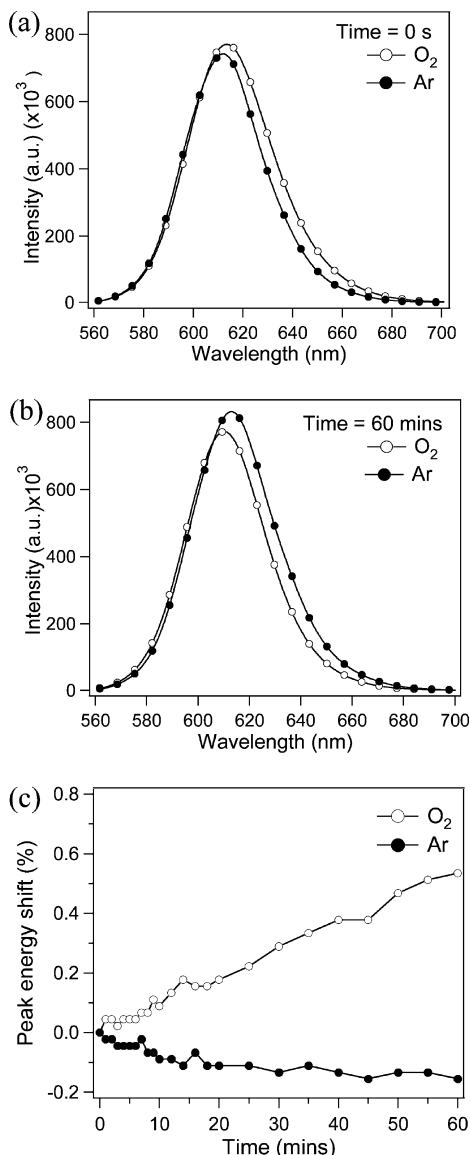
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Figure 2. (a) Photoluminescence spectra of CdSe/ZnS QD samples illuminated under dry oxygen (λ_{max} = 614 nm) and dry argon (λ_{max} = 611 nm) with 532 nm at time = 0. (b) Photoluminescence spectra of CdSe/ZnS QD samples illuminated under dry oxygen (λ_{max} = 609 nm) and dry argon (λ_{max} = 613 nm) with 532 nm at time = 60 min. (c) Plot of peak energy shift of CdSe/ZnS QD samples illuminated under dry oxygen and dry argon with 532 nm light.

similar to that observed by Shu et al.,[31] where the PL spectrum and intensity of CdSe/ZnS QDs were measured as a function of oxygen pressure. This spectral shift was suggested to be a result of a less confined electron wave function in the presence of electronegative oxygen molecule adsorbates.[31] The nonepitaxial shell is considered to be permeable to oxygen, where it is suggested that oxygen molecules pass through to the CdSe core at grain boundaries in the ZnS shell,[10,32] even for QDs with a thick shell.[15]

For the QD samples illuminated under dry argon, there is a very small detectable PFE upon prolonged illumination with 532 nm light (enhancement is only 1.12 after 60 min of illumination). However, there is a continuous red shift in peak energy and an increase in width at the fwhm of the PL spectrum with illumination time. The shift in peak energy can be seen from the emission spectrum illustrated in Figure 2b, where the λ_{max} and fwhm (time = 0) are 612 and 38 nm, respectively, and the λ_{max} and fwhm (time = 60 min) are 613 and 39 nm,

respectively. The shift in peak energy can also be seen in Figure 2c. A similar red shift in the spectral peak maximum has been observed previously where monolayers of, rather than dispersed, colloidal shell-coated CdSe-ZnS QDs were illuminated.[7,14,20,22,33] The observed red shift of the PL peak was previously considered to be due to the Stark effect caused by trapped charges at the core/shell interface or on the QD surface[6,14,20,22,33,34] and/or from interdot nonradiative energy transfer (via dipole−dipole interactions) from small to larger QDs, as observed for close-packed QDs.[35] There is a very small increase in the yield of PL from CdSe/ZnS QDs under dry argon with prolonged illumination. Although Oda et al. also showed that no PFE effect was observed for samples irradiated under vacuum,[7] they found a small PFE in the presence of dry nitrogen. Our sample differs from that of Oda et al.[7] as the illuminated CdSe/ZnS QDs are distributed over a surface (QDs separated), whereas the sample of Oda et al. is a close-packed monolayer of touching CdSe/ZnS QDs on a surface, sensitive to QD−QD interactions.

