Size Control, Shape Evolution, and Silica Coating of Near-Infrared-Emitting PbSe Quantum Dots

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Received August 22, 2006. Revised Manuscript Received February 20, 2007

The physical and optical properties of quantum dots (QDs) are governed by their particle size and shape. In this study, near-infrared-emitting PbSe QDs were synthesized with controlled size (between 7 and 12 nm) and shape (spheres, octahedrons/cubes), with tunable emission from 1200 to 1500 nm. The hydrophobic PbSe QDs were coated with a silica shell to render them water-soluble and non-cytotoxic. The cell viability of NIH-3T3 (mouse fibroblast cells) and HepG2 (human liver cancer cells) was retained at 80% even in the presence of a high QD loading of 100 μg/mL.

Introduction

Near-infrared (NIR) CdTe−CdSe core−shell quantum dots (QDs) have recently been used for sentinel lymph node cancer surgery of large animals.[1] Nanocrystals of the IV−VI semiconductors (e.g., PbS, PbSe, and PbTe) constitute an interesting class of materials because of their unique properties − strong quantum confinement (large Bohr radius of 46 nm in the case of PbSe), small Stokes shift, and bright luminescence.[2−5] The systematic manipulation of nanocrystallite size and shape remains a key synthesis challenge because the QD's size and shape would determine its physical properties.[6,7] PbSe QDs have been derived in different shapes including spheres,[8−10] cubes,[10−12] multipods,[11] rods,[11] octahedrons,[13] wires,[11,13] and rings[13] in organic solvents via organometallic synthesis. Lu et al.[12] ascribed the formation of nanocubes to a two-step evolution mechanism, which is dependent on the growth temperature and time, resulting in the formation of an octahedron and finally of a nanocube. They found that PbSe QDs (3−5 nm in size) resulted in an octahedron shape at a reaction temperature of 230 °C. In this study, the size and shape evolutions of PbSe QDs were examined, and synthesis parameters such as injection temperature and growth conditions were employed for the QD shape control. It was found that the shape evolution could occur even at a relatively low temperature of 100−150 °C with a single-injection technique.

The stable and tunable emission of NIR-emitting QDs make them suitable for applications in telecommunications (1300−1600 nm), biological imaging (transparent tissue windows at 800 and 1100 nm), and solar cells (800−2000 nm).[14] For biological applications, QDs must be water-soluble and buffer-stable.[15] The surface functionalization of NIR QDs for biological applications has received little attention in comparison to their II−VI counterparts. This report addresses these issues using a simple silica coating method in a reverse microemulsion to render PbSe QDs water-soluble and non-cytotoxic. We also demonstrate that the QDs can be encapsulated as a single core within a spherical silica shell or multiple cores within ∼40−160 nm shells.

The encapsulation of single metallic particles (e.g., Au, Ag)[16−18] or semiconductor QDs (ZnS-capped CdSe (ZnS−CdSe) and PbSe) in spherical[19] and thin[20] silica particles has

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10.1021/cm061974e CCC: $37.00
Published on Web 05/24/2007

