

Highly Photo-Stable Type-I PbSe/SnSe and PbSe/SnS Colloidal Core/Shell Quantum Dots

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ABSTRACT

In an effort to improve photo-stability of IV-VI PbSe and PbS quantum dots (QDs) for application of near infrared-based devices, we have synthesized type I core/shell colloidal QDs with PbSe as the cores, and SnSe and SnS as the shells. The new QDs were characterized by photoluminescence, HR-TEM, XRD and EDX analysis. The improved photo-stability was demonstrated both in solution and solid state, and by photo-bleaching tests upon irradiation with a 450 W Xenon lamp. Absolute quantum yields and fluorescence time-life of the core and type I core/shell QDs were also measured. The decreased quantum yields and fluorescent life-time of the core/shells compared with the cores were observed, which was ascribed to the formation of SnO₂ in core/shell structures. These new type I core/shells will provide new opportunities for IV-VI PbSe and PbS QDs in the application of infrared devices.

Keywords: quantum dots, photo-stability, core/shell nanocrystals, type I and type II semiconductors, and colloidal synthesis.

1 INTRODUCTION

The IV-VI PbSe and PbS colloidal semiconductor quantum dots (QDs) have initiated active study in infrared-based applications that include electroluminescent devices,^{1,2} optical gain,^{3a,4} solar cells,⁵ waveguide,⁶ biological markers,⁷ and other opto-electronic devices in recent years due to their high photoluminescence (PL) and size-tunable emission in the near-infrared range.⁸ The photo-stability of these QDs is always a critical factor for device performance. Although nearly 80% quantum yields of PbSe QDs in solution have been reported,^{3,8} the measurements were usually conducted on fresh samples under mild conditions. When PbSe QDs were stored in solid state or in solution for a period, their photoluminescence decreased and a severe blue-shifted emission appeared.⁹ Meanwhile, a fast photo-bleaching of PbSe QDs in solution under a 450 W Xenon lamp irradiation was also observed.⁹ QDs doped into polymer matrix,³ and type II PbSe/PbS core/shell QDs have been claimed to be able to improve photo-stability of PbSe QDs,¹⁰ however, few data were presented to support this.

The epitaxially grown core/shell QDs have either a type I or a type II structure based on the values of band-offsets between core and shell materials.¹¹ Thus far, type I highly photo-stable III-V and II-VI core/shell QDs have been reported.^{12,13} Type II IV-VI PbSe/PbS core/shell QDs, which were prepared following literature procedures in our work did not give much improved photo-stability. They still exhibit severe blue-shifting of the emission when stored in solution and fast photo-bleaching performance close to that of PbSe QDs.⁹ To improve the photo-stability while keep PL properties of the core, type I PbSe based core/shell QDs, which confine both electrons and holes in the cores may address this concern. We present here the first synthesis of type I IV-VI PbSe/SnSe and PbSe/SnS core/shell QDs and their characterization data. Photochemical results show much higher photo-stability of type I QDs both in solution and solid state than the corresponding PbSe core and type II PbSe/PbS core/shell QDs.

2 EXPERIMENTS

2.1 Materials:

Lead (II) oxide, Lead (II) acetate trihydrate (98%), octadecene (90%), oleic acid (90%), trioctylphosphine (90%), selenium (99.5%), tetrachloroethylene (99%), sulfur, tin (II) acetate, and diphenyl ether (99%) were purchased from Aldrich and used without further purification.

2.2 Synthesis of PbSe core QDs.

The synthesis of PbSe nanocrystals followed a modified procedure similar to that reported by Bawendi et al.¹ and including the following steps: 1) 446 mg (2 mmol) PbO was mixed with 1.28 ml (4 mmol) oleic acid (OA) and 30 ml 1-octadecene (ODE). The mixtures were then heated to 120 °C under vacuum to remove excess water. When all yellow PbO were dissolved, the whole mixture would become a clear colorless solution forming Pb(oleate)₂. The solution was then further heated under argon ca. 30 min to remove molecular oxygen. In a separate 10 ml flask added 5 ml trioctylphosphine (TOP) and 158 mg (2 mmol) elemental selenium. The mixture was stirred for 15-30 min under argon to allow the full dissolution of Se. TOPSe was then injected into the first flask to allow the PbSe growth.

The expected core sizes were controlled by the reaction time. It usually takes 4-7 min to grow the PbSe QDs within the ranges of 1300 -1600 nm under the current conditions. The reaction was stopped by pouring the reaction mixture into 100 ml absolute ethanol and the black QDs were then precipitated. The precipitates were washed subsequently with absolute ethanol and acetone for couple of times and dried with air stream and dissolved in tetrachloroethylene. The yields of the above PbSe QDs were ~ 70mg.