Although the initial PL spectrum (time = 0) for the QD sample under dry oxygen is broader and shifted to the red as compared with the PL spectrum of the QD sample obtained under dry argon (Figure 2a), the PL yield at $t = 0$ is similar to that of the CdSe/ZnS QD sample illuminated under argon (also shown in Figure 2a), and there is also no detectable PFE upon prolonged illumination. The only effect of prolonged illumination is a narrowing fwhm and a shift of peak maximum of the PL spectrum from the red to the blue (λ_{max} (at time = 0) is 614 nm and λ_{max} (at time = 60 min) is 610 nm), as illustrated in Figure 2c. This is the opposite effect to that seen for CdSe/ZnS QDs illuminated under argon described above. This spectral shift observed for CdSe/ZnS QDs illuminated under oxygen has previously been interpreted to be a result of oxidation of the QDs and a reduction of the core size.[10] There is not a significant enhancement or reduction of the PL of the QDs with prolonged illumination, which is consistent with previous observations of Cordero et al. where CdSe QDs were illuminated under dry oxygen.[16]

A variety of different studies have been done where CdSe/ZnS QDs have been irradiated under an oxygen-containing environment, and these include under either pure oxygen or air.[10,32] However, unfortunately, it is difficult to establish in every case if the samples have been prepared in such a way that water molecules (i.e., humidity) have been completely excluded. The results provided here demonstrate that there is a small difference in the PL spectrum and a minimal difference in yield for CdSe/ZnS QDs illuminated under a *dry* oxygen or argon environment, and these results are inconsistent with a number of studies where the PFE[16] and FI (blinking)[10,11,15] have been evaluated for CdSe/ZnS QDs under "air". Because such environments (i.e., air) contain both oxygen and water molecules, our next step was to establish the effect of humidity under an inert (argon) and oxygen environment on the PL properties of CdSe/ZnS QDs using similar conditions to those used in our experiments described above.

3.1.2. PL Properties under Argon with Different Humidity Levels. The PL spectra of dropcast CdSe/ZnS QDs were obtained only after passing argon gas at the desired humidity over the sample, for at least 50 min. The initial PL spectrum and yield ($t = 0$) for the QD samples irradiated under an argon atmosphere were shown not to be dependent upon the humidity, as seen in Figure 3a. Only the PFE has a dependence on the humidity content (Figure 3b). For instance, the PL yield increased by 55% within 10 min of illumination for the sample at 1.19 mol/m³ H_2O humidity, as compared with 43% for samples under
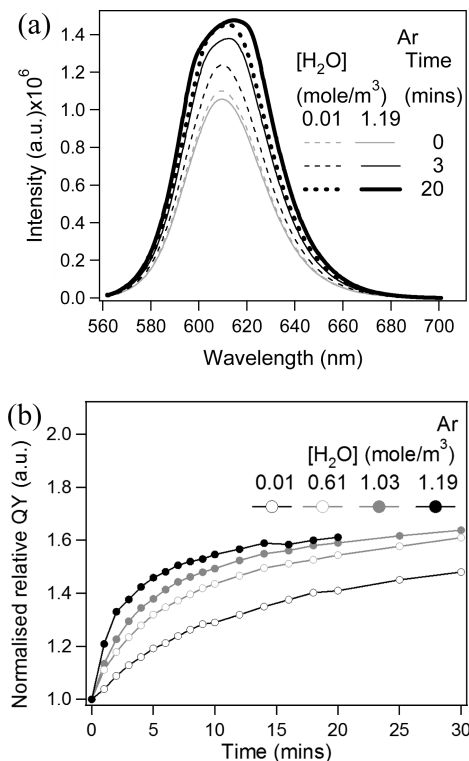
Figure 3. (a) Photoluminescence spectra of CdSe/ZnS QD samples by illumination with 532 nm under humidities of 0.01 and 1.19 mol/m^3 of water, in an argon atmosphere, at time = 0, 3, and 20 min. (b) Plot of quantum yield versus time obtained with continued illumination (532 nm, 4.1 kW/m^2), showing the PFE effect as a function of humidity in an argon atmosphere (all normalized at time = 0).

Figure 4. (a) Photoluminescence spectra of CdSe/ZnS QD samples by illumination with 532 nm under humidities of 1.19 mol/m^3 of H$_2$O and D$_2$O, in an argon atmosphere, at time = 0, 3, and 20 min. (b) Plot of quantum yield versus time obtained with continued illumination (532 nm), showing the PFE effect as a function of humidity in an argon atmosphere (all normalized at time = 0).

0.61 mol/m^3 H$_2$O humidity for the same illumination time. After 20 min of exposure under a high humidity (1.19 mol/m^3 H$_2$O) and argon environment, the PL spectrum is broader and very different to that obtained under dry argon (Figure 2). These spectral changes cannot be clearly interpreted, but what is certain is that the presence of water molecules results in a photoproduct that is different to the starting CdSe/ZnS QDs and this is crucial to the PFE effect. In short, *the initial emission yield (i.e., t = 0) is independent of the humidity, but the PFE is highly dependent on the humidity.*