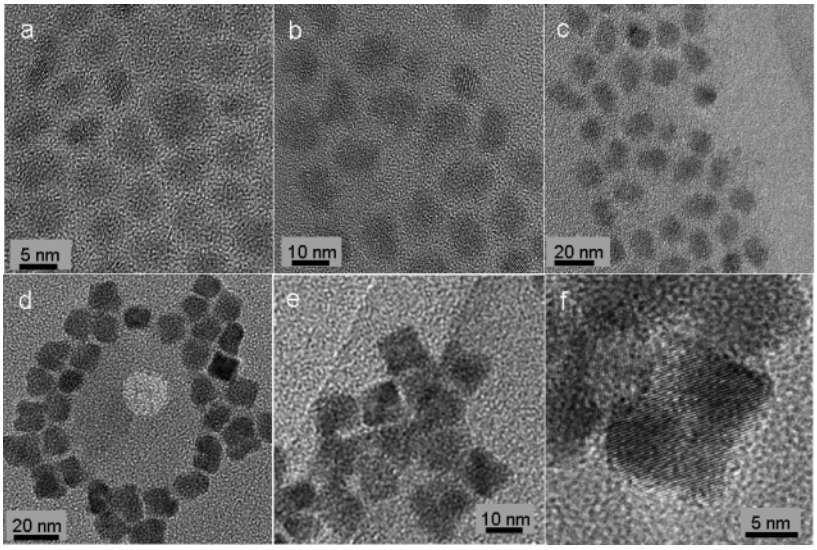
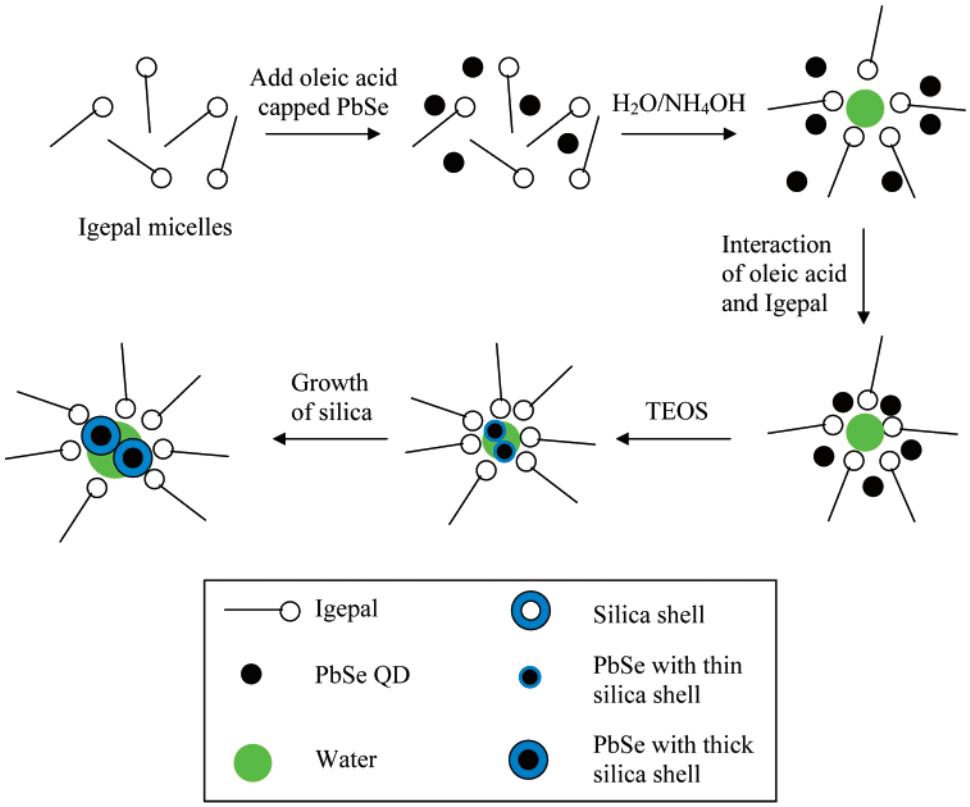


Figure 1. TEM images showing the size evolution of PbSe QDs synthesized at 100 °C with a growth period of (a) 2, (b) 5, and (c) 10 min. TEM images showing the shape evolution of PbSe QDs synthesized at (d) 150 and (e) 180 °C with a growth period of 10 min. (f) HRTEM image of PbSe QDs synthesized at 180 °C with a growth period of 20 min. The lattice fringes are clearly seen.

Scheme 1. Encapsulation of Hydrophobic, Oleic-Acid-Capped PbSe QDs within a Silica Shell Using a Reverse Microemulsion Method



been a topic of interest because of the elegant work by Liz-Marzán, Mulvaney, and co-workers.[16−18] We have recently reported a novel direct silica coating method for hydrophobic ZnS−CdSe QDs[21] and nanocomposites consisting of magnetic nanoparticles and QDs.[22] In this report, we show that this one-pot silica-coating approach can be successfully extended to oleic-acid-capped PbSe QDs, demonstrating the flexibility and versatility of this method.

