

## Photostability of Colloidal PbSe and PbSe/PbS Core/Shell Nanocrystals in Solution and in the Solid State

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The photostability of semiconductor PbSe nanocrystals (NCs) under different storage conditions and the photoluminescence of PbSe NC films on Si substrates under vacuum and under different atmospheres were investigated. The NCs show a small blue shift in both the emission and absorption spectra when stored in solution. This blue shift is accelerated when the particles are stored in room light compared to when the particles are stored in the dark, which indicates that photooxidation is an important process. The photooxidation process is accelerated by irradiating NC solutions with a 450 W xenon lamp. The photobleaching and appearance of a precipitate are attributed to ligand desorption followed by agglomeration. Reversible O<sub>2</sub>-induced luminescence quenching was observed on a PbSe NC film on Si substrates, which could be addressed by two mechanisms: indirect quenching by alteration of PbSe charging and neutralization dynamics or quenching through direct interaction of O<sub>2</sub> with the exciton. To improve the photostability of PbSe NCs, PbSe/PbS core/shell NCs using (TOP)S (TOP = trioctylphosphine) and TMS<sub>2</sub>S (TMS<sub>2</sub> = bis(trimethylsilyl)) as sulfur sources were prepared. However, PbSe/PbS core/shell NCs did not show an increased stability in solution upon irradiation with a xenon lamp when compared with PbSe core NCs. Either the PbS shell is not able to confine the charge carriers or there is incomplete shell passivation with the PbSe core, and as a result these core/shell NCs have comparable stability.

### Introduction

Semiconductor nanocrystals (NCs) attract a great deal of interest due to their size-dependent properties. The optical absorption and emission properties of these NCs can easily be tuned due to quantum confinement. Most studies have focused on the group 12 chalcogenides, in particular the cadmium analogues, the emissions and absorptions of which can be tuned all over the visible range of the electromagnetic spectrum.<sup>1–3</sup> Recently, a liquid-phase synthesis method was reported that allows the growth of PbSe NCs in organic solution.<sup>4</sup> The procedure involves the reaction of lead oleate with trioctylphosphine selenide in diphenyl ether in the presence of an excess of oleic acid to control the growth of and protect the particles after the synthesis. The procedure was slightly modified by others, and optical properties of the NCs have been reported.<sup>5–7</sup> The band gaps of the lead salts are small, but due to the very large Bohr radii of 20 nm for PbS and 46 nm for PbSe,<sup>4,6</sup> the absorption and emission peaks of PbSe NCs can be tuned through the near-infrared from 1 to 2  $\mu\text{m}$ . Recently, even larger PbSe NCs were prepared, which allow tuning of the band gap from 2 to 4  $\mu\text{m}$ .<sup>8</sup> The application of these PbSe NCs is currently

under investigation, and electroluminescence and optical gain have been demonstrated.<sup>9,10</sup> The PbSe NCs were also successfully doped in polymer waveguides.<sup>11</sup> Using very similar synthesis procedures, it was also possible to synthesize oleate-capped PbTe and PbS NCs.<sup>12–14</sup>

Relatively little has been reported on the stability of these NCs in solution and in the solid state. The luminescence of these NCs can be very efficient when the surface of the NC is passivated with organic ligands. The quantum yield of the PbSe NCs synthesized in this method is very high, between 10% and 90% when measured by comparison with an organic dye and 20% when measured directly with an integrating sphere.<sup>10</sup> Schaller et al. reported rapid decay of the PbSe luminescence in solid films under high-power laser excitation, due to ligand desorption.<sup>9</sup> The synthesis of core/shell NCs is usually applied to increase the luminescence stability, and for most of the II–VI semiconductor NCs methods to synthesize core/shell NCs have been reported.<sup>15</sup> A shell of a large band gap semiconductor is grown over the original core in these type I core/shell structures, and the charge carriers (holes and electrons) that are generated in the NC after photon absorption are confined to the core. Surface passivation by organic ligands is less critical in these structures. Recently, type II PbSe/PbS core/shells have been synthesized by Lifshitz et al.;<sup>16</sup> however, they did not

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provide detailed characterization of the photostability. In this work we will address some stability issues of oleate-capped PbSe and PbSe/PbS core/shell NCs in solution and in the solid state, because it is expected that the luminescence stability of the NCs will have a major impact on their application in solid-state devices. The successful synthesis of PbSe/PbS core/shell NCs using TMS<sub>2</sub>S (TMS<sub>2</sub> = bis(trimethylsilyl)) or (TOP)S (TOP = trioctylphosphine) as the sulfur sources will be described as well.

## Experimental Section

**Materials.** Lead(II) acetate trihydrate (98%) was purchased from Caledon, and lead(II) oxide, octadecene (90%), oleic acid (90%), trioctylphosphine (90%), selenium (99.5%), bis(trimethyl)silyl sulfide, squalene (98%), tetrachloroethylene (99%), and diphenyl ether (99%) were purchased from Aldrich and used without further purification.