To further investigate the effect of water molecules on the PFE, the effect of humidity of deuterated water (D$_2$O) was evaluated and compared with similar QD samples irradiated under similar levels of H$_2$O humidity. The use of the H$_2$O/D$_2$O solvent isotope effects have been used in the past to probe electron solvation processes,[36] electron-transfer processes (for instance, organic photoinduced reactions),[37] and electrode/electrolyte[38] electron-transfer systems. The data obtained from these experiments are shown in Figure 4. The intensity of the PL spectra obtained for QD samples illuminated under similar D$_2$O humidities as compared to H$_2$O humidities at time = 0 were lower; an example is shown in Figure 4a for the samples at 1.19 mol/m^3 humidity. In addition, the degree of enhancement of the PFE is greater in H$_2$O, as compared with D$_2$O humidity; this is most evident for the sample under 0.61 mol/m^3 humidity where the PFE is ∼30% (Figure 4b). This is easiest to see for the two samples illuminated under 0.61 mol/m^3 (i) H$_2$O and (ii) D$_2$O where the rate of the PFE is approximately 30% higher for the sample illuminated under H$_2$O humidity. However, for the samples illuminated under 1.19 mol/m^3 humidity, the rate of PFE is higher for the sample illuminated under H$_2$O as
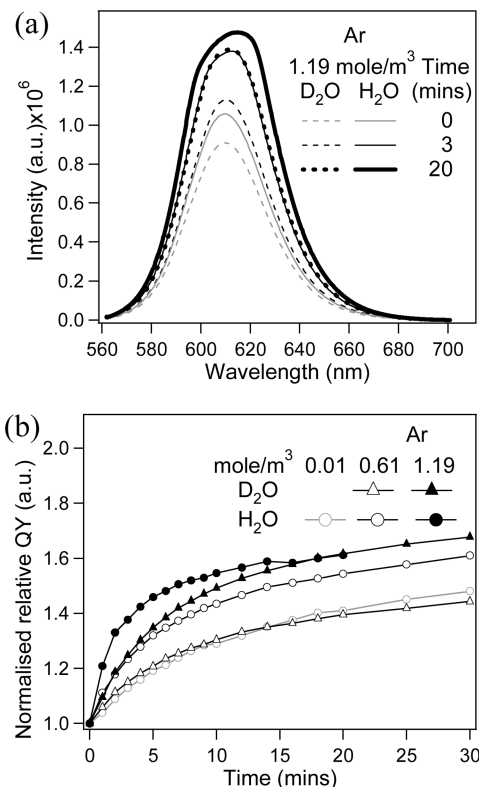
compared with D$_2$O, but both samples reach the same PFE yield after ∼15 min of illumination.

Because the initial PL yield, as reported here, is independent of the level of humidity under argon, and the PFE effect is enhanced in the presence of higher humidity, the most reasonable explanation for the observed PFE effect under argon is that the water molecules play an important role in stabilizing photoinduced charge-separated states, providing a route to preferred radiative decay. We illustrate our explanation by adaptation of the scheme proposed by Jones et al.,[6] which itself is an adapation of that of Bawendi et al.,[39] where a trap state manifold is present (Figure 5). We suggest that the water molecules play a key role in defining the identity of the surface trap (or charge-separated) state, and because a difference between the PFE effect for similar humidities of D$_2$O and H$_2$O is seen, we suggest that the trap state stabilization involves reorganization of the water environment. The isotope effect seen is due to differences in solvent reorganization energy, which is due to differences in the strength and structural order of intermolecular hydrogen bonds formed by H$_2$O and D$_2$O;[40] isotope effects have been observed for electron solvation and electron-transfer processes previously.[37,41,42] What our studies suggest is that solvation of a charged surface trap state ultimately leads to enhancement of the PL of the CdSe/ZnS quantum dots. We suggest that the trap state (TS), also called by others the charged core state,[43] is stabilized by solvation of one of the charges (e or h$^+$) forming a solvated trap state (TS$_{(aq)}$). Our mechanism presented here is in concordance with the proposal that water molecules are photoabsorbed onto the QD surface.[7,16] The initial PL yield is not dependent upon the humidity; hence, the solvated trap state (TS$_{(aq)}$) must only provide an avenue that eventually leads to the PFE effect (discussed further below).
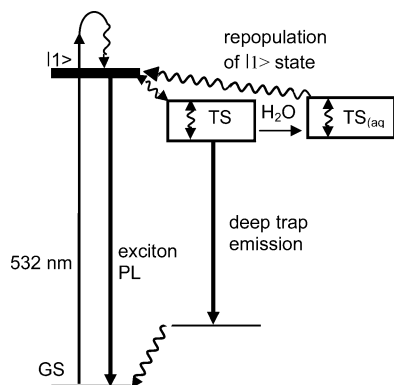
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Figure 5. Schematic illustration, which is modified from that originally proposed by Bawendi et al.[39] and adapted by Jones et al.,[6] of the postulated decay route of an exciton generated in CdSe/ZnS quantum dots and the formation of a trap state (TS) and water-stabilized trap state (TS$_{(aq)}$).

