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Silica-encapsulated ZnSe quandum dots (QDs) were obtained by employing di-2-ethylhexyl sodium sulfosuccinate (AOT) microemulsion methods. When the QDs were coated by silica, well-defined spherical shapes were formed and the photoluminescence (PL) efficiency was decreased from 4.9% to 1.9% with increasing water content W (W = [H_2O]/[AOT]). In addition, ZnSe QDs showed the good photostability. The present method does not require a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor. Moreover, they are cadmium free and less toxic. Therefore, the present method can be a safer and more economical method for obtaining the silica-encapsulated ZnSe QDs, which may be a potential material for Light-Emitting Diode (LED), solar cell, and biosensors.

Keywords ZnSe; quantum dot; microemulsion; silica encapsulation; photostability

Introduction

The II–VI semiconductor nanocrystals (NCs) such as ZnSe attract much interest as novel bright phosphors with tunable photoluminescence wavelength for possible uses including display, LED, and biological labeling [1,2]. Although CdSe is the most studied QDs, its inherent toxicity may hinder its safe use in vivo applications, such as biolabeling procedure. Accordingly, it is natural to seek for cadmium ion substitutes and less toxic labeling materials. For these reasons, a recent report presented ZnSe crystals in the quantum confinement region as potential materials [3]. When colloidal ZnSe QDs are prepared, various synthetic techniques can be utilized. In general, for synthetic technique, the hot-injection [4,5] or the precipitation method [6,7] is employed. However, such a method requires a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor. Therefore, it would be favorable if we can synthesize ZnSe QDs using a safer and more economical method. Recently, in our laboratory, ZnSe QDs were prepared using a safe, simple and one-step synthetic method by employing water-containing AOT reversed micelles (microemulsions) [8]. However, in applying these ZnSe QDs for biosensor media, it is necessary for obtaining the biocompatible QD's. In order to improve the photostability of QDs they need to

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be encapsulated within a rigid matrix. In that respect, metallic and oxide particles can be generally used. Among them, silica encapsulation is one of the great choices to pave the way of protection and biocompatibility of quantum dots under biological conditions [9]. Such silica coating is expected to bring many advantages since the thin silica layer on the QDs increases the mechanical stability, enables a transfer into various organic and aqueous solvents, and protects QDs against oxidation and agglomeration.

In the present work, silica encapsulated ZnSe QDs were prepared using a safe, simple synthetic method by employing water-containing AOT reversed micelles. Then, the silica encapsulated ZnSe QDs were characterized. For characterizing study, UV-visible spectroscopy, X-ray diffraction (XRD) analysis, photoluminescence spectroscopy (PL), and transmission electron microscopy (TEM) were employed.

Experimental

Materials

AOT (Sigma-Aldrich, 99%), $ZnSO_4 \cdot 7H_2O$ (Sigma-Aldrich, 99%), selenium powder (Sigma-Aldrich, 100 mesh), $NaBH_4$ (Sigma-Aldrich, 99%), heptane anhydrous (Sigma-Aldrich, 99%), and cyclohexane anhydrous (Sigma-Aldrich, 99%) were used as received without further purification. Tetraethyl orthosilicate (TEOS) and NH_4OH (99%) was obtained from Aldrich. The water used in all experiments was prepared by distillation and reverse osmosis.

Synthesis of ZnSe Quantum Dots and Silica-Encapsulated ZnSe Quantum Dots

A schematic of the synthetic method is shown in Fig. 1. The first step was to obtain Se^{2-} ions by reducing selenium powder with $NaBH_4$ in water at a high pH. After 30 min, a dark yellow solution was produced. This reducing selenium solution was kept under nitrogen atmosphere at room temperature. Next, 50 ml solutions of 0.1 mol/L AOT in cyclohexane were poured into a reaction flask to form reverse micelles. The obtained microemulsion solution was constantly stirred using a magnetic stirrer. Then pure water was added to form initial W/O microemulsions. To obtain the nanocrystals as a function of water content in reversed micelles W ($W = [H_2O]/[AOT]$), different amount of water was added. Subsequently, an aqueous solution of 0.2 mol/L $ZnSO_4$ was added into the reverse micellar solution. Then, 0.1 mol/L Se^{2-} solutions were injected into the reaction flask using a syringe under vigorous stirring at room temperature. At a fixed surfactant concentration (0.1M), 0.15 ml of $ZnSO_4$ and Se^{2-} solutions were injected. All of these solutions were degassed with a nitrogen purge for more than 20 min, and the reaction flask was continually flushed with nitrogen gas. For the encapsulation, dilute ammonia and tetraethyl orthosilicate (TEOS) in reversed micelles were prepared separately, where the AOT concentration and water content were same with those for the preparation of ZnSe quantum dots. Then, the microemulsions of TEOS were injected to AOT reversed micellar solutions containing ZnSe QDs.