**Synthesis.** PbSe NCs were synthesized by drying 380 mg (1 mmol) of Pb(OAc)<sub>2</sub>·3H<sub>2</sub>O (or PbO) under vacuum at 130 °C for 15 min, followed by the addition of 20 mL of octadecene (ODE) and 635 μL (2 mmol) of oleic acid (OA). This mixture was heated under vacuum for 15 min at 130 °C to form Pb(oleate)<sub>2</sub> and to remove excess H<sub>2</sub>O and acetic acid. This was followed by bubbling Ar through the solution for 1 h to remove O<sub>2</sub>. In a separate flask 5 mL of TOP was put under Ar, followed by the addition of 79 mg (1 mmol) of elemental selenium. The selenium was allowed to dissolve over the course of 15 min. The reaction flask was brought to the injection temperature of 121 °C, and (TOP)Se was then injected into the mixture. The reaction was allowed to proceed without the heating conditions being changed, and samples were taken for photophysical characterization. The samples were purified by precipitation in a 4-fold excess of anhydrous ethanol and separated by centrifugation. The precipitate was washed subsequently with anhydrous ethanol and acetone, dried under an Ar stream, and dissolved in tetrachloroethylene. With an injection temperature of 121 °C and a reaction time of 4 min, this yielded about 40 mg of purified core PbSe NCs. The size of the PbSe NCs was controlled by the reaction time in this work.

Two routes were used to prepare PbSe/PbS core/shell NCs by using bis(trimethylsilyl) sulfide (TMS<sub>2</sub>S) and (TOP)S as the sulfur sources. In both cases, PbSe/PbS core/shell NCs were prepared by first synthesizing the PbSe core NCs in ODE.

When using TMS<sub>2</sub>S as the S source, the PbSe core NCs were redissolved in 10 mL of ODE and 1 mmol of OA with stirring. A solution of 0.25 mmol of Pb(oleate)<sub>2</sub> in 5 mL of ODE and 0.5 mmol of OA were added, and the solution was heated to 130 °C. At this temperature a solution of 0.2 mmol of TMS<sub>2</sub>S in 2.5 mL of TOP was added dropwise. Samples were taken from the reaction mixture after the addition of 0.3, 0.8, 1.8, and 2.5 mL of this solution, and these samples were purified in the same way as the PbSe NCs and dissolved in tetrachloroethylene.

Using (TOP)S as the S source, PbSe/PbS core/shells were prepared by a two-injection process modified from Lifshitz et al.<sup>16</sup> A typical procedure includes the following stages: A 125 mg (0.53 mmol) sample of Pb(OAc)<sub>2</sub>·3H<sub>2</sub>O, 2 mL of ODE, and 1.5 mL of OA (4.7 mmol) were mixed together and heated to 120 °C under vacuum. After the mixture became clear and was heated at 120 °C for 10 min, the vacuum was removed and Ar was bubbled through the solution followed by addition of 6 mL of TOP. The solution was then heated at 120 °C for at least 20 min, after which the mixture was cooled at room temperature for the next step. In a separate flask, 40–50 mg of PbSe NCs

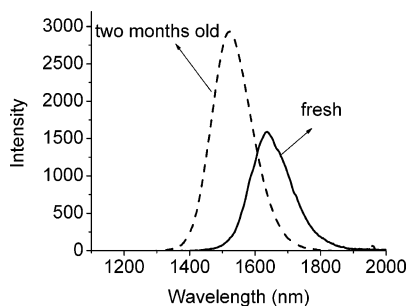
in chloroform was injected and bubbled with Ar to remove the solvent at 45 °C. When all solvent was removed, 1.5 mL of TOP was syringed to redissolve PbSe NCs followed by 80 mg of S dissolved in 0.5–1 mL of TOP solution. The whole mixture in the second flask was then injected into the first solution loaded with Pb(oleate)<sub>2</sub>, excess oleic acid, and solvent. After the combined mixture was stirred for 5 min at 45 °C, it was injected into the third flask containing 15 mL of ODE and preheated at 180 °C for shell growth. The mixture was first heated in a 180 °C oil bath for 1 min and then transferred to a 120 °C oil bath. The reaction time was controlled between 15 and 20 min. Samples were taken from the reaction mixture at different times to supervise the growth of shell materials. The samples were purified in the same way as the PbSe NCs except that the final core/shell samples were dissolved in tetrachloroethylene and filtered through a 0.45 μm glass filter (GMF, Whatman) before characterization.