3.1.3. PL Properties under Oxygen with Different Humidity Levels.

There are significant numbers of conflicting reports on the effect of oxygen on the PL yield and PFE effect.[10,15,16,44] One of the earliest of these studies was that of van Sark et al. where a reduction in the PL of CdSe/ZnS QDs in air was observed along with a PL spectral shift to the blue.[10] It was suggested that the QDs were photooxidized and this resulted in both a reduction in the core size as well as a degradation of the ZnS shell. Also reported is the effect of air on the blinking behavior of these QDs, and this is compared with the results of Koberling et al. Koberling et al.,[8] who studied the oxygen-induced blinking of CdSe/ZnS QDs under normal oxygen pressures, suggested that the adsorbed oxygen can provide extra trap states where the Auger electrons from the QD core are trapped. The Auger electron from the QD core can now not only be transferred to the surrounding matrix or nearby QD environment but also be transferred to the adsorbed oxygen, creating a positively charged, nonemitting QD and a negatively charged oxygen radical. This is suggested to reduce the "on-time" duration in the blinking in individual QDs.

Muller et al. reported an increased PL yield in the presence of air and increased blinking rate to mean that rapid discharging of QDs due to electron transfer from the QD core to adsorbed oxygen can also lead to a PL rise for samples irradiated in air.[15] It was suggested that the low number of water molecules in the air facilitates the electron transfer by broadening the O$_2$ LUMO state of surface-adsorbed oxygen, and this then results in a reduction of the energy barrier that must be overcome during electron transfer. This effect was reversible under evacuation to vacuum. The PL of CdSe/ZnS QDs was reported by Muller et al. to be approximately twice as high in air as compared with nitrogen, and this is suggested to be due to quenching of the defect luminescence. If this is the case, then the time spent in the "dark state" is suggested to be shorter.

On the basis of the experiments reported here, where a very significant impact of humidity was observed for the PFE of CdSe/ZnS QDs under argon, it was clear that we extend our study to provide details about the PL properties of CdSe/ZnS QDs as (i) a function of humidity and (ii) under oxygen. The initial PL yield for QDs illuminated under an oxygen atmosphere, unlike under an argon atmosphere, was observed to be highly dependent upon the humidity (Figure 6). The initial yield (time = 0) of the PL for QD samples irradiated at a humidity of 0.01 mol/m^3 is ~60% lower than for similar QD samples irradiated under oxygen with a humidity of 1.47 mol/m^3. A
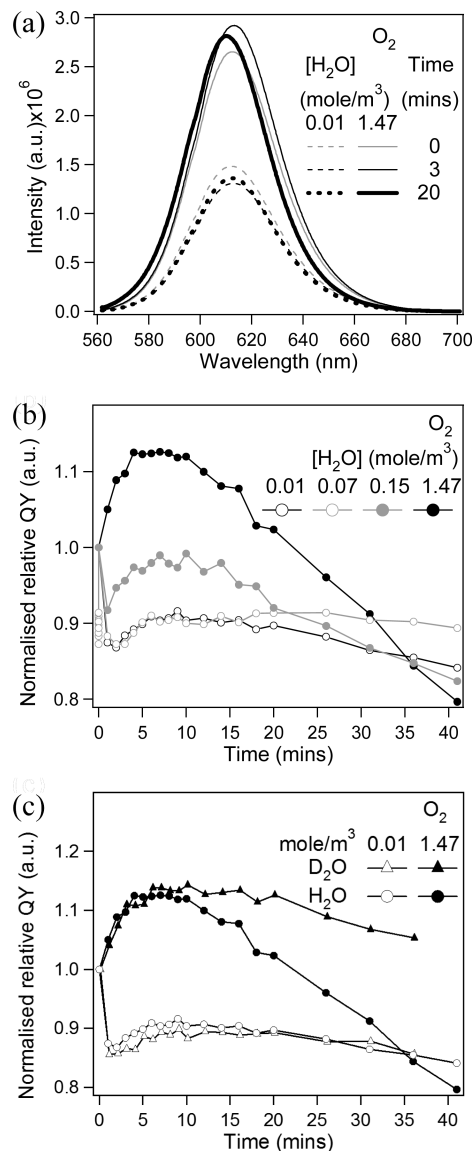

Figure 6. (a) Photoluminescence spectra of CdSe/ZnS QD samples by illumination with 532 nm under humidities of 0.01 and 1.47 mol/m^3 of water, in an oxygen atmosphere, at time = 0, 3, and 20 min. (b) Plot of quantum yield versus time obtained with continued illumination (532 nm), showing the PFE effect as a function of humidity in an oxygen atmosphere (all normalized at t = 0). (c) Plot of quantum yield versus time obtained with continued illumination (532 nm), showing the PFE effect as a function of humidity in an oxygen atmosphere (all normalized at t = 0).