Characterization

For obtaining the image of ZnSe nanocrystals, TEM (JEOL 2100) was utilized after demulsifying the AOT microemulsion system by the addition of acetone. XRD data were collected with a D/MAX-2000/PC using Cu-K radiation (λ is 1.5418Å) for the dried powder sample.

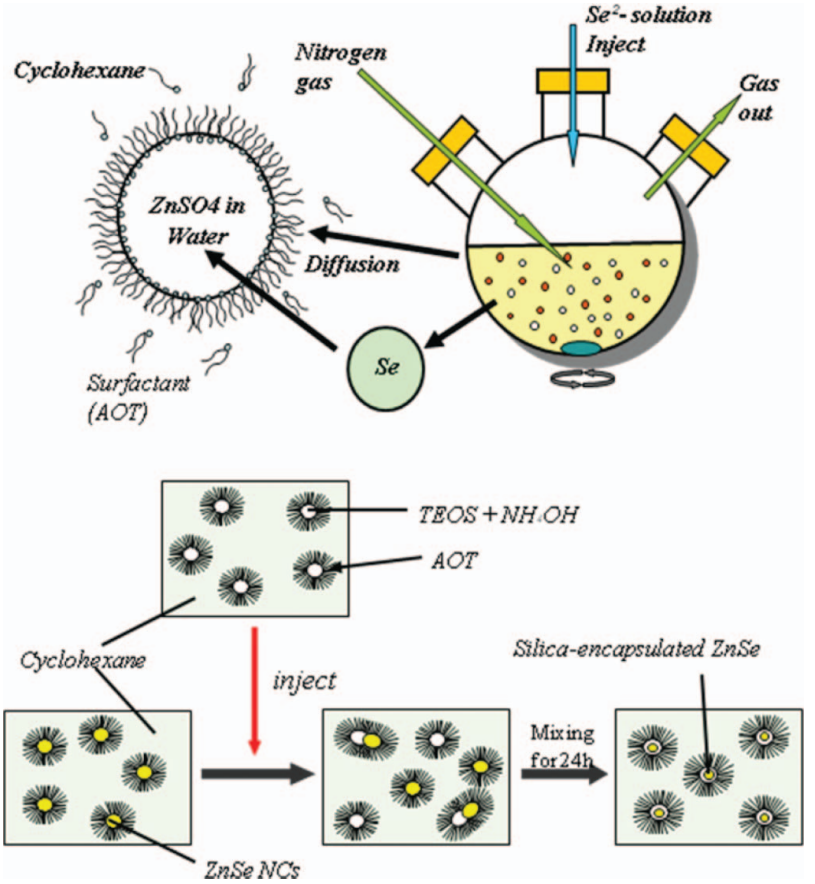

Figure 1. Schematic of microemulsion technique for ZnSe nanoparticle synthesis (top) and silica encapsulated ZnSe nanoparticles synthesis (bottom).

To measure the PL efficiencies of ZnSe quantum dots in reversed micellar solutions, the absolute values of room-temperature PL efficiency of quantum dots were estimated by comparison with solutions of Rhodamine 6G in ethanol. We used the literature value for the room-temperature PL efficiency of Rhodamine 6G (95%) [10].

Results and Discussion

Figure 2 shows the TEM images of silica-encapsulated ZnSe QDs at W = 3. It can be seen that ZnSe QDs with well-defined spherical shapes were formed and the image shows that the average size of ZnSe QDs was about 7 nm. In addition, the figure shows that the ZnSe QDs are encapsulated within a rigid silica matrix. As shown in Fig. 2, by using an inverse microemulsion technique with injection of TEOS in microemulsions, silica-encapsulated ZnSe QDs were successfully prepared without employing a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor. In Fig. 3, the PL spectra were given for ZnSe QDs before and after the encapsulation by silica. Each peak showed single and strong emission peaks at 450 nm and these results are consistent with the results in the PL measurements for ZnSe QDs in cyclohexane reversed micellar solution [8]. In addition,