2.3 Synthesis of Type II PbSe/PbS and Type I PbSe/SnSe and PbSe/SnS QDs.

PbSe/PbS core/shells were prepared by a two-injection process modified from Lifshitz et al.¹⁰ A typical procedure includes the following stages: 125 mg (0.53 mmol) $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, 2 ml ODE, and 1.5 ml 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 further 10 min, the vacuum was removed and argon was bubbled through the solution followed by adding 6 ml TOP. The solution was further heated at 120 °C for at least 20 min then cooled at room temperature for the next step. In a separate flask, the 40-50 mg PbSe QDs as-synthesized above in dichloromethane was injected and bubbled with argon and heated at 45 °C to remove the solvent. When all solvent was removed, 1.5 ml TOP was syringed in to redissolve PbSe QDs and followed 80 mg S dissolved in 0.5-1 ml TOP solution. The whole mixture in the second flask was then injected into the first solution loaded with $\text{Pb}(\text{oleate})_2$, excess OA and solvent. After stirring the combined mixture for 3-5 min at 45 °C, they were injected into the third flask added with 15 ml ODE and pre-heated at 180 °C for the shell growth. The mixture was first heated at 180 °C oil bath for one minute and then transferred to 120 °C oil bath. The reaction time was controlled between 15-20 min. Samples were taken from the reaction mixture at different time to supervise the growth of shell materials. The samples were purified in the same way as the PbSe QDs except that the final core/shell samples will be dissolved in tetrachloroethylene and filtered through 0.45 μm glass filter before the later characterizations.

PbSe/SnSe and PbSe/SnS core/shells were prepared by the same procedures described above except switching $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ to the same molar amount of $\text{Sn}(\text{OAc})_2$. For SnSe shell growth, the elements Se will be used instead of S.

2.4 Characterization Methods

Photoluminescence measurements were done with an Edinburgh Instruments FS/FL 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 (1x1 cm^2) 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. A silicon filter in front of the detector was used throughout the measurements. The emission spectra were corrected for the detector response.

A FEI Tecnai 200 keV Field Emission Scanning Transmission Electron Microscope was used to collect HRTEM images. EDX analysis was performed on a Hitachi S2600N SEM operated at 8kV, with a magnification of 45X. For X-ray diffraction studies, powdered samples were smeared on to a zero-diffraction quartz plate and the diffraction data were collected over the 2 θ range 3 – 100° with $\text{CuK}\alpha$ (40 kV, 40 mA) radiation on a Siemens D5000 Bragg-Brentano Th-2 θ diffractometer. The scanning step size was 0.04° 2 θ with a counting time of 2 s/step. A solution of QDs was placed inside an integrating sphere (Edinburgh instruments, 150 mm in diameter coated with barium sulfate) and was excited by monochromatic light (Xenon lamp, excitation wavelength 890 nm). The PL spectra were detected by InGaAs detector. For fluorescence life-time measurements, the excitation source used was a 10 Hz Q-Switched Quantel Brilliant, pumped by a Nd:YAG laser, attached with an optical parametric oscillator (OPO) excited at 800 nm. The fluorescence is detected with a conventional liquid nitrogen-cooled Hamamatsu R955 photomultiplier tube (PMT). The MSA-300 5 ns multiscaler card was used to count all pluses.

3 RESULTS AND DISCUSSION

3.1 Optical Characterization

Selection of SnSe and SnS as the shell materials was based on their potential to grow into rock-salt structure with less than 5% crystallographic mismatch with the PbSe core,¹⁴ and relatively large energy band gaps (E_g). Approximate band-offsets were evaluated from E_g s and ionization potentials (IPs) of the bulk state. The E_g s of bulk PbSe, PbS, SnSe and SnS are 0.26, 0.37, 0.9 and 1.2 eV, respectively and IPs are 8.8, 9.0, 9.1 and 9.1 eV, respectively.¹⁵ These values predict type I PbSe/SnSe and PbSe/SnS, and type II PbSe/PbS core/shell QDs (Figure 1).