further decrease in PL yield occurred very quickly (i.e., within 1 min.) with continued illumination at low humidity under oxygen (0.01 mol/m^3), and then the PL yield very slightly increased on continued illumination, but never to the original level. A similar initial reduction of the PL yield was found for samples illuminated under 0.07 and 0.15 mol/m^3 H$_2$O humidity; however, for the sample of 0.15 mol/m^3 humidity, a very apparent increase in the PL yield, with continued photoillumination, was seen (Figure 6b). In contrast, at higher humidity levels (1.47 mol/m^3) no evidence of a reduction in PL yield is seen initially (within the first 10 min of illumination), while instead, a PFE effect is observed (Figure 6a,b). For the sample illuminated under high humidity (1.47 mol/m^3), the PL level decreased after ~15 min of continued illumination. The evolution of the PL spectra is also remarkable; at low humidity (0.07 mol/m^3) under oxygen, the spectrum is relatively unchanged

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with continued illumination, whereas for samples illuminated at high humidity (1.47 mol/m^3), the PL spectrum at time = 0 has a λ_{max} at 612 nm and an fwhm of 39 nm and then shifts to the red (i.e., at time = 3 min, λ_{max} at 613 nm, fwhm of 38 nm) and then to blue at times >10 min (i.e., at time = 20 min, λ_{max} = 610 nm, fwhm of 37 nm) (Figure 6a).

The PL properties of samples of CdSe/ZnS QDs were studied under various humidity levels of D$_2$O and under oxygen and compared with similar samples illuminated under various humidity levels of H$_2$O, but obtained concurrently. Very similar results were obtained irrespective of whether H$_2$O or D$_2$O was used for samples illuminated at low humidity (0.01 mol/m^3) (Figure 6c). Two potential effects of using deuterated, versus nondeuterated water, might be expected for the sample illuminated under oxygen with different humidities:

(i) The PL yield is dependent on the same water-dependent process as seen for the CdSe/ZnS QDs illuminated under a humid argon environment, described in section 3.1.2.

(ii) The singlet oxygen lifetime is 10 times longer in deuterated water,[45] and under these conditions, enhanced peroxide products and degradation of the QDs might be expected.

The fact that there is no detectable difference in the PL properties for samples illuminated under comparable humidity levels of H$_2$O versus D$_2$O at 0.01 mol/m^3 suggests that water molecules are not as important in defining the PL properties as seen for CdSe/ZnS QDs with comparable humidity levels, but under argon. For CdSe/ZnS QDs that are illuminated at the higher humidity levels (1.19 mol/m^3) under oxygen, there is a minor difference, but this is only after longer illumination times (which are examined further in section 3.2). Thus, singlet oxygen is *not* the root of the observed differences between illumination under humid argon and oxygen.

The question thus arises as to how the humidity level in the presence of oxygen plays such a significant role in the PL yield at $t = 0$ of the CdSe/ZnS QDs. First, the difference in PL yields at $t = 0$ in the presence of oxygen at different humidities, shown Figure 6, will be discussed. This difference in the PL yield, at $t = 0$, is not seen for similar samples illuminated under argon at different humidities (Figure 3); thus, it is clear that oxygen plays a significant role in defining the PL yield. A possible suggestion is that there is a photoinduced reaction with oxygen. Indeed, oxygen is an excellent electron acceptor, and as suggested by Muller et al.,[15] hydration of oxygen will mean that the LUMO states will be broadened and this will facilitate electron transfer from the QD and yield an oxygen radical anion (superoxide radical). Such a reaction with other electron acceptors, for instance, benzoquinone, has been shown to quench the PL emission of CdSe QDs.[30] Consistent with this, Mulvaney et al. show that injection of holes into CdSe/ZnS QDs results in complete PL quenching.[46] Although we cannot rule out an alternative reaction with oxygen, we suggest that is an electron transfer to the hydrated oxygen molecules and quenching of the emission of CdSe/ZnS QDs (by hole-induced Auger) is most probable. So the question arises as to why the yield at $t = 0$ is greater at higher humidity under oxygen. We suggest that there are two competing processes occurring in the presence of oxygen and water molecules, as shown in Figure 7. At low humidity levels, the major process is reaction with oxygen, whereas at high humidity levels, the photoinduced interactions of the CdSe/ZnS QDs with water molecules predominates. The hydration of the charge-separated state (TS) to yield the solvated trap state (TS$_{(aq)}$) occurs in competition with the reaction with hydrated oxygen, and thus, at high humidity levels, higher initial PL yields are seen (see Figure 5). The water-stabilized trap state (TS$_{(aq)}$)
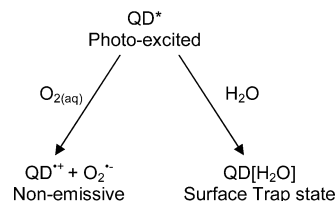

Figure 7. Schematic illustration showing the proposed interaction of hydrated oxygen and water molecules with photoexcited CdSe/ZnS QDs.

must also ultimately lead to a PL event because the PL yield is higher at $t = 0$ for samples illuminated under higher humidity levels in an oxygen environment (see Figure 6). Thus, we suggest that these water-stabilized charge-separated trap states (TS$_{(aq)}$) repopulate an exciton state more efficiently than nonradiative decay processes. In addition, the water-stabilized charge-separated trap states TS$_{(aq)}$ are not sufficiently reactive (or reducing to react) with hydrated oxygen.

