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마이크로에멀전을 이용한 실리카에 담지된 ZnSe 양자점 제조

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Encapsulation of ZnSe Quantum Dots within Silica by Water-in-oil Microemulsions

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ZnSe 양자점을 AOT 마이크로에멀전을 이용해서 제조하였으며, tetraethyl orthosilicate (TEOS)를 직접 주입하는 방법으로 실리카에 담지된 ZnSe 양자점 소재를 얻었다. 양자점이 실리카에 담지되었을 때, 상대적으로 고른 구 형태의 ZnSe 양자점을 얻을 수 있었고 그 크기는 약 7 nm이었다. 아울러 마이크로에멀전상의 ZnSe 양자점이 실리카에 담지되면 photoluminescence 효율은 8%에서 1.1%로 감소하였다. 그러나 금표면에 실리카에 담지된 ZnSe 고체 박막을 형성시켰을 때, 양자점의 광학안정성은 크게 증가함을 알 수 있었다. 특히 ZnSe 양자점은 카드뮴이 없어 독성이 작으며 기존의 ZnSe 제조 시 Se 전구체로 사용하는 맹독성의 H_2Se 가스나 높은 반응 온도를 필요로 하지 않는다. 따라서 바이오센서용 등으로 사용이 가능한 실리카에 담지된 ZnSe 양자점을 안전하고 경제적인 방법으로 생산할 수 있는 방법을 제시할 수 있었다.

ZnSe quantum dots (QDs) were prepared by employing water-containing Dioctyl sodium sulfosuccinate (AOT) reversed micelles (microemulsions) and the silica-encapsulated ZnSe QDs were obtained by a direct injection of tetraethyl orthosilicate (TEOS) into the microemulsion system. When the QDs were coated by silica, well-defined spherical shapes were formed and the average size of the QDs was near 7 nm. In addition, the photoluminescence (PL) efficiency of the QDs was reduced from 8.0 to 1.1% as they were encapsulated by silica. However, the solid layers of the silica-encapsulated ZnSe QDs on gold surfaces showed the excellent photostability. In particular, they are cadmium free and thus, less toxic. Moreover, the present method does not require a hot reaction temperature or extremely toxic H2Se gas as a Se precursor. Accordingly, the method can be a safer and more economical process for producing silica-encapsulated ZnSe QDs, which may be a potential media for biosensors.

Keywords: *ZnSe, quantum dot, microemulsion, silica encapsulation, photostability*

1. Introduction

Over the years, extensive attention has been paid to the preparation of selenide in the quantum confinement region due to its optoelectronic advantages over commonly used organic fluorophores. Its advantages are related not only to its size tunable optical properties but also to its active surface and low photodegradation rate[1]. Although CdSe is the most studied quantum dots (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[2]. When colloidal ZnSe QDs are prepared, various synthetic techniques can be utilized. In general, for synthetic technique, the hot-injection[3-6] or the precipitation method[7,8] is employed. However, such methods require 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)[9]. However, in applying for biosensor media, it is necessary for these ZnSe QDs to be biocompatible. In order to improve the photostability of QDs they need to be encapsulated within a rigid matrix. In that respect, metallic or oxide particles can be good candidate materials. Among them, silica encapsulation is one of the great choices to pave the way of protection and biocompatibility of quantum dots under biological conditions[10]. In fact, methods for silica coating of gold, silver, CdS and CdTe nanoparticles have been reported[11-14]. Such silica coating are expected to bring many advan-

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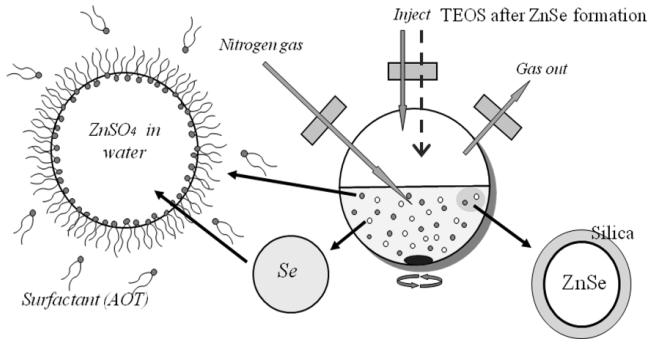


Figure 1. Schematic of microemulsion technique for silica encapsulated ZnSe nanoparticles synthesis.

tages 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 addition, silica is chemically inert, optically transparent and allows the dispersion of hydrophobic QDs in aqueous solutions at high concentrations and high ionic strength. Moreover, the surface of the silica can be easily modified for linking bioconjugators. Accordingly, it is possible to bind different compounds, such as bio-molecules, useful for bio analytical applications.