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Experimental Section

Synthesis of PbSe QDs. PbSe QDs of different sizes and morphologies were synthesized according to the literature procedures with some modifications.[8,9] The reagents used were lead acetate trihydrate, selenium (Se), oleic acid, diphenyl ether, and trioctylphosphine (TOP). For a typical synthesis, 0.1 g (0.26 mmol) of lead acetate, 0.34 mL (1 mmol) of oleic acid, and 5 mL of diphenyl ether were introduced to a 50 mL three-necked flask connected to a condenser circulating with cold water. The mixture was then vigorously stirred at 100 °C and purged with argon for 1 h. On the other hand, 0.2 g (2.5 mmol) of Se was dissolved in 1.6

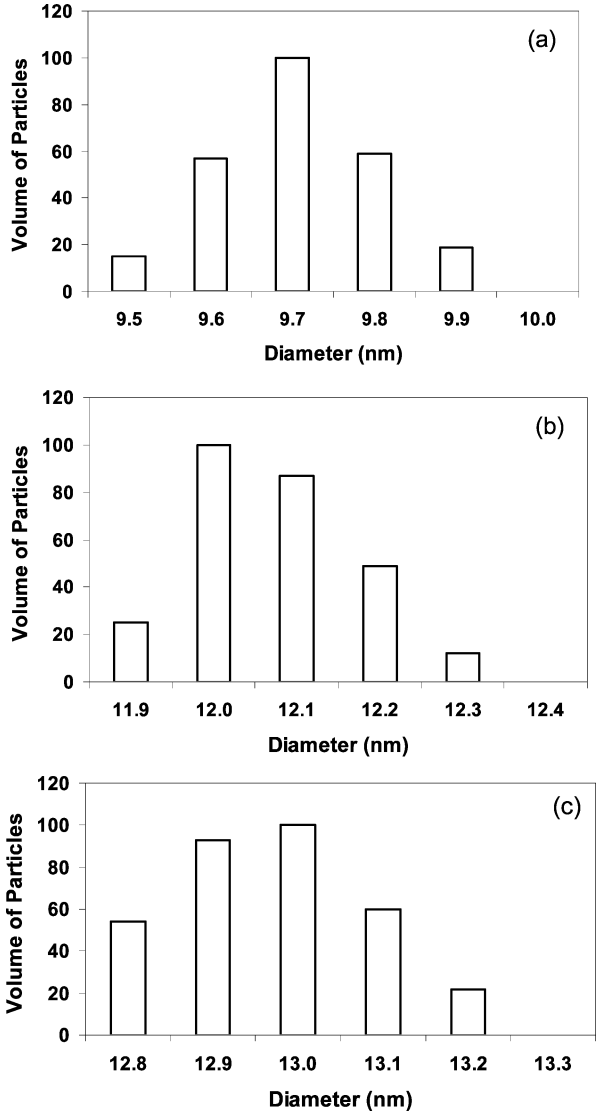

Figure 2. Volume-weighted particle size distribution of PbSe QDs synthesized at 100 °C with a growth period of (a) 45 s, (b) 5 min, and (c) 10 min. The average particle sizes are 9.7, 12.1, and 13.0 nm, respectively.

mL of TOP. The Pb:Se molar ratio was 1:10. To initiate the synthesis, the temperature of the lead salt mixture was adjusted to the desired temperature (100, 150, or 180 °C), and the TOP−Se mixture was quickly injected. Upon injection of TOP−Se, the colorless mixture turned to light brown. As the reaction proceeded, the color intensified to dark brown because of the nucleation and growth of PbSe QDs stabilized in the presence of oleic acid and TOP. Aliquots of samples were taken at different time intervals, precipitated with methanol, and then separated by centrifugation. The PbSe nanocrystals were then redispersed in chloroform for analysis or in cyclohexane for silica coating.

Silica Coating of PbSe QDs. PbSe QDs passivated with oleic acid were precipitated with methanol once, and the precipitate was dried under nitrogen to remove the methanol. Initially, reverse micelles were formed by dissolving 0.25 g of Igepal CO-520 in 4.5 mL of cyclohexane (the oil phase) and stirring for 30 min. Next, 10−50 μL of aminopropyl trimethoxysilane (APS)-modified PbSe QDs (0.5 mL, 1 mg/mL of cyclohexane) were introduced into the reverse micelles and stirred for another 30 min. Fifty to one hundred microliters of 29.5% NH_4OH (the aqueous phase) was then introduced and stirred for 1 h to form a water-in-oil microemulsion. Finally, 2−100 μL of tetraethylorthosilicate (TEOS) were added and stirred for 24 h to obtain uniform SiO_2 formation within the