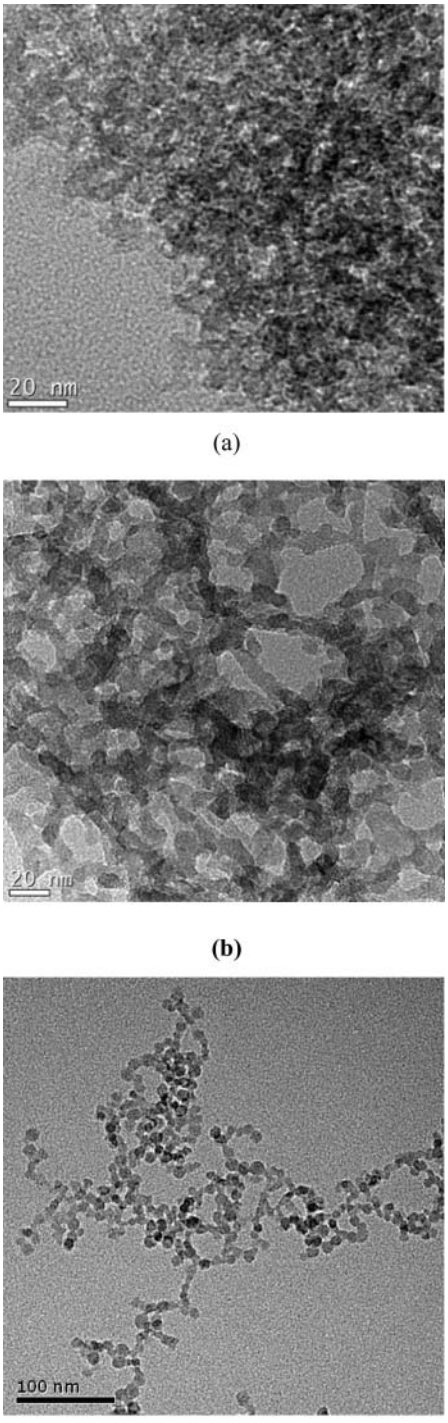

Figure 2. TEM images of silica-encapsulated ZnSe quantum dots prepared by AOT reverse micellar solution: (a) W = 3, (b) W = 5, (c) W = 8.

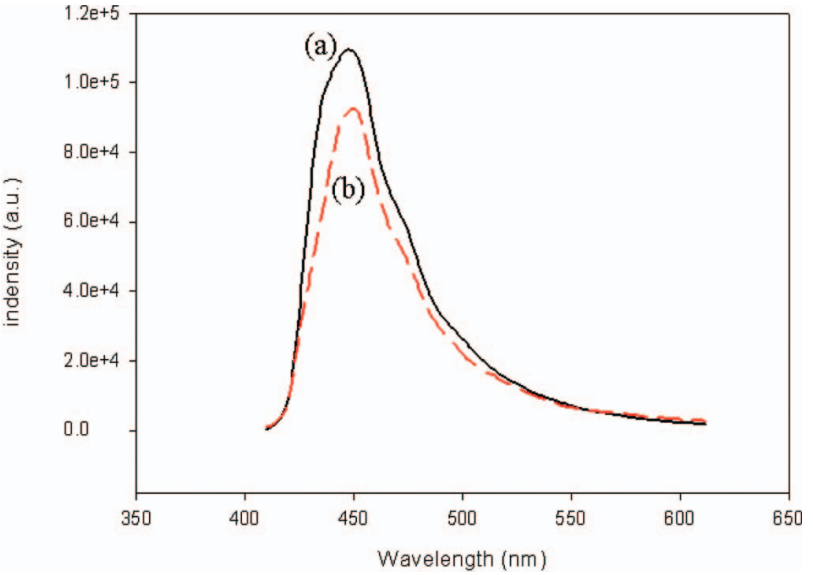

Figure 3. PL emission spectra of AOT/water/cyclohexane reversed micellar solutions: (a) ZnSe QDs (b) silica-encapsulated ZnSe QDs.

the maximum peak height for QDs after encapsulation was slightly decreased. This result is presumably due to the presence of chemicals like ammonia and TEOS [11]. In Table 1, the PL efficiency and the size of ZnSe QDs encapsulated with silica are given. The PL efficiency was decreased from 4.9% to 1.9% with increasing water content, W. On the other hand, the size of the QDs was increased with increasing W from 7 to 10 nm. These results are consistent with the previous work [8], since the PL intensity and quantum yield (QY) of ZnSe QDs are decreased as the size of quantum dot (ZnSe) increases in the same AOT/cyclohexane system. Figure 4 shows the X-ray diffraction patterns of silica-encapsulated ZnSe QDs as a function of water content W. The X-ay diffraction peaks arising from (111), (220) and (311) showed that the peaks match the standard peaks corresponding to cubic blende ZnSe, confirming that the present synthetic method provides crystalline ZnSe at room temperature. However, it should be noted that the crystalline nature of the QDS are almost unchanged even though the size of the QDs increased because the X-ay diffraction peaks are almost same as given in Fig. 4.

