Sensitivity versus Stability: Making Quantum Dots More Luminescent by Sulfur Photocuring without Compromising Sensor Response

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Treatment of CdSe quantum dots with a solution of elemental sulfur, followed by UVA or visible photoactivation, leads to as much as a 500% luminescence enhancement and stabilization as a result of the modification of surface sites by short sulfur oligomers. These modified quantum dots show excellent response to solution quenchers and are promising materials for the development of quantum dot-based sensors.

Introduction

Quantum dots (QDs), in particular CdSe semiconductor QDs, have found numerous applications that reflect their interesting luminescent properties.[1,2] In the case of CdSe QDs, their synthesis is relatively simple, and they can be prepared with luminescence across most of the visible spectrum by tuning their size.[3] In spite of their useful properties, QDs do suffer from a number of disadvantages, such as blinking, luminescence quantum yields that depend on their "quality" (i.e., subtle variations in their synthesis), their age, the exposure to air, the history of light exposure, and other ambient conditions.[4] Numerous efforts have been made to enhance and stabilize the QD luminescence, some of them with considerable success. For example, CdSe "core-shell" QDs, containing a shell of ZnS, are quite stable[5,6] and are readily available commercially. Similarly, the fluorescence of QDs can be stabilized with polymers containing amine ligands.[7] In a recent comparative study of core and core−shell CdSe QDs we showed that the presence of a shell greatly reduces their sensitivity toward solution quenchers,[8] something that may be desirable for simple label-type applications but is a problem for the development of QD-based sensors. In this contribution, we describe the effects of the treatment of CdSe QDs with elemental sulfur, combined (or not) with light exposure. In particular we show that treatment with elemental sulfur followed by UVA or visible irradiation leads to a remarkable enhancement of QD luminescence and to QD with improved luminescence stability. In addition, we have made a point of measuring the luminescence quantum yields before and after treatment, using emission standards with good spectral overlap with our QD samples, a consideration that has been overlooked in at least some reported studies and may have contributed to the large variability of fluorescence quantum yields in the literature.

Our studies also show that the enhanced luminescence of sulfur-treated QDs is accompanied by an improved response to solution quenchers, a property that we illustrate with 4-amino-2,2,5,5-tetramethylpiperidine oxide (4AT), a persistent free radical with excellent QD binding and quenching properties.[9]

QDs were also treated with cadmium oxide without significant change and with elemental selenium, which also gave an emission enhancement; not surprisingly, quantitative aspects of this reaction involving two solids in suspension were hard to reproduce.

Experimental Section

Materials. Tetradecylphosphonic acid (TDPA) and tri-*n*-octylphosphine (TOP) were purchased from Alfa. Selenium powder 99.99%, cadmium oxide (CdO), tri-*n*-octylphosphine oxide (TOPO), sulfur 99.999%, and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-aminoTEMPO or 4AT) were purchased from Aldrich. Methanol

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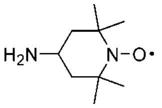
was purchased from Fisher. Chloroform OmniSolv was purchased from EM Science. All chemicals and solvents were used without further purification. All reactions were performed in a 50 mL three-neck round-bottom flask under an argon atmosphere. The injection solutions were all freshly prepared just prior to injection.



4AT

Spectroscopy and UVA Exposure Instrumentation. All the absorbance spectra were run using a Cary-50-Bio UV−visible spectrophotometer. Fluorescence spectra on liquids were done using a luminescence spectrometer from Photon Technology International. The photoreactor LZC-4 and the UVA lamps centered at 350 nm were all purchased from Luzchem Research. Fluorescence lifetime experiments were performed on an EasyLife LS from Photon Technology International, and the filters were purchased from Thorlabs Inc.

CdSe QD Synthesis. Typically, a mixture of CdO (0.0514 g, 0.40 mmol), TOPO (3.78 g, 9.77 mmol), and TDPA (0.223 g, 0.80 mmol) was heated to 300 °C and then allowed to cool down to 270 °C. A solution of Se (0.0410 g, 0.52 mmol) in TOP (2.4 mL) was swiftly injected into this hot solution. The temperature would then be allowed to drop to 250 °C for the growth of CdSe nanocrystals. Once the desired size/color (approximately 3 nm) was reached, the hot solution was poured into cold methanol, and the unused starting materials were separated from the nanocrystals by repeated centrifugation/decantation in methanol. The final product was redispersed in chloroform and kept in the dark under air for measurement and further applications.