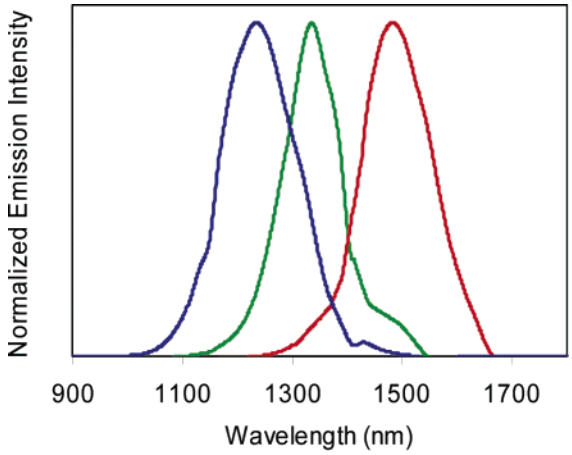

Figure 3. Photoluminescence spectra of PbSe QDs synthesized at 100 °C with a growth period of (blue) 45 s, (green) 5 min, and (red) 10 min.

Table 1. Effect of Growth Period on Crystallite Size and Emission of PbSe QDs

	particle size (nm)		
growth period[a]	DLS	TEM	emission peak (nm)
45 s	9.7	6.9	1238
5 min	12.1	10.1	1338
10 min	13.0	11.3	1516

[a] Injection temperature: 100 °C. Varying the injection temperature from 100 to 150 °C with a growth period of 10 min would change the QD shape from spheres to octahedrons/cubes.

aqueous domains by alkoxide hydrolysis and polycondensation. The silica-coated PbSe QDs (SiO_2/PbSe) were extracted by ethanol addition and centrifugation (10 000 rpm) for 30 min. The precipitate was washed and centrifuged with ethanol twice to remove excess surfactants and then dispersed in water.

Characterization of PbSe and SiO_2/PbSe QDs. The QDs synthesized were characterized using NIR fluorescence spectroscopy, X-ray diffraction (XRD), dynamic light scattering (DLS), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray (EDX) analysis. A FEI Technai G^2 HRTEM was used to image the PbSe and SiO_2/PbSe QDs. Samples were prepared by placing a few drops of the particle suspension onto a carbon-coated Cu grid. Absorption and fluorescence spectra were acquired with UV−vis spectrophotometer (UV-3600 Shimadzu) and spectrofluorometer (Fluorolog-3 FL3-2T with TRIAX 320 imaging), respectively. DLS experiments were performed with a Brookhaven 05-LHP-928 laser light scattering system (He−Ne laser, 35 mW). Before the measurements, 3 mL samples were filtered ~10 times using a 0.2 μm filter to ensure that the samples were of high quality (i.e., free from dust particles and particle agglomerates). XRD patterns were obtained with a Philips Analytical X'pert PRO diffraction system equipped with PW3040/60 console and PW3050/6X goniometer.

Cytotoxicity of SiO_2/PbSe QDs. NIH 3T3 and HepG2 cells were trypsinized and resuspended in Dulbecco's modified Eagle's medium (DMEM) with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin. The cells were seeded at a density of 0.2−1 million cells/well in a 96-well plate at 37 °C and 5% CO_2 for 24 h and washed with PBS. One hundred microliter SiO_2/PbSe samples of desired concentrations (10−100 μg/mL) were added to each well with 6 duplicates for each concentration. After 48 h of incubation, the supernatant was removed, and the cells were washed with PBS three times. To evaluate cell viability, we added 100 μL of MTT solution to each well and incubated the mixture at 37 °C for 4 h. After incubation, each well was treated with 100 μL of dimethyl-