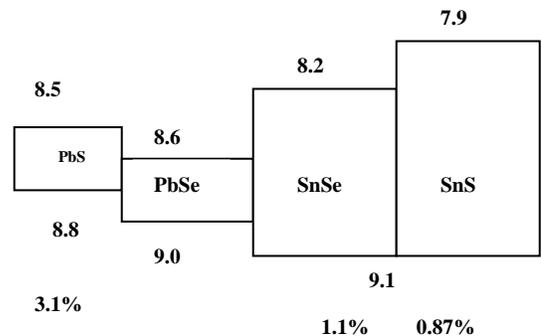


Figure 1. Band-offsets (in eV) and lattice mismatch (in %) between the PbSe cores and IV-VI semiconductor PbS, SnSe and SnS shells.

The predication of the type II QDs matches well with the calculation and experimental results.^{10,16}

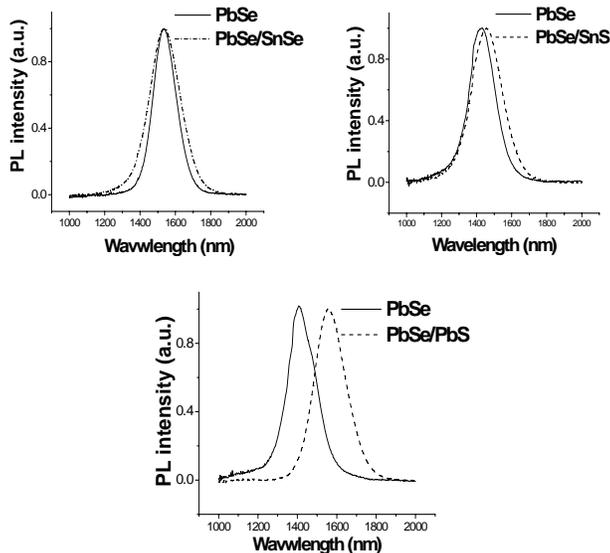


Figure 2. Normalized emission spectra of the PbSe/PbSe (up-left), PbSe/SnS (up-right) and PbSe/PbS (bottom) core/shells compared with their corresponding PbSe cores

Figure 2 shows the emission spectra of the PbSe/SnSe, PbSe/SnS and PbSe/PbS core/shells compared with their corresponding PbSe cores. The emission peak differences between PbSe core and the corresponding PbSe/SnSe and PbSe/SnS core/shells are 0 and 25 nm, respectively. For all PbSe/SnSe and PbSe/SnS core/shells (over 20 trials), the red-shift emission peak relative to the corresponding PbSe cores are generally varied between 0-50 nm (0-0.04 eV). For PbSe/PbS core/shells, the red-shift peaks compared with cores were usually larger and over 90 nm (>0.07 eV) depending on the loadings of Pb and S resources. In Figure 2 (bottom) of PbSe/PbS core/shell QD, the difference is 147 nm (0.12 eV). These fluorescent results match well with the predication of the type I and II QDs.¹¹⁻¹³

3.2 Photo-Stability of Solution

The much improved photo-stability of the new type I QDs compared with cores was observed in solution and solid state through the long-time storage and photo-bleaching tests.

The emission spectra of three separate PbSe/SnSe QD solutions and corresponding cores were measured after two-month storage under ambient conditions. The blue-shifts of the emission peaks for core/shell QDs were 64, 24, 24 nm, while for the cores they were 248, 36 and 98 nm, respectively. Upon irradiation with a 450 W Xenon lamp, photo-bleaching of PbSe QD solutions was observed within 15 seconds and their emission died very fast (Figure 3, up-left); while clear brown type I QD solutions remained the same solution color and over 80% emission intensity for a couple of minutes in the case of PbSe/SnSe core/shell QDs

(Figure 2, up-right). Figure 3 (bottom) shows the relative PL intensity left of four QDs after being illuminated. Type I core/shell QDs clearly show much improved photo-stability in solution.

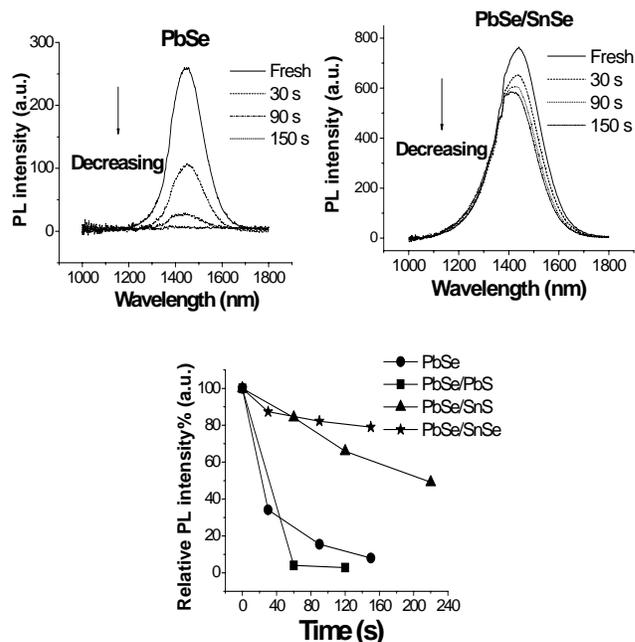


Figure 3. Upon irradiation with a 450 W Xenon lamp of PbSe (up-left) and PbSe/SnSe (up-right) QD solutions. Bottom: Relative emission intensity remained for core and three core/shells before and after being irradiated. Original intensities of four QDs were normalized to 100% and lines are drawn to guide the eye.