CdSe QDs Characterization. The photochemical properties of each batch of QDs are determined with absorption and emission spectroscopy. The average size and concentration of the QDs were obtained from UV−visible absorption and fluorescence measurements following the calibration reported by Yu et al. The average size is determined using eq 1:[10]

$$D = (1.6122\times10^{-9})\lambda^4 - (2.6575\times10^{-6})\lambda^3 + (1.6242\times10^{-3})\lambda^2 - 0.4277\lambda + 41.57 \qquad (1)$$

where D is the average size of the particles (in nm) and λ the emission wavelength maximum of the solution. Then the concentration is derived using

$$c = \frac{A}{l\times\varepsilon} = \frac{A}{l\times5857(D)^{2.65}} \qquad (2)$$

where ε [$\varepsilon = 5857(D)^{2.65}$] is the molar extinction coefficient, A the maximum absorbance, l the path length, and c the concentration.

The full-width at half-maximum (fwhm) was used as an indicator of dispersity, where a fwhm < 30 nm indicates close to monodisperse samples.

CdSe QD Treatment with Elemental Sulfur (S_8). Elemental sulfur is added to the chloroform solution of CdSe at a weight percentage of 1% with respect to solvent. The solution is left to sit for 24 h in the dark, under air. Since S_8 is fully dissolved in the solvent, the QDs are precipitated in methanol followed by centrifugation and extraction, following a procedure similar to that employed in the separation following synthesis (vide supra). This ensures that no excess sulfur remains in solution as residual S_8 could have a screening effect during the irradiation process. The treated and extracted QDs are then redispersed in chloroform and kept in the dark under air for further experiments.

CdSe QD Treatment with Cadmium Oxide or with Selenium. Cadmium oxide or elemental selenium was also added to the chloroform solution of CdSe at a weight percentage of 1% for treatment (see more detail in the Supporting Information).

CdSe QDs Irradiation under UVA Light. QDs were irradiated with Luzchem UVA lamps centered at 350 nm. Each fused silica cell is placed in a photoreactor containing six lamps (corresponding to 48 W input power); these lamps deliver about 39 W/m^2 light with approximately 4% spectral contamination, mostly visible and UVB light; Luzchem photoreactors limit temperature increases to 3 °C above ambient temperature, even upon prolonged irradiation. The effect of irradiation is followed by steady-state fluorescence measurements and pursued until maximum fluorescence emission is reached.

Comparison of Irradiation at Different Wavelengths. A comparison was carried out of the effectiveness of irradiation with UVA lamps (as above), visible lamps, and lamps centered at 420 nm; the spectra of these lamps are available in the Supporting Information. For this purpose an expo panel fitted with five lamps was used, the illuminance and spectral distribution at the sample were monitored with a Luzchem SPR-4001 spectroradiometer, and the changes in absorbance and fluorescence were monitored with a Luzchem MSL spectrometer.

Quantum Yield of Fluorescence (Φ) Calculation. To obtain meaningful quantum yields it is necessary to select an appropriate reference compound. To measure relative quantum yields this reference must have an emission spectrum overlapping extensively with that of the QD and have suitable absorption so that the reference and sample can be excited at the same wavelength. Unfortunately, most spectrofluorimeters have poor spectral correction, and if the sample and reference spectra do not overlap, the yields measured can have very large errors. Further, instruments used for steady state quantum yield measurements should not have gated detection (or the gates should be much longer than the relevant lifetimes).

A dilute solution of QDs is prepared in its solvent, such that its absorbance at the excitation wavelength (λ_{ex}) would be <0.10, as well as a diluted solution of the reference of comparable absorbance. Then an emission spectrum is recorded using this λ_{ex}, and the quantum yield is obtained by

$$\Phi_{QD} = \Phi_R \frac{A_{fluoQD}}{A_{fluoR}} \frac{\alpha_R}{\alpha_{QD}} \frac{{\eta_{QD}}^2}{{\eta_R}^2} \qquad (3)$$

where R stands for reference, Φ are the quantum yields, A_{fluo} is the area under the fluorescence peak, α is the fraction of light absorbed, and η is the refractive index of the solvents.[11]

Fluorescence Quenching. Solutions of 4-amino TEMPO (4AT) were prepared in the solvent of study, in this case chloroform. The stock solution is made at [4AT] = 10 mM to have an increase of concentration upon addition from 0 to 2500 μM. The treated (QD_{S8}) and nontreated (QD) CdSe QD solutions are diluted in chloroform to obtain a final concentration of CdSe QD of 6 μM for both samples.