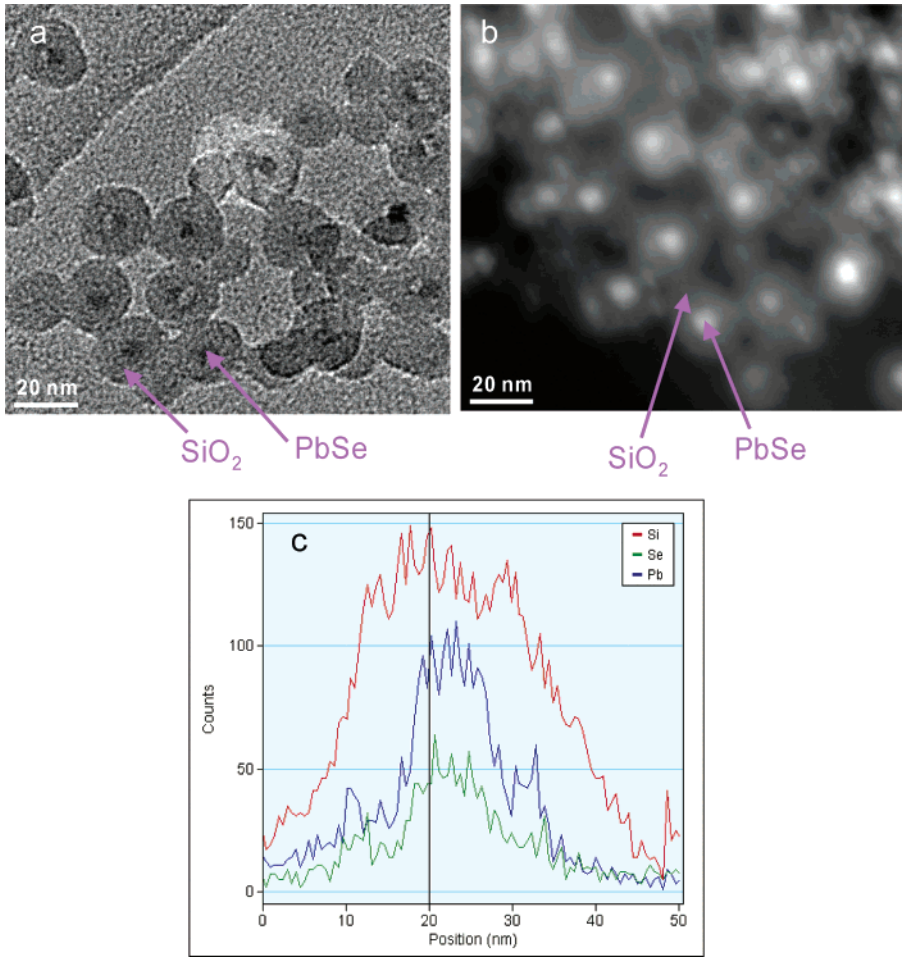

Figure 4. (a) TEM and (b) STEM images of SiO_2/PbSe. (c) EDX profile of (red) Si, (blue) Pb, and (green) Se across one core−shell particle shown in (b).

sulfoxide (DMSO) for 3−5 min. The optical absorbance was measured at 570 nm on a plate reader. Each data point was the average from 6 wells, and 100% viability was determined from the untreated cells.

Results and Discussion

At the synthesis temperature of 100 °C, samples were taken at different time intervals (45 s and 2, 5, and 10 min) to investigate the size evolution of the QDs. Highly crystalline and nearly monodispersed crystallites of 6.9−11.3 nm were obtained. Figure 1a−c shows that the crystallite size of QDs increases with increasing reaction time because of grain growth. Particle sizes determined by DLS measurements (Figure 2) were ∼2 nm larger than the crystallite size estimated by TEM, which could be attributed to the surfactant molecule (oleic acid) surrounding the PbSe crystallites.

The shape evolution of PbSe QDs could be affected by the synthesis temperature, growth period, choice of solvents, multiple injections, and noble metal seed particles.[22] In our synthesis, shape evolution was observed at relatively low temperature and short growth period with a single injection. Figure 1c−e shows that at a growth period of 10 min, an increase in temperature from 100 to 180 °C gave rise to a shape transition from spheres to a mixture of octahedron and cubic structures. The HRTEM image of QDs synthesized at 180 °C with a growth period of 20 min revealed a cubic structure with clear lattice fringes (Figure 1f). A mixture

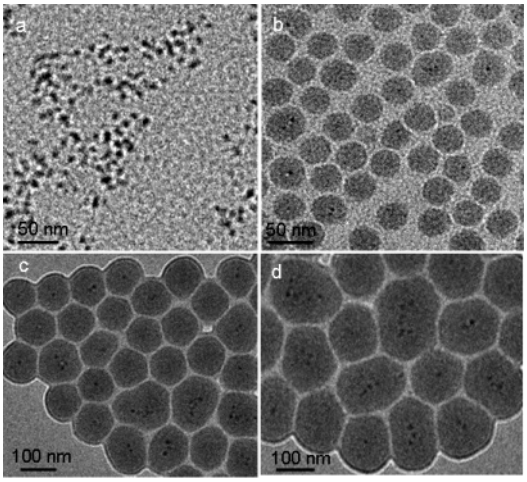

Figure 5. TEM images of SiO_2/PbSe nanoparticles prepared in Igepal reverse microemulsion with (a) 2, (b) 10, (c) 50, and (d) 100 μL of TEOS. The average particle diameter varies from ∼40 to 160 nm with an increase in TEOS volume (b−d).

of octahedron and cubic structures were also observed at 100 °C with a long growth period of 80 min (see the Supporting Information, Figure S2).