In the present work, silica encapsulated ZnSe QDs were prepared using a safe, simple synthetic method by employing water-containing AOT reversed micelles (microemulsions). For the encapsulation, diluted ammonia and tetraethyl orthosilicate (TEOS) were injected directly to AOT reversed micellar solution after the formation of ZnSe QDs. Then, the silica encapsulated ZnSe QDs were characterized. In addition, we prepared the layer of silica-ncapsulated ZnSe QDs on gold surface by simple dipping method for applying those layers to biosensor media. For characterizing study, photoluminescence spectroscopy (PL), focused ion beam system (FIB) and transmission electron microscopy (TEM) were employed.

2. Experiments

2.1. Materials and Synthesis

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) was obtained from Aldrich. The water used in all experiments was prepared by distillation and reverse osmosis.

2.2. Synthesis of ZnSe Quantum Dots and Silica-encapsulated ZnSe Quantum Dots

A schematic of the synthetic method is shown in Figure 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 reduced selenium solution was kept under nitrogen atmosphere at room temperature. Next, 50 mL solution of 0.1 mol/L AOT in cyclohexane was poured into a reaction flask to form reverse micelles. The obtained microemulsion solution was constantly stirred using a magnetic stirrer. Then 0.15 mL of pure water was added to form initial W/O microemulsions. Subsequently, an aqueous solution of 0.2 mol/L $ZnSO_4$ was added to the reverse micellar solution. Then, 0.1 mol/L Se^{2-} solution was injected into the reaction flask using a syringe under vigorous stirring at room temperature. At a fixed surfactant concentration (0.1 M), 0.15 mL of $ZnSO_4$ and Se^{2-} solutions were injected. All of these solutions were degassed with a nitrogen purge for over 20 min, and the reaction flask was continually flushed with nitrogen gas. When the $ZnSO_4$ solution was added to the microemulsion solution, there was no change in color, but upon the addition of the Se^{2-} solution, a change in color from white to yellow was observed due to formation of ZnSe QDs. After formation of ZnSe QDs, silica-encapsulated ZnSe QDs were prepared by direct injection of 0.02 mL of diluted ammonia (14 wt%) and 0.05 mL of TEOS. The reaction time was 24 h.

2.3. Preparation of Layer of ZnSe QDs

The layers of silica-ncapsulated ZnSe QDs were prepared by simple dipping method. Gold wafers (1 cm × 1 cm) were dipped into reverse micellar solutions of ZnSe QDs (or silica-encapsulated ZnSe QDs). The layers were then heated at 400 ℃ to remove all organic materials including AOT.

2.4. Characterization

PL measurement was performed on colloidal solutions of ZnSe QDs (or silica encapsulated ZnSe QDs) using a photofluorometer (PTI Quanta Master TM). To measure the PL efficiencies of ZnSe QDs in reversed micellar solutions, the absolute value of room-temperature PL efficiency of quantum dots was estimated by comparison with solutions of Rhodamine 6G in ethanol. The literature value for the room-temperature PL efficiency of Rhodamine 6G (95%) was used[15]. For observing the ZnSe layer and silica encapsulated ZnSe layer, focused ion beam system (FIB, Nova) was employed and for the image of ZnSe QDs, transmission electron microscopy (TEM, FEI, Tecnai, F30 S-Twin) was utilized after demulsifying the AOT microemulsion system by the addition of acetone.

3. Results and Discussion

Figure 2 shows the TEM images of the silica-encapsulated ZnSe QDs with direct injection of TEOS into AOT reversed micelles containing ZnSe. The ZnSe QDs with well-defined spherical shapes were formed and the image shows that the average size of the ZnSe QDs was about 7 nm. In addition, the figure shows that the ZnSe QDs were encapsulated within a rigid silica matrix. One of the purposes of the present work is to prepare stable QD for sensor media, which allows the eventual introduction of a specific surface functionality such as hydroxy and carboxyl group. In fact, silica coatings of gold, silver, CdS and CdTe nanoparticles have been reported[16]. As shown in Figure 2, the silica-encapsulated ZnSe QDs were successfully prepared without