A consensus for the mechanism of the PFE effect has not been reached,[6,7,14,16−23] but our results indicate clearly that water molecules play a significant role in yielding a product that is responsible for the PFE effect. Thus, our results are consistent with the proposal that the PFE effect is a result of photoactivation. In our view, this product could be from photoinduced chemisorbtion or physiosorbtion of water and these products may have higher yields of radiative as compared with nonradiative processes when illuminated again. This mechanism is consistent with a number of proposals, including that of Cordero et al.,[16] where photoinduced absorption of water is proposed; the adsorbed water molecules passivate trap states, and as a result, an increased PL is seen. An alternative proposal is that rapid carrier trapping at surface sites can follow photoexcitation and a charge state is produced, which, with subsequent excitation, can yield a charged exciton.[43] Thus, a stabilized solvated trap state (TS(aq)) may result in higher yields of charged excitons or may contribute to the photoelectrication effect consistent with the proposal of others, including Uematsu et al.[14,23]

3.2. Photoproducts of CdSe/ZnS QDs from Illumination under a Humid Oxygen Environment. We now focus on the question why there is a reduction of the emission of the CdSe/ZnS QDs sample after 15 min of illumination under oxygen. This could be a result of chemical degradation of the shell or core. To identify what are the chemical processes involved in the photoluminescence and degradation of CdSe/ZnS QDs under highly humid oxygenated environments and to verify the proposal of van Sark et al. that both the ZnS shell and the CdSe core are degraded by oxidation,[10] we used X-ray photoelectron spectroscopy (XPS) to evaluate the photoproducts. XPS spectra were taken of samples obtained by photoillumination (532 nm, 3 W/m^2) of CdSe/ZnS QDs under humid (H$_2$O = 1.47 mol/m^3) oxygen and were compared to those that had not been illuminated (Figure 8). Figure 8a shows survey spectra (binding energy = 0−1200 eV). The spectrum acquired following photoillumination of the CdSe/ZnS QDs is shown in (i), and the spectrum of CdSe/ZnS QDs that were unilluminated, but treated otherwise in the same manner, are shown in (ii). These spectra contain a number of lines assigned to elements of the starting CdSe/ZnS QDs and products. The samples also contain lines assigned to oxygen 1s and carbon 1s, and these are most likely from the capping layer of hexadecylamine. Silicon 2s and 2p lines, from adventitious silicon, are also seen. The spectrum of the unilluminated CdSe/ZnS QDs (ii) exhibits peaks attributed to a greater range of elements, including Cd and Se. A
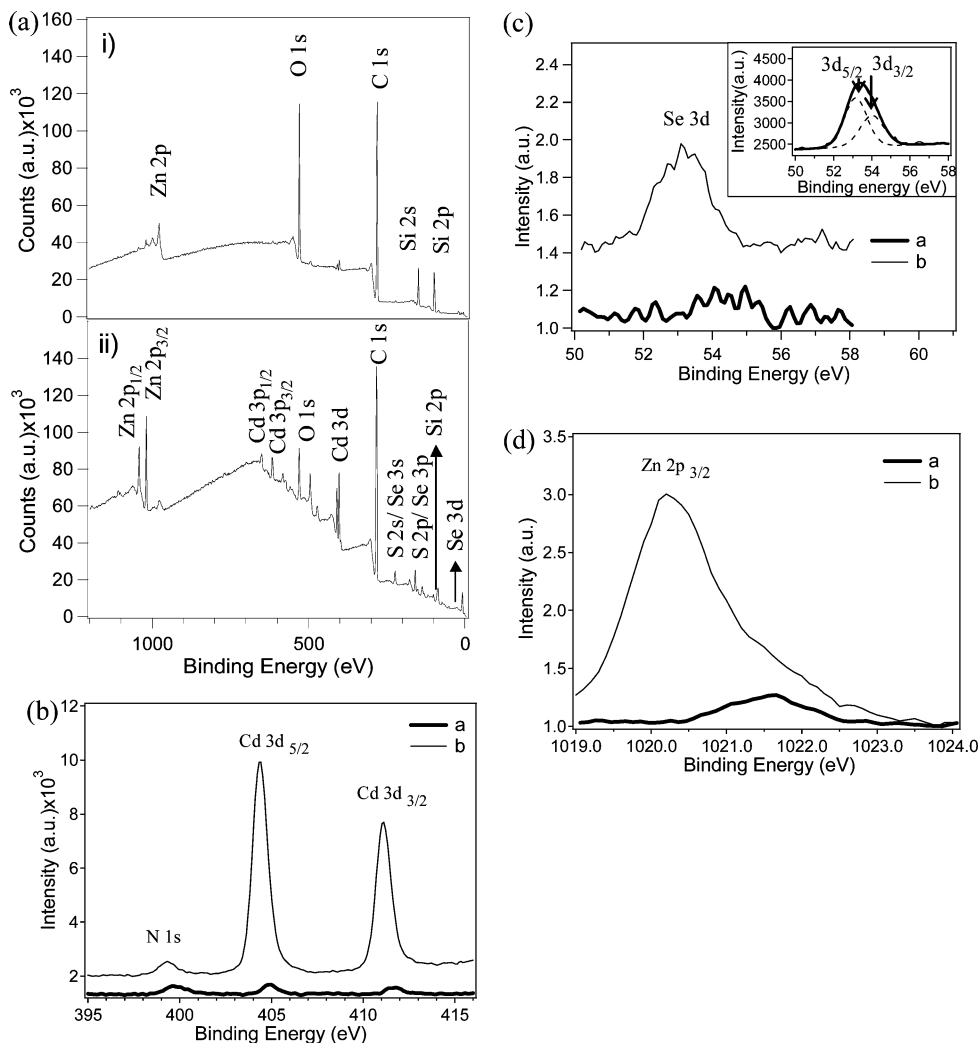
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Figure 8. (a) X-ray photoelectron spectroscopy spectra for (i) CdSe/ZnS QDs illuminated with 532 nm light (3 W/m^2) under oxygen (1.20−1.47 mol/m^3 H$_2$O) and (ii) unilluminated CdSe/ZnS QDs. (b) X-ray photoelectron spectroscopy spectra showing the Cd 3d$_{3/2}$, Cd 3d$_{5/2}$, and N 1s lines for (a) CdSe/ZnS QDs illuminated with 532 nm light under oxygen (1.20−1.47 mol/m^3 H$_2$O) and (b) unilluminated CdSe/ZnS QDs. (c) XPS spectra showing the Se 3d lines for (a) CdSe/ZnS QDs illuminated with 532 nm light under oxygen (1.20−1.47 mol/m^3 H$_2$O) and (b) unilluminated CdSe/ZnS QDs. Inset: the Se 3d signal is made up of two peaks (Se 3d$_{5/2}$ and Se 3d$_{3/2}$), separated by 0.85 eV. (d) XPS spectra showing the Zn 2p$_{3/2}$ line for (a) CdSe/ZnS QDs illuminated with 532 nm light under oxygen (1.20−1.47 mol/m^3 H$_2$O) and (b) unilluminated CdSe/ZnS QDs.