NIR emission spectra were recorded for PbSe QDs synthesized at 100 °C with a growth period of 45 s, 5 min and 10 min. These QDs, which have TEM-estimated average crystallite sizes of 6.9, 10.1, and 11.3 nm, respectively, gave rise to emission peaks at 1238, 1338, and 1516 nm (Figure 3). The emission shifted toward longer wavelengths with

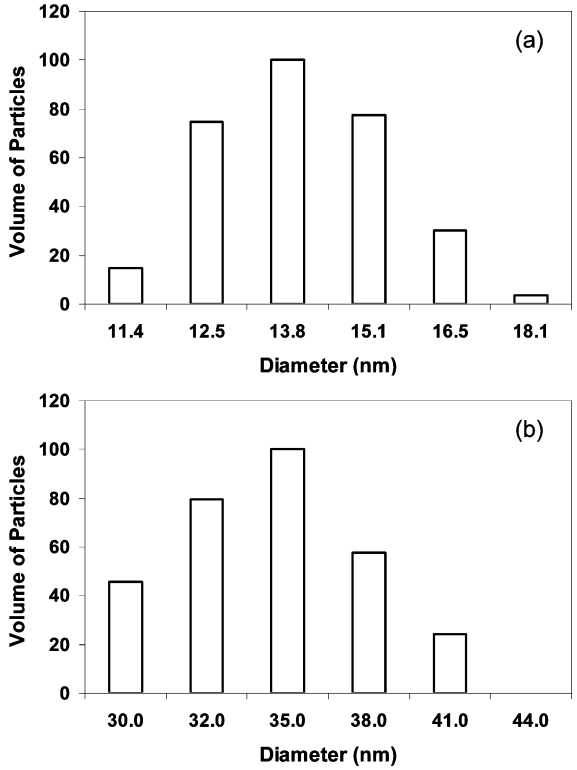

Figure 6. Volume-weighted particle size distribution of SiO_2/PbSe nanoparticles in water for the samples corresponding to images a and b in Figure 5. The average particle sizes are (a)13.8 and (b) 35.0 nm, respectively.

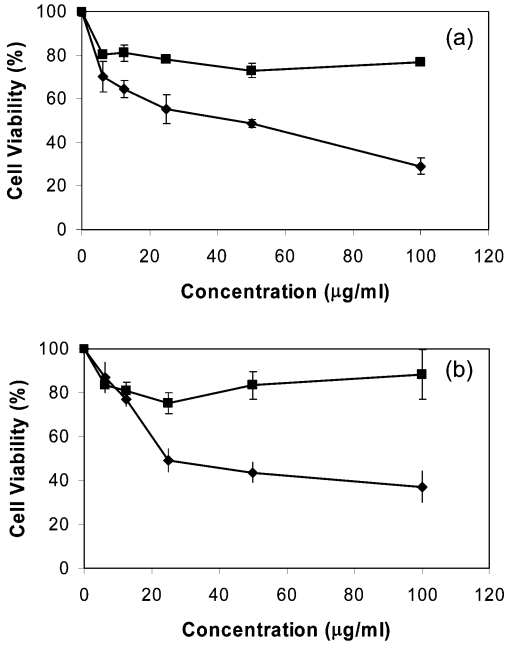

Figure 7. In vitro cell viability of (a) NIH-3T3 and (b) HepG2 in the presence of the specified concentrations of (■) SiO_2/PbSe and (◆) PA/PbSe nanoparticles.

increasing crystallite size because of the quantum confinement effect. This illustrated that the band gap of PbSe was tunable by controlling the crystallite size of the QDs. Our PbSe QDs exhibited sharper emission peaks than Du et al.'s PbSe QDs.[9] The optical properties of PbSe QDs were studied by different groups,[8,9] and crystallite sizes ranging from 3 to 8 nm were produced with narrow size distributions at temperatures ranging from 80 to 150 °C.[9] Table 1 summarizes the effect of growth period on crystallite size, and the corresponding emission of our PbSe QDs.

