Highly Photoluminescent PbS Nanocrystals: The Beneficial Effect of Trioctylphosphine

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Received September 7, 2007
Revised Manuscript Received May 6, 2008

Colloidal lead chalcogenide nanocrystals (NCs), PbX (X = S, Se, and Te), have actively been studied for their applications in optoelectronics and as biological markers in recent years owing to their unique intrinsic properties.[1–9] Of particular interest are high-quality NCs that operate in the telecommunication wavelengths of 1.3−1.6 μm or the biologically transparent window of 0.7−1.1 μm.[7,10] Compared to their visible and ultraviolet light emitting counterparts, lead chalcogenide semiconductors are well suited for the near-infrared (NIR) because their small bulk band gaps (PbS, PbSe, and PbTe have bulk band gaps of 0.41, 0.28, and 0.31 eV, respectively) and large exciton Bohr radii (for instance, 20 nm for PbS) allow for relatively large nanocrystals while still maintaining quantum confinement.[4,9] PbS NCs in particular are a practical alternative to the more widely studied PbSe NCs because of the reduced toxicity level of sulfur compared to selenium, but to date PbS NCs have shown significantly lower photoluminescence.[1–3,11]

Colloidal organometallic synthetic routes for hydrophobic PbS NCs that have size-tunable NIR emission were first reported by Hines and Scholes.[3] They used highly reactive bis(trimethylsilyl) sulfide [$(TMS)_2S$] as the sulfur source and a Pb/S molar ratio of 2:1 to synthesize PbS NCs with an emission peak full width at half-maximum (fwhm) of ~100 meV, a size dispersion of 10−15%, and a luminescence quantum yield of ~20% (relative to the dye IR-125). It is well-known that capping ligands, surfactants, reaction temperature, and reagents are all factors that influence the size, shape, and optical properties of colloidal NCs.[12,13] In Hines and Scholes's synthesis, the reaction temperature and oleic acid (OA), which was used as reagent and capping ligand, were the main factors that controlled the properties of the final PbS NCs. Trioctylphosphine (TOP) and octadecene (ODE) were also used as dilution solvents for $(TMS)_2S$, but the authors reported no perceivable effects of these dilution solvents on the synthesis products. Yet, recent NMR studies have shown that TOP may play an important role in the formation of metal chalcogenide NCs.[14,15] Furthermore, using high-resolution X-ray photoelectron spectroscopy (XPS), Lobo et al. showed that OA ligands preferentially bind to lead atoms on the NC surface and leave the sulfur atoms unpassivated, which allows for possible hole traps; however, when they synthesized PbS NCs in the presence of both OA and TOP, they found that the TOP ligands efficiently bonded to the sulfur surface sites, but no optical studies were shown.[16]

In this communication we reinvestigate the synthesis of PbS NCs to determine the specific influence of TOP on their morphological and photochemical properties. We present a modified synthesis of high-quality NCs using TOP and also examine the effects of the molar ratios of reactants and dilution conditions on the properties of the NCs. We found that the introduction of TOP does have a strong positive effect on the quality of the PbS NCs produced and ultimately on their emission properties and have obtained NCs with a narrow size distribution and quantum yields as high as 80%.

Initially, reactions were guided by Hines and Scholes's synthesis, but the reactants were diluted with 20 mL of ODE (a noncoordinating solvent), and $(TMS)_2S$ was diluted in either ODE or TOP prior to injection to avoid highly concentrated reactants and fast local NC nucleation. Following their reported synthesis, we used a Pb/S molar ratio of 2:1.[3] The PbS NC nucleation and growth step typically ended at almost the same time, and relatively broad size distributions were observed (~150 meV). This is probably due to the highly reactive $(TMS)_2S$, which causes very fast NC nucleation and growth. Meanwhile, PbS NCs obtained from reactions incorporating TOP possessed increased photoluminescence intensities and slightly narrower FWHMs than those obtained without the incorporation of TOP. Reactions were then further optimized by reducing the $(TMS)_2S$ molar ratio in the presence of TOP. After increasing the Pb/S ratio above ~10:1, a distinct difference between nucleation and the growth step was observed. Finally, TOP was incorporated into the reaction flask directly rather than using it to dilute $(TMS)_2S$. The final optimized conditions include an increased solvent dilution, a higher Pb/S molar ratio, and the incorporation of TOP directly into the reaction