**Methods.** Absorption spectra were measured on a Cary 5 UV–vis–NIR spectrophotometer. Photoluminescence measurements were done with an Edinburgh Instruments FLS 920 instrument with a 450 W Xe arc lamp as the excitation source. The excitation light was fed to a monochromator (single grating, 600 lines/mm) and focused on a square quartz cuvette (1 × 1 cm<sup>2</sup>) containing the nanoparticle solution or on a glass substrate for solid-state measurements. The emitted light was fed to a second monochromator (600 lines/mm grating) and collected on an InGaAs detector. The emission spectra were corrected for the instrument response. PbSe solid films at a density of 0.6–1.0 g/cm<sup>3</sup> were made by depositing NC solutions onto quartz slides, which were stored under ambient conditions in the dark for subsequent periodical emission measurements. Optical densities were kept between 0.1 and 0.2. For luminescence measurements under vacuum and different atmospheres, PbSe films on Si substrates were prepared by drop casting from toluene or tetrachloroethylene onto Si(100) wafer pieces. The samples were transferred into a vacuum chamber pumped by a roughing pump and with a 1 mm glass window. A 635 nm diode laser was focused onto the sample (3.5 mW, spot size ~15 μm), and the luminescence was collected by a 10× long working distance objective lens and analyzed by a Fourier-transform spectrometer with an InGaAs photodiode detector. Spectra were corrected for the instrument response. To track changes in the luminescence intensity, the total detector signal was recorded using a computer-based data acquisition system. High-purity gases (99.998% N<sub>2</sub> and 99.999% O<sub>2</sub>) were used; moist N<sub>2</sub> was obtained by bubbling N<sub>2</sub> through H<sub>2</sub>O. The O<sub>2</sub> pressure dependence was obtained by starting under vacuum and increasing the O<sub>2</sub> pressure in discrete steps; the intensity at each pressure was recorded 5 min after the pressure change.

For X-ray diffraction studies, powdered samples were smeared onto a zero-diffraction quartz plate, and the diffraction data were collected over the 2θ range 3–100° with Cu Kα (40 kV, 40 mA) radiation on a Siemens D5000 Bragg–Brentano θ–2θ diffractometer. The scanning step size was 2θ = 0.04° with a counting time of 2 s/step.

EDS (energy-dispersive X-ray spectroscopy) was conducted on an Oxford Instruments Link ISIS EDS X-Ray Microanalysis System implemented on the S-3500N scanning electron microscope.

An FEI Tecnai 200 keV field-emission transmission electron microscope at the Simon Fraser University Nano-Imaging Facility was used to collect HR-TEM images. TEM specimens



**Figure 1.** Comparison of the emission spectra ( $\lambda_{\text{ex}} = 980$  nm) of a PbSe NC solution directly after synthesis (solid line) and after storage under air in room light for 2 months (dashed line).

were prepared by dipping a copper grid (600 mesh), coated with an amorphous carbon film, into NC solutions and drying at room temperature.

## Results and Discussion

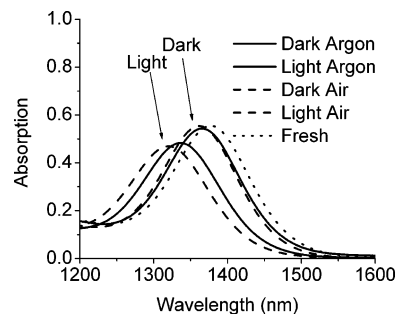
**PbSe Synthesis.** The NC synthesis was conducted by using the solvents diphenyl ether, squalene, and ODE under the same reaction conditions. PbSe NCs synthesized in ODE exhibit the best size dispersity, which is illustrated by the absorption spectra shown in Figure S1 in the Supporting Information.<sup>17</sup> ODE was selected as the solvent for the PbSe synthesis.

The size of the PbSe NCs was controlled by the reaction time in this work. The evolution of the absorption and emission spectra of a reaction in ODE is shown in Figure S2 in the Supporting Information. The growth of the NCs can be followed by the shift in the absorption spectrum. The wavelength of the first absorption peak shows a linear relationship with particle size, and it is therefore easy to determine particle sizes from the absorption spectra.<sup>7</sup> The NCs that were isolated after 1 min in the reaction showed an absorption peak at 1250 nm, which corresponds to a size of about 4 nm, and after 15 min in the reaction the NCs had grown to a size of about 6.5 nm. The emission spectra show a small Stokes shift from the peak of the absorption spectrum of about 30 nm in all samples. A similar dependence of the emission peak wavelength on the particle size is observed. The emission intensity of the samples shows a maximum after 2 min, after which the intensity slowly decreases.

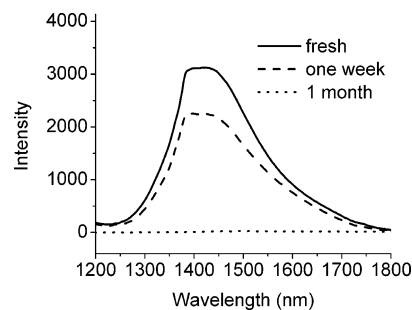
**Solution Stability.** The stability of the emission in solution was investigated by comparing the emission spectrum of a freshly prepared PbSe sample with the emission of the same sample stored in tetrachloroethylene solution under ambient conditions and in room light for 2 months. The spectra are shown in Figure 1.

A clear blue shift in the emission peak wavelength is observed, from 1637 nm for the freshly prepared sample to 1523 nm for the 2 month old sample. This blue shift in the emission spectrum is probably caused by some surface oxidation and corresponds to an effective size decrease of the PbSe core of about 0.3 nm. Furthermore, a slight increase in emission intensity is observed for this sample. An increase in emission intensity after exposure to air has been observed before with CdSe NCs under a fluorescence microscope, which was attributed to neutralization of charged particles by  $\text{O}_2$ ,<sup>18</sup> but probably this mechanism does not play a role here with these low excitation powers. We attribute the increase in intensity to improved surface passivation by surface oxidation.