Quenching data were analyzed as Stern-Volmer plots. A typical Stern-Volmer plot for simple systems follows eq 4.[12]

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$$\frac{\Phi^0}{\Phi} = \frac{I^0}{I} = 1 + k_q\tau[\text{quencher}] \qquad (4)$$

where Φ^0 and Φ are the luminescence quantum yields in the absence and presence of quencher, I^0 and I are the corresponding experimental emission intensities, k_q is the bimolecular rate constant for quenching, and τ is the fluorescence lifetime. A nonlinear Stern-Volmer plot (as observed here) is a sure sign of a more complex mechanism involving states with multiple lifetimes or reactivities or the presence of different sites for the quencher on the QD surface.

Fluorescence Lifetimes. Each lifetime experiment was done with a class-I short-pulse LED matching as closely as possible the excitation wavelength of our sample (e.g., λ_{ex} = 440 nm). Long-pass cutoff filters were used to lower the spectral contamination of the decay signal (FEL 550 nm: transmits light from 550 nm and above).

Transmission Electron Microscopy (TEM). High-resolution and conventional TEM images were performed with a transmission electron microscope (TEM) JEM-2100F from JEOL Ltd. Nano-dispersed samples are deposited over 300 mesh carbon-coated gold grids from Electron Microscopy Sciences. Typically, a drop of the sample is put on the grid the day before the analysis and left to dry under vacuum overnight. No heating is performed as it might alter the dispersity of our nanoparticles.

X-ray photoelectron spectroscopy (XPS). The XPS experiments were done on the system Axis Ultra DLD from Kratos Analytica. XPS samples are prepared on a MOD 2 polished silicon wafer from Mitsubishi Silicon America. Typically, a drop of the sample is put on the wafer two days before the analysis and left to dry under vacuum overnight. It is then left to dry further in the vacuum chamber of the XPS instrument overnight.

Results

For this study we have selected rather small core QDs (2.6 nm, $\lambda_{em\ max} \sim$ 520 nm) that were prepared by the well-known TOPO method reported by Peng et al.[13] and were separated at relatively short times to prevent the formation of larger particles. Smaller QDs are known to have more surface defects and also to be more sensitive to quenching by solutes.[8,14] This makes them more challenging to stabilize but ideal substrates for our work.

At the concentration required for this work, elemental sulfur (S_8) can be dissolved in many organic solvents, including chloroform. For all our experiments, we would always compare the control QDs (QD) to the sulfur-treated QDs (QD_{S8}) first without and then with irradiation (QD(i) and $QD_{S8}(i)$, respectively). Treatment with sulfur had little effect on the fluorescence in the absence of UV irradiation, but UV exposure led to a large enhancement with a final stabilization at a fluorescence quantum yield around 0.15 (Table 1 and Scheme 1). Figure 1 shows a comparison of the response to photoexcitation of two samples differing only in that one of them had been pretreated with S_8. The actual pretreatment lasted 24 h, where the CdSe QDs were left in an environment containing elemental sulfur (QD_{S8}). However, the sample irradiated did not contain S_8 in solution, since the QD_{S8} were extracted prior to any experiment (see Experimental Section). Scheme 1 shows a graphic representation of the overall procedure.

Table 1. Quantum Yields for Fluorescence Emission before and after UVA Irradiation[a]

sample	before irradiation	after 3 h irradiation
control batch 1	0.024	0.052
S_8-treated batch 1	0.034	0.159
control batch 2	0.029	0.056
S_8-treated batch 2	0.057	0.144
control batch 3	0.054	0.012
S_8-treated batch 3	0.110	0.151
Se-treated batch 1[b]	0.028	0.042

[a] The fluorescence reference compound is fluorescein. [b] For details of the selenium treatment see Supporting Information.