For utilizing these QDs, the photostability of the QDs is very important. Accordingly, to investigate the photostability of the ZnSe QDs, the PL emission spectra were obtained as a function of time. In Fig. 5, PL spectra of silica-encapsulated quantum dots ($[H_2O]/[AOT] = 3$) are shown in AOT/water/cyclohexane reversed micellar solutions. As given in the figure, the PL was almost unaltered even after two and four weeks, respectively. On the other

Table 1. PL efficiency and the size of ZnSe QDs encapsulated with silica

$W = [H_2O] / [AOT]$	3	5	8
PL efficiency (%)	4.9	4.0	1.9
Diameter (nm)	7.2	8.8	10.7

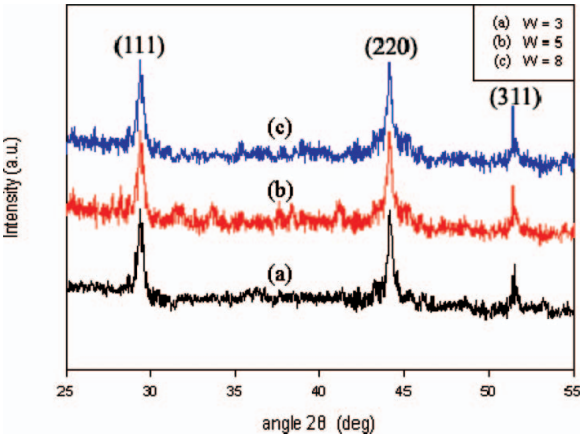

Figure 4. X-Ray diffraction traces for silica-encapsulated ZnSe nanocrystals as a function of water content W.

hand, as shown in Fig. 6, PL peak was remarkably reduced even after 3 days in the same cyclohexane solutions when the ZnSe QDs were not encapsulated with silica. In our previous work [12], it has been also shown that the drastic reduction of PL intensity when the pure QDs were exposed to air, but the photostability could be increased after ZnSe QDs were encapsulated by silica.

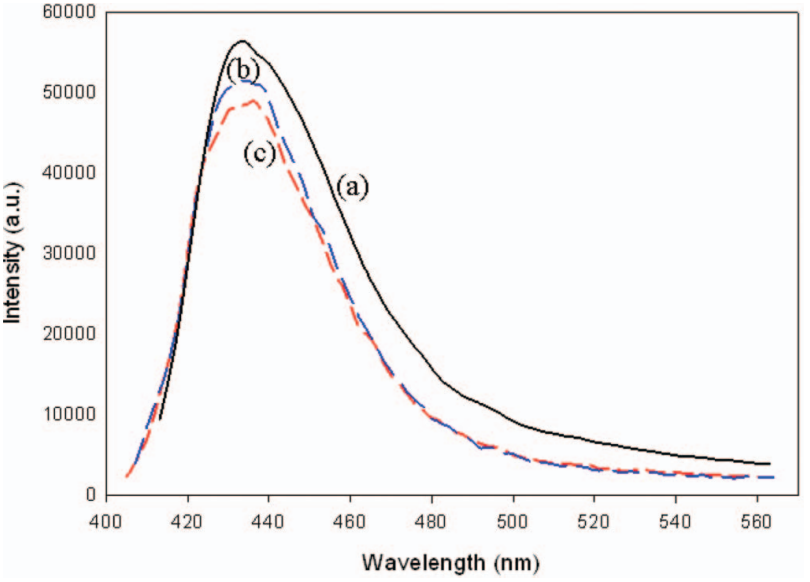

Figure 5. PL spectra of silica-encapsulated ZnSe QDs (W = 3) in AOT/water/cyclohexane reversed micellar solutions as a function of time: (a) on preparation, (b) after 2 weeks, (c) after 4 weeks.

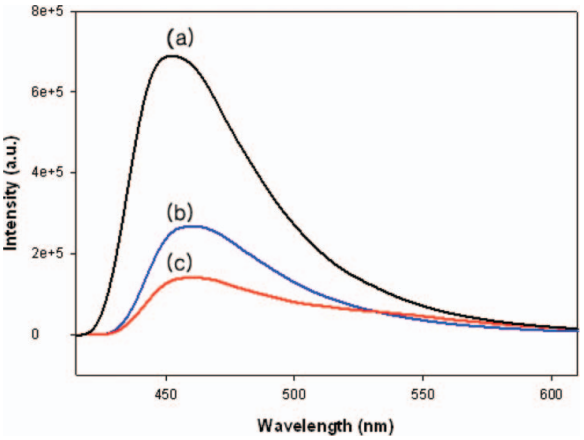

Figure 6. PL spectra of ZnSe QDs AOT/water/cyclohexane reversed micellar solutions as a function of time: (a) On preparation, (b) after 1 day, (c) after 3 days.

Conclusions

By employing water-containing AOT reversed micelles (microemulsions), silica-encapsulated ZnSe QDs were successfully prepared. The PL efficiency was decreased and the size of the QDs was increased with increasing W. In addition, ZnSe QDs showed the good photostability. Such silica coating is expected to bring many advantages since the silica layer on the QDs increases the mechanical stability and protects QDs against oxidation. In particular, they are cadmium free and less toxic. Moreover, the present method does not require a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor. Therefore, the present work proposed a safer and more economical method for obtaining the silica-encapsulated ZnSe QDs, which may be a potential material for LED, solar cell, and biosensors.

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