To look at this surface oxidation process in more detail, a PbSe NC solution was stored under different conditions. The



**Figure 2.** Absorption spectra of PbSe NCs stored for 42 days under different conditions. The NCs with the largest blue shift compared to the fresh sample were stored in room light; the other two were stored in the dark. The dashed spectra are of NCs stored under ambient conditions; the solid lines are of NCs stored under Ar.



**Figure 3.** Emission spectra ( $\lambda_{\text{ex}} = 980$  nm) of PbSe NCs evaporated on a glass substrate right after the synthesis (solid line), after one week of storage in the dark and in air (dashed line), and after one month of storage in the dark under air (dotted line).

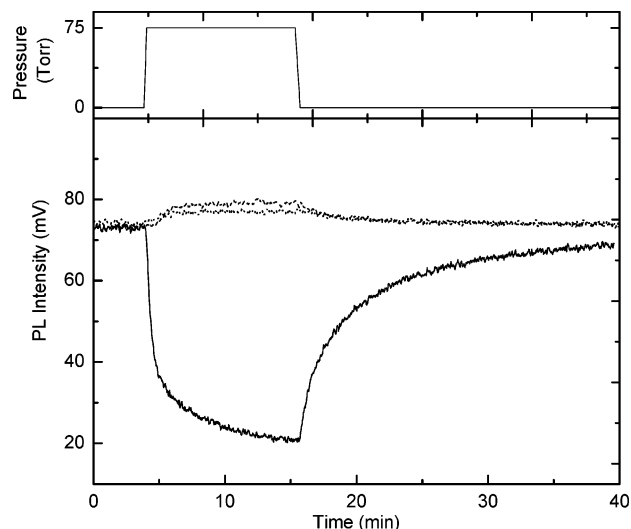
absorption spectra of PbSe NCs stored under Ar or air and in room light or in the dark are compared in Figure 2.

The largest blue shift in the absorption spectrum is observed in the samples that were stored in room light. Only a small difference between samples stored under ambient conditions and stored under Ar was observed. This experiment demonstrates that the absorption of photons accelerates the oxidation of the particle surface significantly. The small shift observed in the samples stored in the dark under Ar was probably from the ligand etching on NCs.<sup>12</sup>

**Solid Film on Quartz Slides.** The luminescence of the PbSe NCs in the solid state was measured by evaporating a drop of the NC solution on a quartz substrate. The emission spectrum is shown in Figure 3.

The emission peak of the solid-state sample does not have the Gaussian shape that the solution spectra have, which is probably caused by partial reabsorption of the emitted light or energy transfer between NCs in the relatively thick solid-state film.<sup>19,20</sup> The emission of this sample was checked after one week and after one month, after storage in the dark under air. After one week the emission intensity is only slightly lower than that of the freshly prepared sample, but after a month no emission could be observed anymore. In the solid state the decrease in emission intensity is clearly faster than in the solution phase. This could be a result of increased contact with  $\text{O}_2$  in the solid film, which is corroborated by measuring photoluminescence of PbSe NC films on Si substrates (see below).

**Photoluminescence of PbSe NC Films on Si Substrates.** Initial work revealed that PbSe NC films were substantially more luminescent under vacuum than under ambient conditions, and that these differences in intensity might be reversible. This motivated a more detailed study of the effects of different gases



**Figure 4.** Effect of 11 min of exposure of different gases on PbSe luminescence: (solid line) O<sub>2</sub>, (dotted line) N<sub>2</sub>, and (dashed line) N<sub>2</sub>/H<sub>2</sub>O.

on PbSe NC luminescence in the solid state, using laser excitation at 635 nm.

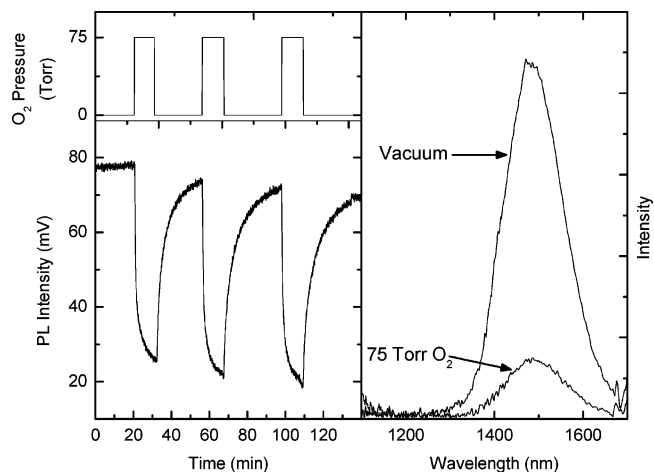
Under vacuum, the luminescence was observed to decay rapidly from an initial maximum after exposure to laser excitation (Figure S3 in the Supporting Information), with a time constant on the order of 15 s. The steady-state luminescence intensity was found to be about 65% of the initial value. A short interval without illumination (5 min) was sufficient for sample relaxation to the initial more luminescent state.