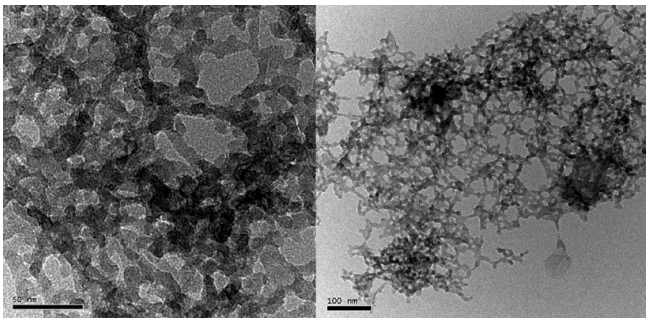


Figure 2. TEM images of silica-encapsulated ZnSe QDs with different magnifications.

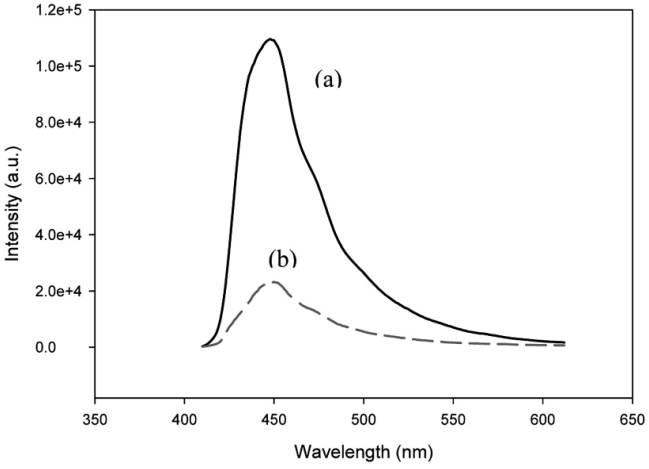
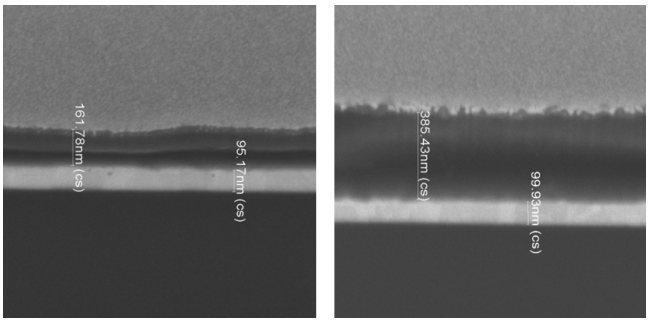


Figure 3. PL spectra of silica-encapsulated ZnSe QDs : (a) in solution and (b) solid layer after removing solvent. Excitation wavelength = 370 nm.



(a) (b)

Figure 4. FIB images of thin layers on gold surface after removal of surfactant and solvent : (a) ZnSe layer and (b) silica-encapsulated ZnSe QDs layer.

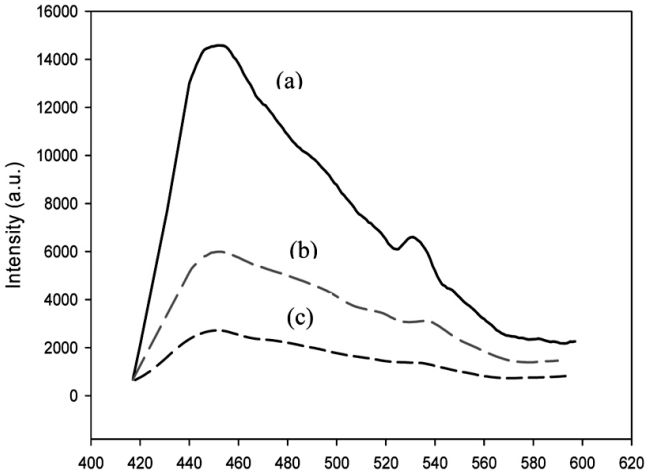


Figure 5. PL spectrum of thin layer of ZnSe on gold surface after removing solvent and surfactant : (a) on preparation, (b) after 1 day, and (c) after 2 days.