Solid films of core and core/shell QDs were prepared by depositing QD solutions onto quartz slides, which were stored at room atmosphere for emission measurements periodically in three months (Figures not shown). After three months, emission peaks of PbSe QD film shifted to blue over 150 nm (= 0.12 eV) and emission spectra had broadened compared with the fresh film. As for core/shell films, emission peaks had only small shifts (< 0.03 eV) and they kept their spectral shape. Meanwhile, the FWHM values of PbSe, PbSe/SnSe and PbSe/SnS QD films increased to 30, 0 and 10 nm, respectively, from the fresh films. The results indicated that PbSe QDs without shell protection have undergone significant physical and chemical changes.

3.3 Characterizations with TEM, EDX and XRD Analysis.

Spherical particles, size and size distribution of the new type I PbSe/SnSe QDs were determined from low and high-resolution TEM imaging (HR-TEM) (Figure 4). Size dispersions for core and core/shell QDs in Figure 4 (right) are 5.6% and 7.7%, which are consistent with the slightly broader FWHM of the core/shell emission spectrum (Figure 2, up). Crystalline fringes are clearly shown in HR-TEM, indicating the consistent crystalline structure between the

core and shell phases. The ca. 1 nm shell thickness indicates that 2-3 monolayer shell materials had been grown. Similar QD shape, size and TEM images were observed for PbSe/SnS core/shell QDs.

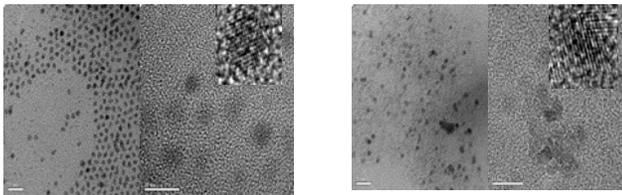


Figure 4. TEM and HRTEM of PbSe core (left) and PbSe/SnSe core/shell (right). Scale bar = 20 nm for TEM and 10 nm for HRTEM. Sizes for PbSe insert is ca. 4 nm and 5 nm for PbSe/SnSe.

EDX analysis on PbSe/SnSe core/shell samples shows signals of Sn, Pb, Se and O elements. The molar ratio of Pb/Sn was decreasing when more Sn resources were added. Our XRD results show the diffraction patterns due to the PbSe, SnSe and SnS crystalline phases, but also show significant amount of crystalline SnO₂, which is consistent with the O signal in EDX spectrum. Since the synthesis was conducted under oxygen-free conditions, the formation of SnO₂ was probably due to the work-up and storage. The amount of SnO₂ increases with storage time observed through XRD. The interaction between the oxygen and tin vacancies in SnO₂ could create defects,¹⁷ and these defects might be responsible for the decreased emission intensity of core/shell QDs in the solid state. As a consequence, quantum yields and fluorescent lifetime of core/shell QDs compared with PbSe cores were also decreased.

Absolute quantum yields (QYs) of each PbSe, PbSe/SnSe and PbSe/SnS QD sample (fluoresces in the 1500-1600 nm range) solution have been measured using the integrating sphere technique,¹⁸ which were 7.7%, 2.9% and 1.0%, respectively. Fluorescent life-time of PbSe was found to be 600 ns, while PbSe/SnSe and PbSe/SnS were 335 ns and 320 ns, respectively. The life-time of PbSe is 280 ns shorter than the PbSe sample fluoresces in the 1300-1500 nm range and was prepared in different solvent.^{3b} More detailed study of these new type I core/shell crystalline structure and resultant properties, and the efforts to synthesize SnO₂-free core/shell QDs is in progress.

In conclusion, we have synthesized new type I PbSe/SnSe and PbSe/SnS core/shell QDs with much improved photo-stability both in solution and the solid state.¹⁹ These new type I core/shells will provide new opportunities for IV-VI PbSe and PbS QDs in the application of infrared devices.

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