The time scale of this decay suggests that the luminescence is strongly affected by some relatively slow processes in the NC film. A similar initial luminescence bleaching has been observed for CdSe NCs as well.<sup>21</sup> The reduction in intensity for CdSe has been explained by the formation of charged, nonemissive NCs under excitation.<sup>22–24</sup> PbSe NCs have also been shown to become charged under laser illumination.<sup>25</sup>

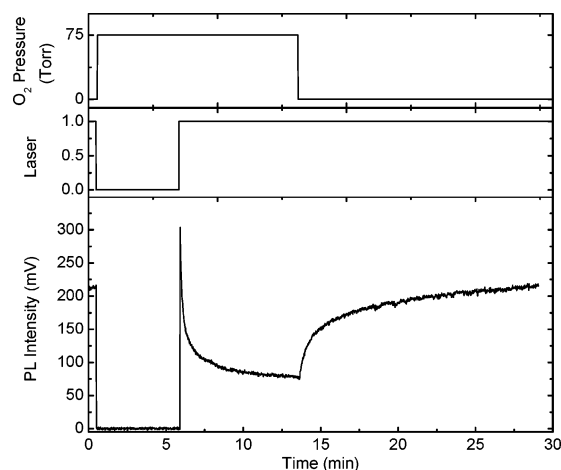
The quenching effect of the main atmospheric gases was investigated by measuring the luminescence of the PbSe NC films while introducing separately O<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub> saturated with H<sub>2</sub>O (Figure 4). While both dry and moist N<sub>2</sub> caused a modest increase in the luminescence (4% and 10%, respectively), the presence of O<sub>2</sub> reduced the luminescence to 20–30% of its steady-state vacuum value. In all cases, the luminescence recovered to its original value once vacuum was reestablished.

The lack of response of PbSe to moisture stands in contrast with PbS, for which strong moisture-related quenching is reported.<sup>26</sup> Molecular oxygen is known to affect NC luminescence,<sup>18,21,27–30</sup> and as such it was investigated in more detail. Under constant illumination, exposure of the PbSe NC film to O<sub>2</sub> strongly reduced the luminescence intensity in a reversible manner (Figure 5, left). There was no substantial shift or broadening of the emission spectrum (Figure 6, right), and the luminescence was always observed to recover to the vacuum level after O<sub>2</sub> exposure. However, some degradation (~10%) was observed over the course of several days of measurements. This is in contrast with the effect of O<sub>2</sub> on CdSe, where irreversible bleaching is observed even after a few minutes of illumination in the presence of O<sub>2</sub>.<sup>18,21,28,29</sup>

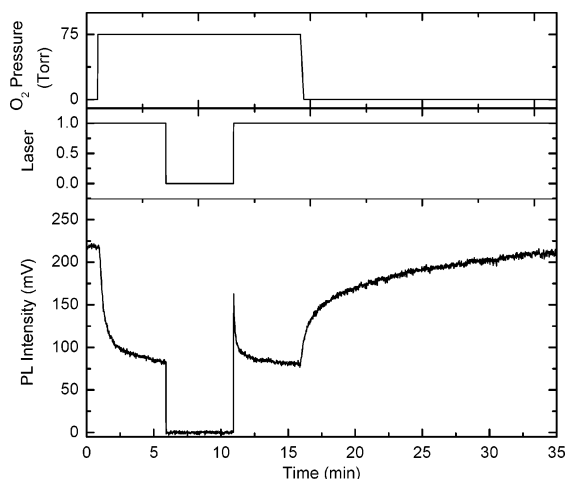
When O<sub>2</sub> was introduced before laser illumination, the initial luminescence intensity was higher than the steady-state vacuum level and then decayed to the steady-state level under O<sub>2</sub> (Figure 6). This implies that the quenching occurs through an interaction between O<sub>2</sub> and a product of laser excitation. In addition, it



**Figure 5.** (Left) PbSe luminescence quenching by repeated 11 min exposures to 75 Torr of O<sub>2</sub>. (Right) PbSe luminescence spectra under vacuum and O<sub>2</sub>.



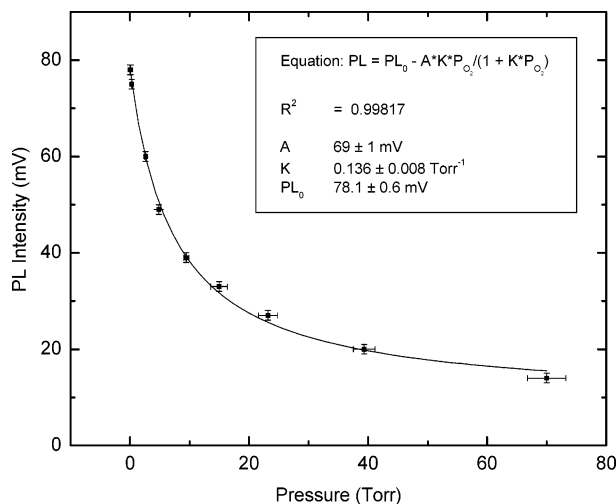
**Figure 6.** Effect of O<sub>2</sub> introduction prior to laser illumination.