employing a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor by using an inverse microemulsion technique with simple injection of TEOS. In order to investigate the properties of the ZnSe QDs, the PL emission spectra were obtained before and after incorporating them into the silica matrix. As shown in Figure 3, strong emission peaks were observed at near 490 nm but the intensity was decreased when the QDs were encapsulated by silica. In the present case, the PL efficiency of the ZnSe QDs was 8.5% and that of the silica-encapsulated ZnSe QDs was 1.1%, respectively. This result is presumably due to the growth of the ZnSe QDs since the water pool size of AOT microemulsion was increased when additional aqueous ammonia solution was introduced during encapsulations of silica. According to the previous work[9], the PL intensity and quantum yield (QY) of ZnSe QDs were decreased as their sizes increased in the same AOT/cyclohexane system. In addition, the decrease of the PL intensity could be due to the presence of chemicals like ammonia and TEOS [17]. Although the intensity was decreased, the silica-encapsulated ZnSe QDs are probably utilized as biosensor media when the photostability of the QDs is improved. Accordingly, the photostability of the ZnSe QDs was investigated. The layer of the silica-encapsulated ZnSe QDs was prepared on gold surface since the thin solid layers on solid substrate are generally employed for sensor fabrications. For the layer fabrication, a simple and economical dipping method was used, i.e., a gold substrate was perpendicularly immersed into the solution of the silica-encapsulated ZnSe QDs. Then the layers were heated at 400 ℃ (4 h) to remove all organic materials including AOT. Figure 4(a) and 4(b) show the FIB images of the pure ZnSe layer and the silica-encapsulated ZnSe QDs layer, respectively. The images clearly show the bright gold layers (95 nm and 99 nm) and the dark dry ZnSe QDs layers. The thickness was 161 nm for the ZnSe QDs layers and that for the silica-encapsulated ZnSe QDs layer was 385 nm, respectively. After formation of solid layers, the PL spectra of the films were obtained as a function of time in order to evaluate the photostability of the QDs. Figure 5 shows the PL spectra for the pure ZnSe QD layer. 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 solution. However, the broadened peaks were observed for the solid layers when compared to those for the ZnSe QDs in solutions. After the ZnSe QDs were assembled and transferred from solution onto the silica surface, the average inter-QD distance became much shorter. Moreover, it has been proposed that shortening the distance in fluorphore molecules may cause red-shift phe-

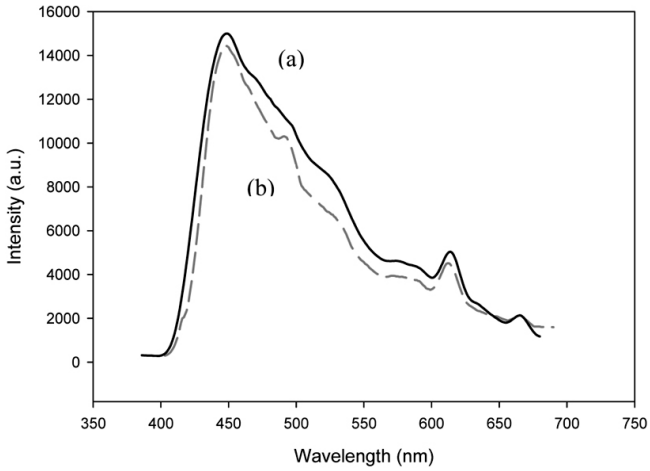


Figure 6. PL spectrum of thin layer of silica-encapsulated ZnSe QDs on gold surface after removing solvent and surfactant : (a) on preparation and (b) after 2 weeks.

nomena in PL spectra[18]. Accordingly, it appears that the peak broadening was ascribed to the shortening of the average inter-QD distance in solid layers. In addition, the figure shows that the drastic reduction of PL intensity after 2 days. Thus, the pure ZnSe QDs in the layer were easily quenched. On the other hand, the PL intensity measurements for the silica-encapsulated ZnSe QDs revealed that the PL intensity was almost unaltered even after two weeks as shown in Figure 6. Therefore, the photostability of the ZnSe QDs could be remarkably improved by encapsulation of silica.

4. Conclusions

By employing water-containing AOT reversed micelles (microemulsions) and using a direct TEOS injection method, silica-encapsulated ZnSe QDs were successfully prepared. In addition, the layers of silica-encapsulated ZnSe QDs could be obtained on gold surface by dipping method. Although the PL efficiency was reduced when the ZnSe QDs were encapsulated by silica, the ZnSe QDs in solid layers showed the excellent photostability. 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. In particular, they are cadmium free and thus, 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 media for biosensors.

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