Scheme 1. Sulfur Treatment Leading to Emission Enhancement

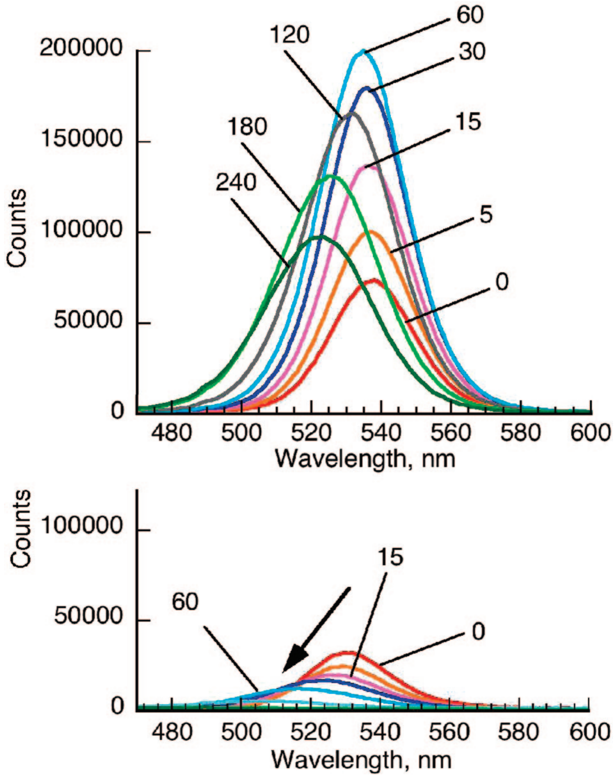

Figure 1. Luminescence behavior under UVA irradiation of CdSe QD(i) (bottom) and of CdSe $QD_{S8}(i)$ (top). Note that the vertical scales are the same for both panels. Times of UVA exposure are given in minutes.

Interestingly, several samples of $QD_{S8}(i)$ all led to approximately the same quantum yield ($\sim$0.15) after treatment (see Table 1). We note that it is not uncommon for different batches of QDs to show variable quantum yields, probably reflecting surface differences. Moreover, the irradiation of QD(i) does not always lead to fluorescence enhancement (see Control batch 3).

Quenching studies reveal that in spite of their higher luminescence, QD_{S8} are quenched more readily than QD; in

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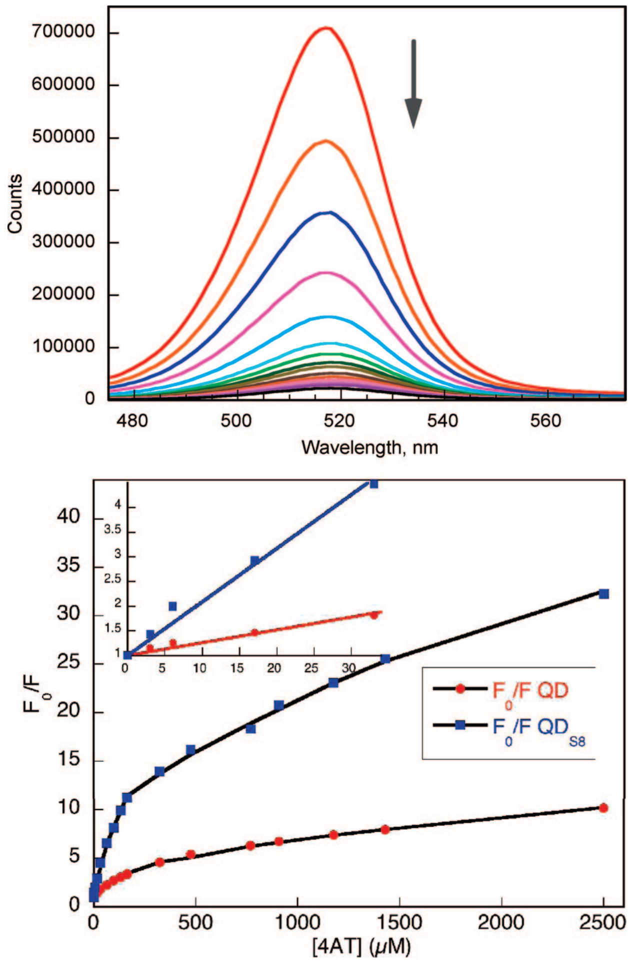

Figure 2. Quenching of the fluorescence of QD (6.0 μM) by 4AT in chloroform solutions. Top: Fluorescence emission spectra (λ_{ex}= 440 nm) of the first exciton band of QD_{S8} for various 4AT concentrations. The corresponding plot for the QD sample and the actual concentrations are given in the Supporting Information. For comparison, the prequenching counts were 709 000 for QD_{S8} and 157 000 for QD. Bottom: Stern-Volmer quenching plots calculated from spectra recorded with the same samples (F = fluorescence intensity at 510 nm, F_0 = fluorescence intensity at 510 nm with no 4AT). Inset: expansion of the Stern-Volmer plots for the low 4AT concentrations.

fact, at high quencher concentrations their emission is comparable to that of QD at the same quencher concentration (see Supporting Information for the quenching of QD). It is possible that at high concentrations the quenching is determined by TOPO exchange, as we have proposed in other systems,[8] and thus surface treatment has little impact under these conditions. The corresponding quenching plots for 4-amino-TEMPO (4AT) as a quencher are shown in Figure 2 and reveal the characteristic downward curvature observed in other studies using the same quencher.