**Figure 7.** Luminescence recovery under O<sub>2</sub> without laser illumination.

suggests that the decay dynamics observed when O<sub>2</sub> is introduced with laser illumination (Figure 5, left) are not limited by O<sub>2</sub> diffusion into the NC film.

A 5 min interruption of the laser illumination during O<sub>2</sub> exposure allowed a partial recovery of the luminescence to about twice the steady-state level under O<sub>2</sub> (Figure 7). The lack of complete luminescence recovery in this situation suggests that illumination under O<sub>2</sub> creates some long-lived, nonemissive PbSe species.



**Figure 8.** Pressure dependence of PbSe quenching by O<sub>2</sub>. The solid line is the fit of the Langmuir adsorption equation.

The luminescence quenching was found to obey an inverse relationship with O<sub>2</sub> pressure (Figure 8) and was reproducible from one sample to another. This pressure dependence was described quite well by the Langmuir monolayer adsorption model:

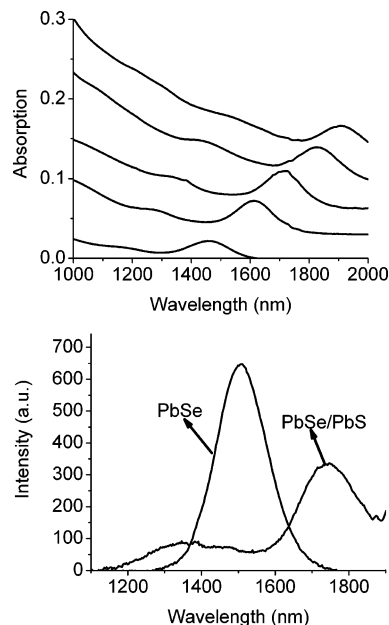
$$PL = PL_0 - \frac{AKP_{O_2}}{1 + KP_{O_2}}$$

where PL<sub>0</sub> is the vacuum luminescence intensity, P<sub>O<sub>2</sub></sub> is the O<sub>2</sub> pressure, and A and K are constants. The observed isotherm thus suggests that O<sub>2</sub> adsorption to a species within the film is the rate-limiting step of the quenching process.

There are literature reports of both reversible quenching<sup>21</sup> and enhancement<sup>18,29</sup> of CdSe NC luminescence by O<sub>2</sub>. In the case of quenching, a correlation with a shortening of the bright state of the blinking NCs was found. On the other hand, the O<sub>2</sub>-induced enhancement was assigned to passivation of surface states<sup>29</sup> or neutralization of charged NCs by electron transfer to O<sub>2</sub>.<sup>18</sup> In particular, Shu et al. found that the pressure dependence supported a monolayer adsorption mechanism.<sup>29</sup> Without any absolute measure of luminescence efficiency, these contradictory reports most likely indicate that the NC synthesis conditions play a critical role in determining the surface passivation quality and the associated sensitivity to external agents.

For PbSe, two quenching mechanisms seem possible: indirect quenching by alteration of PbSe charging and neutralization dynamics and quenching through direct interaction of O<sub>2</sub> with the exciton. It has been reported that the optical properties of semiconductor NCs can be further influenced by the nature of the substrate.<sup>31–34</sup> However, for the relatively thick films considered here, interactions with the substrate are not likely to be relevant.

Charged semiconductor NCs have been reported to be nonemissive, although this has not been shown directly for PbSe. The dynamics of luminescence quenching by O<sub>2</sub> appear to operate on time scales similar to that of the initial luminescence decay observed under vacuum (Figure S3). It would seem probable that the introduction of O<sub>2</sub> alters the processes associated with this decay, in particular by stabilizing any species receiving an Auger electron from an NC. The partial recovery observed with the laser turned off (Figure 7) also indicates that quenching is mediated by relatively slow pro-

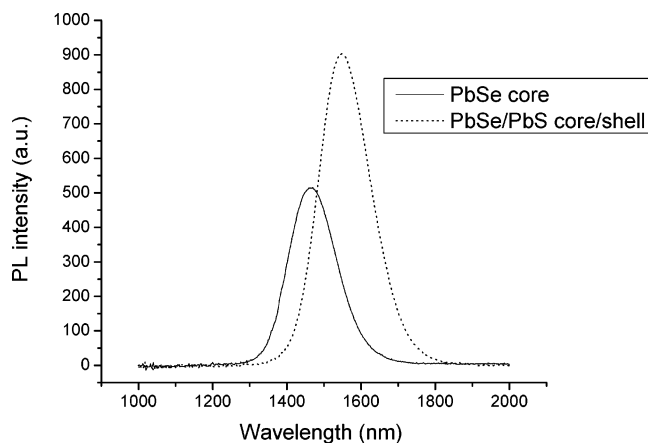


**Figure 9.** (Top) Absorption spectra of PbSe NCs and PbSe/PbS core/shell NCs. The bottom spectrum is of the PbSe NCs, and the spectra above that are from PbSe/PbS core/shell NCs after the addition of 0.3, 0.8, 1.8, and 2.5 mL of the TMS<sub>2</sub>S solution in TOP, respectively. The offset is for clarity. (Bottom) Comparison of the emission spectra of PbSe NC and PbSe/PbS core/shell NCs.

cesses. It is less clear why moist N<sub>2</sub> enhanced the luminescence, but it may be that while O<sub>2</sub> is only expected to interact with negatively charged species, H<sub>2</sub>O molecules also interact with the positively charged PbSe NC, in a manner that increases the luminescence yield.