The XRD pattern of PbSe QDs grown at 180 °C for 10 min is shown in Figure S3 in the Supporting Information. All diffraction peaks corresponded to the rock salt structure of PbSe, as observed for nanocubes[8] and quantum rods.[23] The presence of Pb and Se in the nanocrystals was confirmed by EDX (see Figure S4 in the Supporting Information).

Silica coating was introduced to the PbSe QDs using a reverse microemulsion method, employing Igepal CO-520 (polyoxyethylene nonylphenylether) as the nonionic surfactant. The surfactant interaction prior to silica coating allowed the hydrophobic QDs to be encapsulated within the aqueous domains of the reverse microemulsion (Scheme 1). This involved the hydrophilic carboxylate and polyoxyethylene groups of oleic acid and Igepal, respectively. Oleic acid and Igepal were surfactants present on the QD surface and in the reverse microemulsion, respectively.

The TEM images of SiO_2/PbSe are shown in Figure 4. The 9 nm PbSe nanocrystals were encapsulated as single cores within the spherical silica shells. The diameter of the silica-encapsulated QD particles was ~25 nm. The STEM image (Figure 4b) showed that the bright white particles were the QD cores, surrounded by SiO_2 coatings (in gray). The EDX profiling (Figure 4c) on one core−shell particle indicated the presence of Si, Pb, and Se in the silica-coated QDs. The peak locations illustrated the co-localization of Pb and Se in the ~9 nm core of the particle. Si was present across the particle diameter of ~25 nm, confirming that a single PbSe QD was encapsulated within the SiO_2 shell.

Figure 5 illustrates that the surface silanization worked well for different silica thicknesses. The particles were well-dispersed. The thin silica shell obtained with a low volume of 2 μL of TEOS in Figure 5a was difficult to discern. The overall particle diameter varied from ~40 to 160 nm with an increase in TEOS volume (from 10 to 100 μL; Figure 5b−d). The shapes of the silica particles seemed to be dependent on the arrangement of PbSe particles.

Panels a and b of Figure 6 show the volume-weighted particle size distributions of SiO_2/PbSe nanoparticles in water; the samples corresponded to those in images a and b of Figure 5, respectively. The mean DLS particle diameters were estimated to be 13.8 and 35.0 nm, respectively. In addition, there was a very small volume (~1.2 units) of aggregated particles of 100−160 nm.

The cytotoxicity effects of silica-coated QDs (CdSe and ZnS−CdSe) have been documented in the literature.[24,25] Figure 7 shows the in vitro cytotoxicity effects of SiO_2/PbSe and polyanhydride-coated PbSe QDs (PA/PbSe) on NIH-3T3 and HepG2 cell lines. SiO_2/PbSe was potentially less toxic compared to the water-soluble PA/PbSe.[26] The inhibitory particle loadings corresponding to 50% cell viability

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(IC_{50}) were 50 and 25 μg/mL for PA/PbSe in NIH 3T3 and HepG2, respectively. In contrast, SiO_2/PbSe maintained greater than 80% cell viability even at particle loadings as high as 100 μg/mL. The much lower cytotoxicity of SiO_2/PbSe was attributed to the effective prevention of PbSe dissolution by the silica coating.

Conclusion

In conclusion, we have demonstrated that the size control of spheres (7−12 nm) and shape evolution (spheres to octahedrons/cubes) of PbSe QDs could occur even at a relatively low temperature of 100−150 °C with a single injection. We have also shown that the band gap of QDs was manipulated by the crystallite size in the synthesis; sharp, tunable emission in the range of 1238−1516 nm could be achieved. We have successfully extended the direct silica coating approach developed in our laboratory to hydrophobic (oleic-acid-capped) PbSe QDs. The in vitro experiments conducted on two different cell lines illustrated that the SiO_2/PbSe QDs were much less cytotoxic than the polymer-coated PbSe QDs.

Acknowledgment. This work is funded by the Institute of Bioengineering and Nanotechnology (Biomedical Research Council, Agency for Science, Technology and Research, Singapore).

Supporting Information Available: Materials, DLS, shape evolution, XRD, STEM, and EDX analyses of PbSe QDs, silica coating of PbSe and ZnS−CdSe QDs, colloidal stability and solution properties of SiO_2/PbSe QDs, and cytotoxicity of coated PbSe and ZnS−CdSe QDs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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