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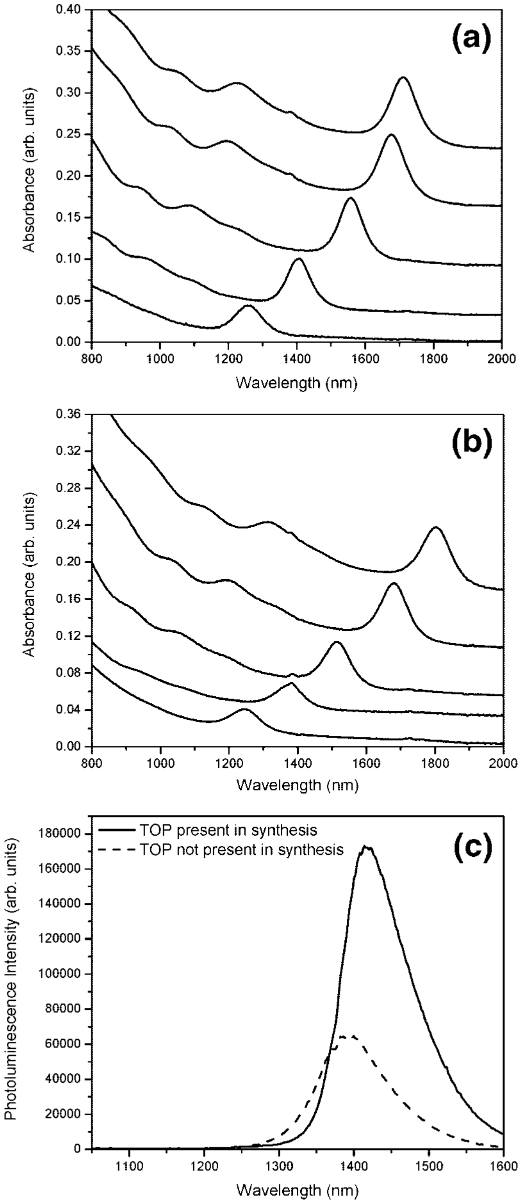

Figure 1. Absorption spectra for PbS NCs synthesized with (a) and without (b) TOP, showing increasing NC size from left to right (reaction times of 30 s and 1, 2, 4, and 8 min). Emission spectra (c) for PbS NCs (λ_{ex} = 980 nm) with and without TOP (measured with a NIR-PMT detector and having similar optical densities).

flask. The reaction was also performed under the same conditions without the addition of TOP for comparison purposes (see Supporting Information for specific details).

A high Pb/S molar ratio could result in NCs with different surface stoichiometries than those typically observed and would result in different optical properties, as has previously been speculated upon.[17] However, in our case energy dispersive X-ray spectroscopy (EDX) showed a stochiometric ratio of ~1:1 (Pb/S) for the PbS NCs (Supporting Information). Therefore, it is likely that the high Pb/S ratio and increased dilution serve only to slow down NC growth and counter the high reactivity of $(TMS)_2S$.

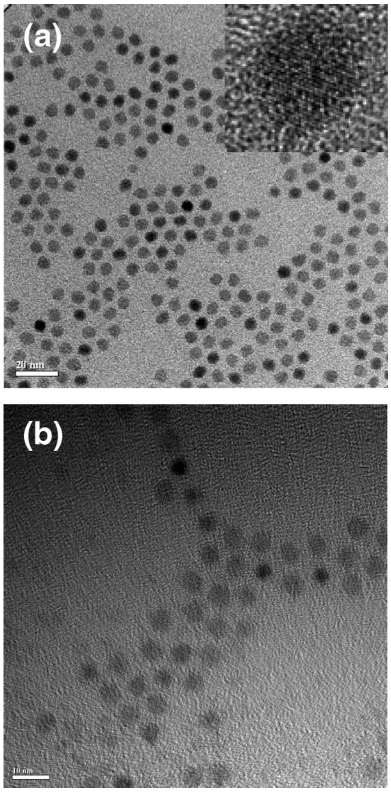

Figure 2. (a) TEM and HR-TEM (inset) images of PbS NCs synthesized in the presence of TOP (scale bar = 20 nm). Average diameter: 5.9 nm with a size dispersion of 3.7% and emission peak of 1591 nm. (b) TEM image of PbS NCs synthesized without adding TOP (scale bar = 10 nm). Average diameter: 5.7 nm with a size dispersion of 8.7%.

Figure 1 presents absorption spectra for reactions with (a) and without (b) the addition of TOP employing a Pb/S molar ratio of 26:1 (all subsequent figures represent samples made with the same molar ratio for consistency). Figure 1c shows emission spectra for both experiments measured under identical conditions (equivalent optical densities). Reactions conducted with TOP present consistently produced more emissive NCs than reactions without TOP. In general we noticed more symmetric and narrower spectral shape in the absorption and emission spectra which indicates more uniform NCs. These highly emissive PbS NCs have a fwhm as low as 49 meV and a Stokes shift as low as 7 meV (an overlay spectrum is presented in Figure S1, Supporting Information).