Direct interaction of O<sub>2</sub> with the PbSe exciton is also possible and would be expected to be a fast process. In molecular photochemistry, O<sub>2</sub> is a well-known excited-state quenching agent.<sup>35</sup> Due to the low energy of the PbSe exciton (~0.8 eV), quenching through formation of the O<sub>2</sub> singlet state can be excluded, as the O<sub>2</sub> triplet-singlet transition requires 1.0 eV. That a threshold for photooxidation exists near 1 eV is illustrated by recent results for PbS NCs.<sup>36</sup> Smaller PbS NCs, emitting at 1.3 and 1.2 eV, were found to photooxidize, while larger NCs, emitting at 0.87 eV, did not. Although the size dependence of PbS photooxidation was ascribed to trap site oxidation effects,<sup>36</sup> it is likely to be more directly due to the minimum energy required for excitation of O<sub>2</sub> to its highly reactive singlet state. Other O<sub>2</sub>-mediated quenching routes (e.g., O<sub>2</sub>-mediated internal conversion,<sup>35</sup> where O<sub>2</sub> essentially acts as a nonradiative recombination center) are difficult to exclude with the present data. If the rate-limiting step is in fact O<sub>2</sub> adsorption, as suggested by the pressure dependence, then a direct quenching mechanism cannot be dismissed. It should be noted that these direct and indirect quenching mechanisms would be easily distinguishable in single-particle blinking studies, as they would respectively shorten the bright-state lifetime and increase the dark-state lifetime.

**PbSe/PbS Core/Shell.** Inorganic surface passivation was investigated by the synthesis of PbSe/PbS core/shell NCs. These NCs were synthesized in a two-step process in which the PbSe core nanoparticles were synthesized first and in a separate reaction the PbS shell was formed with an excess of lead oleate and TMS<sub>2</sub>S or (TOP)S as the sulfur source. The evolution of the absorption spectrum during the shell growth reaction with TMS<sub>2</sub>S as the S source is shown in Figure 9.



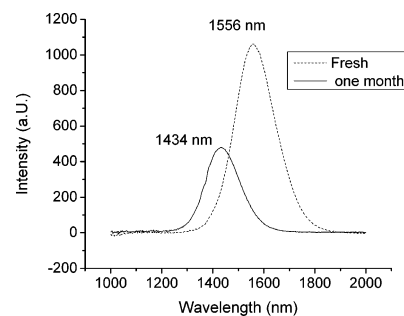
**Figure 10.** Normalized emission spectra for PbSe (solid line) and the corresponding PbSe/PbS core/shells (dashed line) in tetrachloroethylene.  $\lambda_{\text{ex}} = 890$  nm.

A comparison of the emission spectra of the PbSe core NCs and a core/shell sample is also shown in Figure 9. The core/shell sample shows two emission peaks in contrast to the core sample that shows only one emission peak. The first emission peak of the core/shell sample centered at 1350 nm is attributed to PbS NCs. Due to the high reactivity of the TMS<sub>2</sub>S sulfur reagent, it could not completely be prevented that some PbS NCs nucleated during the shell growth. The second emission peak is red-shifted (400 nm) from the emission peak of the core NCs, just like the absorption peak, which indicates that core/shell NCs were successfully synthesized. There is a small energy barrier between the core and shell. The electronic wave function of the PbSe core will then extend into the shell easily, and thus, the energy will be decreased. As a result, the emission peak will move to the lower energy, exhibiting the red shift. XRD patterns of the PbSe/PbS core/shell as synthesized are shown in Figure S5 in the Supporting Information, which present clear diffraction patterns of PbSe and PbS.

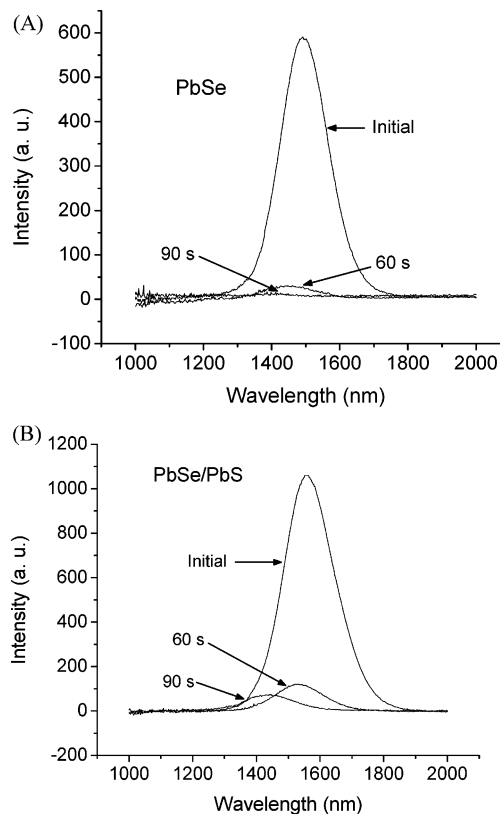
Since the PbS-only peak was almost unavoidable during the synthesis of PbSe/PbS core/shell NCs when the active TMS<sub>2</sub>S was applied, the route of using (TOP)S, a less active sulfur source, to prepare PbSe/PbS core/shells was also conducted.<sup>16</sup> By carefully controlling the Pb and S source, the PbS-only product could be avoided (Figure 10). The emission peak difference of the core and core/shell is only 86 nm, and the spectrum is Gaussian in shape.