comparison of the area of the peaks for zinc 2p versus cadmium 3d and sulfur 2p, respectively, shows that the ratio changes from 3:1 to 2.1 (Zn/Cd) and 1:1 to 4:1 (Zn/S) between the spectra of the unilluminated (ii) versus the illuminated (i). In addition, the selenium 3d line cannot be detected for the illuminated sample (i). This suggests either loss of cadmium, sulfur, and selenium or that the shell of the CdSe/ZnS QDs has become thicker, (i.e., oxidation of the zinc) and a resulting reduced contribution of the QD core elements to the XPS spectra. These changes are emphasized by the spectra illustrated in Figure 8b−d and discussed below. Figure 8b shows the XPS spectra of the Cd$_{5/2}$ and Cd$_{3/2}$ lines, revealing a slight shift in the position of the Cd$_{5/2}$ line from 404.4 eV in the starting QDs to 404.9 eV in the photoilluminated sample. The position of this line is between that previously recorded for cadmium oxide (404.2 eV)[47] and cadmium selenide within a CdSe QD (405.6 ± 0.2 eV)[48] and CdSe/ZnS QD (405 eV).[49] Thus, it is not possible to state definitively that the photoilluminated sample is entirely composed of either CdSe or CdO. Figure 8c is the XPS spectrum showing the 3d$_{5/2}$ and 3d$_{3/2}$ lines for selenium. The unilluminated sample contains evidence for selenium (CdSe is at 54.0 eV and is composed of two peaks, namely, 3d$_{5/2}$ and 3d$_{3/2}$ lines separated by 0.85 eV, as a result of spin−orbit coupling). However, there

is no evidence for the presence of selenium in the sample that has been photoilluminated, which is most likely a result of photooxidation and evaporation of selenium dioxide in the vacuum pump during the XPS sample preparation.