Relative emission intensities were determined by comparing the absorbance at the excitation wavelength (980 nm) and the integrated area under the emission spectra for NCs synthesized with and without TOP. TOP improves the photoluminescence for PbS NCs by three times on average (as seen by the emission peaks in Figure 1c). Absolute quantum yield measurements were performed with an integrating sphere for reactions containing TOP. The quantum yield was found to be as high as 80% (typically seen for 4 out of 10 reactions) for the smaller NCs (emission peaks in the range of ~1100−1300 nm) and were otherwise between 40−60%. For larger NCs (~1300−1600 nm) the quantum yield was found to be between 25−40%. These quantum yields are the highest recorded to date for PbS NCs in this size regime.[1,3,17]

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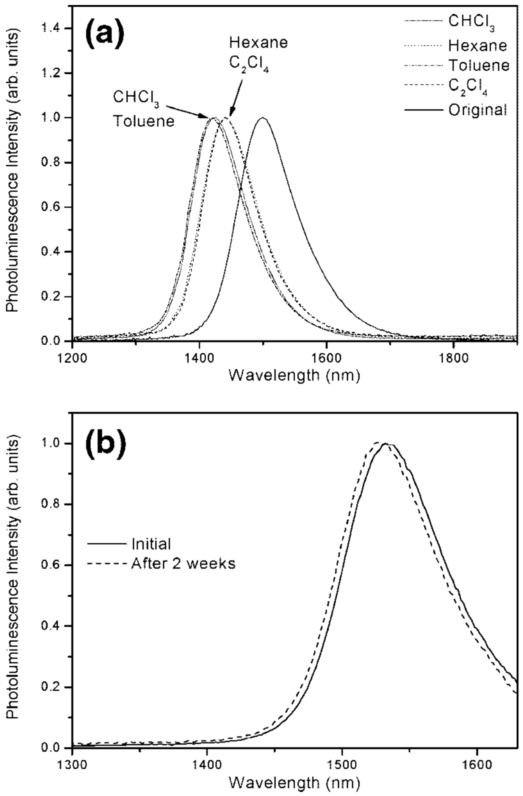

Figure 3. (a) Emission spectra for PbS NCs stored in different solvents for 4 days under ambient lighting conditions (measured with an InGaAs detector). (b) Emission spectra for PbS NCs before and after a 2 week storage period in TCE in the dark (measured with a NIR PMT detector).

Transmission electron microscopy (TEM) images of these PbS NCs are shown in Figure 2. The synthesis with added TOP only produced spherically shaped NCs (Figure 2a). The high resolution TEM (HR-TEM) (Figure 2a, insert) image shows clear lattice fringes, and the size dispersion is below 5%, indicative of highly crystalline and narrowly size-dispersed NCs. The X-ray diffraction pattern is shown in the Supporting Information (Figure S3). The synthesis without TOP (Figure 2b) also produced relatively narrow size distributions, though not to the extent of reactions containing TOP. Therefore, reactions performed using these modified conditions, both with and without TOP, produced NCs with narrower size distributions than those reported by Hines and Scholes.[3] We attribute the increase in photoluminescence with TOP to increased surface passivation rather than a change in overall nanocrystal quality, although it is possible that TOP influences the reaction kinetics and growth of the NCs as well. Phophorous was found to be present in the EDX spectrum of the final product (Supporting Information, Figure S2), indicating the presence of TOP. Presumably TOP ligands are bound to the surface of the NCs at sulfur sites, supported by the XPS work of Lobo et al.[16]

PbS NCs synthesized with TOP were redissolved into different solvents: chloroform, hexane, toluene, and tetrachloroethylene (TCE). After a 4-day storage period under ambient lighting conditions, the absorption and emission spectra of these NCs present small blue shifts, which we attribute to photo-oxidation, and the spectral shapes had hardly changed (Figure 3a). When the PbS NCs were stored in TCE for a period of 2 weeks in the dark (Figure 3b), the shift in emission peak was almost negligible. These results indicate that these PbS NCs synthesized present higher photostability than PbS NCs previously reported.[3,17] Although both the syntheses presented as well as that of Hines and Scholes require no postsynthesis size-selective precipitation, the latter required a significant size-focusing aging process afterward in an organic solvent to narrow the size dispersion. An interesting observation is that no size focusing is required in the synthesis presented (with or without TOP) to obtain high-quality NCs, though very small improvements in the absorbance spectral shape were noticed as well as small improvements in photoluminescence intensity (accompanied by small blue shifts). Therefore the large size-focusing observed by Hines and Scholes seems to be very dependent on reaction conditions since the PbS NCs grown using the synthesis presented herein produce NCs of high quality immediately following the reaction.

In conclusion, very photostable and highly photoluminescent PbS nanocrystals with narrow size distributions were synthesized by carefully optimizing the reaction conditions presented in previously reported syntheses and by incorporating TOP as a capping ligand. Experimental results show that in dilute solvent conditions with high Pb/S molar ratios, TOP improves the PbS NC quality to result in NCs with significantly higher photoluminescence than NCs obtained without adding TOP. The PbS NCs synthesized with our modified conditions exhibit unprecedented quantum yields that are comparable to those reported for PbSe NCs, which would make them more appealing candidates for application purposes and future studies.

Acknowledgment. The Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation (CFI), and the British Columbia Knowledge Development Fund (BCKDF) are all gratefully acknowledged.

Supporting Information Available: Detailed synthesis procedures for PbS NCs, characterization information, XRD, EDX, and optical data (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

CM702564A