Lifetime studies done at $\lambda_{ex} = 440$ nm revealed different behaviors for QD and QD_{S8} samples. Fluorescence decay of the $QD_{S8}(i)$ is rather stable under irradiation, whereas for QD(i) fluorescence intensity drops dramatically (see Figure 3a). Each aliquot displayed three distributions of lifetimes: one in the subnanosecond region, one around 11 ns, and one above 50 ns. Under irradiation, gradually more of the fluorescence of the untreated aliquot is due to the shortest lifetime (around 35 ns). In contrast, more of the fluorescence is gradually due to the longest lifetime for the $QD_{S8}(i)$ aliquot (see Figure 3b).

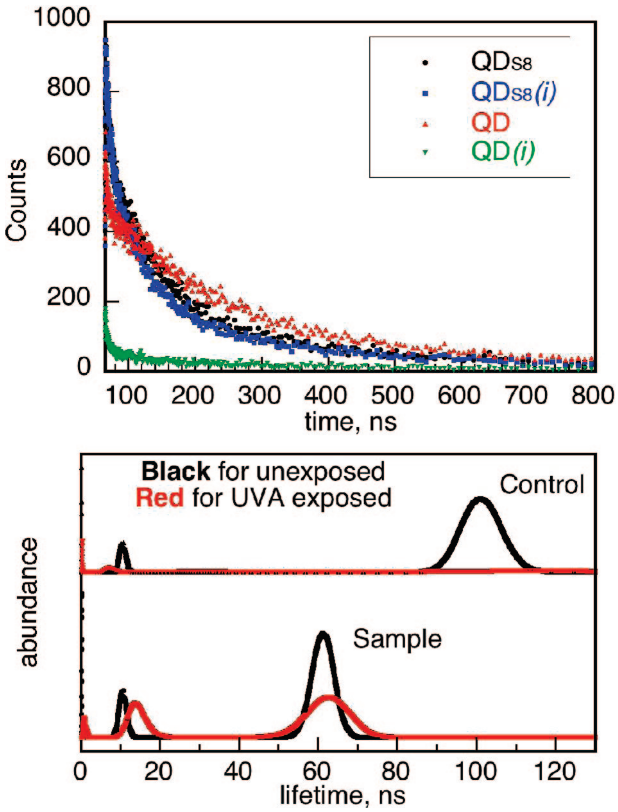

Figure 3. Lifetime study. Top: Intensity decay of QD, QD(i), QD_{S8}, and $QD_{S8}(i)$ QDs before and after UVA irradiation. Note that the control was exposed for 75 min, while the more robust S_8 treated sample was exposed for 360 min. Bottom: Lifetime distribution for each decay.

CdSe QDs absorb light in their characteristic visible band but essentially at all wavelengths in the ultraviolet region.[1] In contrast, elemental sulfur has a very weak absorption in the visible region but a very significant one in the ultraviolet region, where irradiation is known to lead to intermediates such as S_3 and S_4.[15] To evaluate which spectral region was most effective, a sample that had undergone sulfur treatment and purification was divided in several aliquots. They were irradiated with broadband visible, 420 nm, and UVA light. Our studies reveal that visible light irradiation, either broadband or at 420 nm, is also able to induce a fluorescence enhancement. This suggests that light absorption by QD (not just S_8) is capable of inducing decomposition of S_8 causing surface modifications that lead to fluorescence enhancements. Irradiation of the visible QD band is known to induce chemical changes in surface bound organic molecules.[16] Fluorescence enhancement studies combined with radiometric measurements (see Supporting Information) indicate the order of efficiency is

$$\text{UVA} > 420\text{ nm} > \text{broadband visible}$$

The differences are relatively small and may incorporate differences in light absorption.

XPS was run for both QD and QD_{S8}. XPS is a surface chemical analysis technique that allowed us to have an

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elemental analysis at the surface of our perfectly dry QD. This study confirmed the presence of the sulfur at the surface of the treated dots (see Supporting Information).

Finally a TEM image was used to compare the size of QD and QD_{S8}. For all our samples TEM characterization showed no effect on the particles size with and without treatment (see Supporting Information for an example). There was no significant difference between images acquired for treated and untreated QDs (i.e., QD and QD_{S8}).