Figure 8d is the XPS spectrum for the zinc attributed to the 2p$_{3/2}$ line, although the Zn 2p signal is also a doublet with a separation of 23 eV between the two peaks (only the 2p$_{3/2}$ line is shown). The XPS spectrum for the QD sample that has been illuminated contains a 2p$_{3/2}$ signal at 1021.8 eV, which is consistent with zinc oxide.[50] The spectrum for the unilluminated sample contains a Zn 2p$_{3/2}$ signal that is consistent with zinc sulfide. Comparison of the the XPS spectral region (157−167 eV) for the S$_{2p}$ and Se$_{3p}$ lines is not shown, although signals for the unilluminated sample can be broken down into individual contributions from the Se 3p$_{5/2}$, Se 3p$_{3/2}$, S 2p$_{5/2}$, and S 2p$_{3/2}$ lines, whereas the signals for the illuminated sample could not be detected (though this is complicated by low levels of silicon contamination detected). We note again that, if there is oxidation of the sulfide and the selenide, the products will be volatile and lost from the sample.

The most reasonable explanation for the XPS data for the signals attributable to cadmium and selenium is that the CdSe core is oxidized. CdSe nanocrystals have previously been

exposed to hydrogen peroxide and the products evaluated similarly by XPS.[51] The more surprising result here is the XPS signals attributable to zinc, which indicate that the ZnS shell of the QDs is oxidized to ZnO when illuminated under humid oxygen atmosphere. In our view, the oxidation of zinc sulfide as a result of a photoreaction is unlikely; hence, we suggest that the zinc oxide is a product of hydrogen peroxide or a peroxide radical resulting from the oxygen radical anion. Similar XPS data for the treatment of ZnS colloidal dispersions with hydrogen peroxide have been obtained.[50]

ZnS is structurally similar to and has a higher band-gap material than the CdSe core: the CdSe core is usually protected by a nonepitaxial shell of ZnS, which is suggested to passivate surface trap states,[29] increasing the emission yield. In addition, the ZnS shell is suggested to prevent photooxidation (CdSe/ZnS, TOP/TOPO QDs under air[16]); however, photooxidation has been observed (under ambient air) for core−shell CdSe/ZnS QDs.[32] This is explained by partial core exposure to oxygen due to incomplete core coverage by the ZnS shell[44] or too low a ZnS thickness[14] However, even so, a thick (4 monolayers) ZnS shell is not impermeable to oxygen, which is suggested to pass through to the core at grain boundaries in the shell.[10,32] Suggested oxidation products for core−shell QD oxidation include formation of $CdSeO_x$, where $x = 2$ or 3, at the core−shell boundary for thick, nonepitaxially grown shell,[32] or SeO_2 if the CdSe core is only partially/sparsely covered by the ZnS shell.[44] For core CdSe QDs, either SeO_2 forms if a Cd-passivating TOPO coating is present, leaving unpassivated surface Se atoms free to react with adsorbed oxygen, or a compound oxide forms, such as $CdSeO_3$, if no coating is present, leaving both Cd and Se unpassivated surface sites.[48]

4. Conclusions

The PL properties of CdSe/ZnS QDs are significantly affected by the presence of water molecules. Under inert environments (i.e., argon), the only effect is a PFE and this is proportional to the water humidity; there is no difference in the initial PL yield irrespective of humidity. It is suggested that the PFE is a result of a solvation of a charged state, a "solvated" surface trap state; this is implied by the remarkable difference in the PL properties under comparable D_2O humidity levels. Under oxygen environments, the initial PL yield is highly dependent upon the humidity, with a significant reduction in initial PL yield at low humidity levels, but at high humidity, there is a significant PFE effect and no initial PL yield reduction. We thus suggest that two competing processes must occur: (i) photoinduced electron transfer of the CdSe/ZnS QDs to generate a nonemissive QD and generation of an oxygen radical anion and (ii) water stabilization of a highly emissive surface trap state, as seen for samples illuminated under argon. With high humidity under oxygen, the PFE effect is predominant, and under low humidity levels, the photoinduced electron-transfer process is predominant. The eventual reduction in PFE of CdSe/ZnS QDs illuminated for longer time scales under a humid oxygen environment is suggested to be a result of chemical degradation of the ZnS shell by peroxide products and the core, as confirmed by XPS analysis.

Up until now, there has been a level of disagreement in the literature with respect to the PL properties of CdSe/ZnS QDs under oxygen or air environments. Our results demonstrate that the emission under oxygen is highly dependent upon the subtle differences in the humidity level. Our interpretation of the results is based upon the suggested reaction of photoexcited CdSe/ZnS QDs with oxygen that can only occur in hydrated

conditions. However, we suggest that the ionized CdSe/ZnS QDs are nonemissive, as also suggested by Mulhaney et al.[46]

CdSe/ZnS QDs are of great interest for a number of applications, including biological imaging,[5] single photon sources,[52] and photovoltaic devices.[53] In light of our observations here, we suggest that the water environment plays a significant role in the PL properties and that oxygen quenches the emission of CdSe/ZnS QDs. This information will be important in the effective use of CdSe/ZnS QDs for future applications in these areas.

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