The epitaxial growth of the PbS shell onto the PbSe core has been characterized by EDS, XRD, and HR-TEM measurements, which are presented in Figures S4–S6, respectively. From EDS results, the concentrations (atom %) of Pb, S, and Se were 1.03, 0.63, and 0.49, which matched well with a ratio  $(S + \text{Se})/\text{Pb} \approx 1$  for the PbSe/PbS core/shell. In addition, from EDS results, approximately 30 wt % PbS was determined, which is in good agreement with the XRD (Figure S5) and HR-TEM results. The spherical shape of PbSe/PbS core/shell NCs and clear fringes in the HR-TEM picture indicate the epitaxial growth of PbS onto the PbSe core (Figure S6). By measuring the particle size and HR-TEM of PbSe and PbSe/PbS NCs, a 1 nm thick PbS layer has been grown onto the PbSe core, which is close to ~30 wt % PbS.

The core/shell NCs prepared from both routes did not, however, show an increased fluorescence stability in solution compared to the PbSe core NCs, because they both presented blue-shifted properties during the storage in solution. One example is shown in Figure 11 in which the emission spectra of the freshly prepared (1556 nm) and one month old (1434



**Figure 11.** Comparison of the emission spectra ( $\lambda_{\text{ex}} = 890$  nm) of a PbSe/PbS core/shell NC solution directly after synthesis (dashed line) and after storage in tetrachloroethylene in dark room light for one month (solid line).



**Figure 12.** Emission spectra ( $\lambda_{\text{ex}} = 890$  nm) for PbSe (A) and PbSe/PbS (B) core/shell NC solutions after irradiation with a 450 xenon arc lamp at different times.

nm) PbSe/PbS core/shell are compared. We ascribe the blue shift of the core/shell NCs in solution to the inability of the PbS shell to confine the charge carriers to the PbSe core, resulting in oxidation of the core/shell NCs. On the other hand, an incomplete passivation of the PbSe core by PbS, i.e., a partial shell, cannot be ruled out, and this could be responsible for the instability during the storage.

The photooxidation process was accelerated significantly by irradiating the sample with a 450 W xenon arc lamp. When PbSe and PbSe NC solutions were placed very close to the lamp, both NCs precipitated from solution and their emission intensity died almost immediately. The emission spectra for these results are presented in Figure 12, clearly showing the instability of the core as well as the core/shell quantum dots. Very quickly after exposure to light, a precipitate formed, which is a strong indication that a massive ligand desorption took place for both core and core/shell NCs under these high illumination powers.

These “naked” quantum dots then agglomerated, followed by precipitation.

## Conclusion

Colloidal PbSe and PbSe/PbS core/shell NCs were prepared, and their photostability in solution and in the solid state was investigated. A blue shift in the emission of the NCs is observed upon prolonged storage in solution, which is attributed to a surface oxidation process. The surface oxidation process can be accelerated by irradiation with high-intensity light. This irradiation results in desorption of the ligand from the surface of the NCs, and as a result the surface would be better accessible for O<sub>2</sub> or H<sub>2</sub>O from the solution or the atmosphere. The oxidation process is faster in the solid state, which is attributed to irreversible ligand desorption.

In the solid state, the PbSe NC luminescence was reversibly quenched by O<sub>2</sub> on time scales of tens of minutes. The reversibility of this effect is strikingly different from that of all the other NC material systems. This is most likely due to the low energy of the PbSe NC exciton, which effectively prevents singlet O<sub>2</sub> formation. On longer time scales, the quenching was irreversible.

The synthesis of a PbS shell around the PbSe NCs was successful, but the PbS shell was not able to confine the charge carriers to the PbSe core. This is likely a result of the small difference in the band gap between PbSe and PbS, which results in a very small energy barrier between the core and shell.

The growth of shell materials of different semiconductors with larger band gaps is under investigation, because it is expected that these core/shell NCs would substantially increase the stability of the PbSe NCs, which would be beneficial for many of the applications of these NCs.

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**Supporting Information Available:** Figure S1 showing absorption spectra of PbSe NCs, Figure S2 showing the evolution of the absorption and emission spectra of a reaction in ODE, Figure S3 showing the rapid decay of luminescence, and Figures S4–S6 showing EDS, XRD, and HR-TEM measurements of the PbSe/PbS core/shell. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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