All the samples that had been treated with elemental sulfur and kept in the dark under air displayed a more stable fluorescence emission than their untreated counterparts over time. Their fwhm remained below 30 nm, proof that they remained fairly monodisperse.

Discussion

We have shown that a pretreatment of CdSe QD with elemental sulfur followed by UVA photoactivation leads to a systematic enhancement of the fluorescence quantum yield. Our experiments also reveal some detail of the mechanism leading for fluorescence enhancement. Thus, treatment with elemental sulfur but without light must lead to the deposit of S_8 on the QD surface that persists after washing and resuspension of these TOPO-coated QDs. However, this treatment by itself is not enough to cause a significant increase in QD fluorescence.

To achieve a significant enhancement of fluorescence (sometimes as much as 500%), the sulfur-treated QD_{S8} needs to be photoactivated. This activation occurs using UVA or visible light; in the latter case, only the QD have significant absorption, suggesting that energy transfer from the QD to S_8 probably occurs, leading to significant activation of surface sulfur. Irradiation leads to a major luminescence enhancement and based on incident dose is somewhat more efficient in the UVA region (See Figure S8 in the Supporting Information). The solution photochemistry of S_8 is known to yield at least S_3 and S_4, most likely in their open form.[15] We assume that the same intermediates may be formed from surface-bound S_8. These small oligomers of sulfur are most likely more reactive than S_8 itself and bind to the CdSe surface, as revealed also by XPS; from the weak magnitude of the signals, we suggest that the amount of sulfur coverage required for fluorescence enhancement is in fact quite low. The emission data in Figure 1, as well as TEM analysis, suggest that for at least the first 30 min of irradiation this enhancement occurs without any significant decrease in size, while prolonged irradiation leads to a blue shift of the emission maxima and a small decrease of the overall emission intensity (note data at 1 h and 2 h in Figure 1); the shift indicates the particle size is decreasing with anticipated changes in surface properties. Degradation upon long-term aerobic UVA exposure is not uncommon.[16]

The lifetime experiments corroborate this trend: $QD_{S8}(i)$ displays a good stability whereas $QD(i)$ degrades fairly quickly under UVA irradiation.

It is also interesting to note at that point that the behavior observed for treated QDs is quite reproducible from one batch to another. The fluorescence is always enhanced under irradiation, and the QD_{S8} are always more responsive to quenching than the QD. The only factor that varies is the relative change between "before" and "after" manipulation. For example, a sample that already displayed good spectroscopic features without treatment has a small enhancement, whereas a poor material shows spectacular improvement. This observation supports the assumption that small oligomers of sulfur bind specifically to the surface traps (defects) of the dot and hence have more or less impact depending on the original amount of defects that were present on the surface of the QD.

The most common way of enhancing QD luminescence while improving stability is to use a "shell" of semiconductor materials with a larger band gap than the core material.[6] For CdSe QD this is frequently achieved with a ZnS shell, and this type of core−shell particles is readily available commercially. In earlier studies we have shown that core−shell nanoparticles are less prone to solution quenching than core-only particles.[8] Thus, in terms of response to quenching, the following order seems to prevail:

$$QD_{S8}(i) > \text{core QD} > \text{core−shell QD}$$

For applications as fluorescent markers, it is clear that a robust nanoparticle with minimal response to environmental quenchers would be best. On the other hand, for sensor development one would like a particle with good luminescence quantum yield and a very sensitive response to environmental quenchers; from this point of view the QD_{S8} appear promising, with excellent performance in the case of 4AT quenching.

Conclusion

In this contribution, we have shown that treatment of CdSe QDs with elemental sulfur leads to a fluorescence enhancement and excellent stability. When combined with UVA or visible light exposure, a treated sample displays a fluorescence enhancement that will depend on its initial quantum yield. We believe the elemental sulfur binds onto the surface of the QDs and more particularly at the surface defects on the nanocrystal. S_8 is known to decompose under UVA to photogenerate short oligomers such as S_4 and S_3 that appear responsible for the passivation of surface traps present on the dots; these passivated QDs show a substantial fluorescence enhancement. Such QDs are highly responsive to environmental quenchers and are thus promising materials for the development of QD-based sensors.

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Supporting Information Available: Details of cadmium oxide and selenium treatment, quantum yield determination and the importance of proper spectral overlap, additional data on 4AT quenching, and XPS and TEM data. Comparison of QD irradiation with different wavelengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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