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Article

온도센서용 실리카에 담지된 ZnSe 양자점 소재

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Silica-encapsulated ZnSe Quantum Dots as a Temperature Sensor Media

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초 록

본 연구에서는 polyoxyethylenenonylphenylether (NP5) 계면활성제와 sodium bis(2-ethylhexyl) sulfosuccinate (AOT) 계면활성제가 형성하는 두 종류의 W/O 마이크로에멀젼을 이용해서 실리카에 담지된 ZnSe 양자점을 제조하였다. 본 방법으로 3 nm 크기의 cubic zinc blende 결정 구조를 갖는 ZnSe 입자를 합성하였으며 약 20 nm 크기의 실리카 입자에 효과적으로 담지 시킬 수 있었다. 합성된 입자의 photoluminescence (PL) 주변 온도 의존성을 30 ℃에서 60 ℃ 범위에서 확인한 결과, 온도가 증가함에 따라 PL intensity가 감소하였으며 PL intensity와 온도와는 높은 상관관계를 나타내었다. 아울러 PL intensity와 온도의 상관관계는 온도를 낮은 곳에서 올려가며 측정한 경우와 반대로 낮추며 측정한 경우 같은 상관도를 나타내어 온도 의존성이 가역적임을 알 수 있었다. 그 결과 실리카에 담지된 ZnSe 양자점이 온도 센서로 사용될 수 있는 잠재적인 매체임을 확인하였다.

Abstract

Silica encapsulated ZnSe quantum dots (QDs) were prepared by employing two microemulsion systems: AOT/water/cyclohexane microemulsions containing ZnSe quantum dots with NP5/water/cyclohexane microemulsions containing tetraethylorthosilicate (TEOS). Using this method, cubic zinc blende nanoparticles (3 nm in diameter) were synthesized and encapsulated by silica nanoparticles (20 nm in diameter). The temperature dependence of photoluminescence (PL) for silica-encapsulated ZnSe QDs was investigated to evaluate this material as a temperature sensor media. The fluorescence emission intensity of silica-encapsulated ZnSe nanoparticles (NPs) was decreased with an increase of ambient temperature over the range from 30 ℃ to 60 ℃ and a linear relationship between the temperature and the emission intensity was observed. In addition, the temperature dependence of PL intensity for silica-encapsulated ZnSe NPs showed a reversible pattern on ambient temperature. A reversible temperature dependence of the luminescence combined with its insensitivity toward quenching by oxygen due to silica coating established this material as an attractive media for temperature sensor applications.

Keywords: *microemulsion, ZnSe, silica-encapsulation, photoluminescence, temperature-dependence*

1. Introduction

The II-VI semiconductor nanoparticles (NPs) such as ZnSe attract much interest as novel bright phosphors, i.e., quantum dots (QDs) with tunable photoluminescence (PL) wavelength for possible uses including light-emitting devices[1-3], and biological labeling[4,5]. In particular, ZnSe NPs do not contain toxic cadmium. Accordingly, it is favorable when these nanoparticles are applied for biosensors. Up to date, several methods of synthesizing monodispersed nanoparticles have been utilized such as coprecipitation, hydrothermal synthesis, reverse micelles, sol-gel method, and spray pyrolysis[6]. Among these methods, water-in-oil (W/O) microemulsion (i.e., reverse micelle) technique is one of the most recognized methods. In our previous work, we have prepared cadmium-free ZnSe NPs successfully using this method[7]. However, the ultra-sensitive nature of their fluorescence to the surface states hinders their applications to a great extent[8]. Therefore, it is natural to seek an effective method to remove this problem. One of the most notable examples is the formation of a core/shell structure. Overcoating QDs core with higher band gap semiconductor materials such as ZnS or CdS permits passivation of the surface states, which improves the photoluminescence quantum yields and enhances the photochemical stability substantially. Such core-shell structures such as CdSe/ZnSe, CdSe/ZnS, and CdTe/CdS have been explored. On the oth

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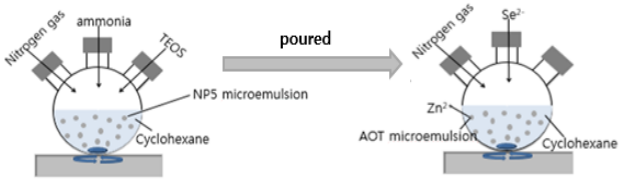

Figure 1. Schematic of synthetic method for silica-encapsulated ZnSe quantum dots.

er hand, another important issue is how to make QDs biocompatible when we use those QDs for biological labeling, or biosensor. Silica is an ideal choice, since it will protect the QDs from oxidation and agglomeration. Furthermore, the QDs will benefit from having a silica shell to impart biocompatibility and surface of silica can be easily modified to link bioconjugators[9]. Earlier, Wilson et al. have reported that silica is a suitable material to be a coating or encapsulating inert substance[10,11]. In fact, silica coatings of gold, silver, CdS and CdTe nanoparticles have been reported[12]. In order to encapsulate semiconductor nanoparticles with silica shells, two methods may be used, i. e., the Stöber method and the microemulsion method. The Stöber synthesis of colloidal silica was first described in 1968 and silica particles with a diameter less than a μm range could be obtained[13]. By the Stöber method, both organic-soluble and water-soluble NPs were encapsulated with silica successfully. However, the Stöber method needs the multiplie preparation steps that are difficult to control. As an alternative method, microemulsion method is very robust against reaction conditions and can yield more uniform spheres with smooth surfaces due to the uniform size of a water pool, which is a reaction field for the formation of silica spheres[14].

In the present work, silica encapsulated ZnSe QDs were prepared using a safe, simple synthetic method by employing microemulsions. Silica-encapsulated ZnSe NPs were prepared by employing two microemulsion systems : AOT/water/cyclohexane microemulsions containing ZnSe quantum dots with NP5/water/cyclohexane microemulsions containing tetraethylorthosilicate (TEOS). Then, the temperature dependence of the PL for silica-encapsulated ZnSe particles on the ambient temperature was investigated to evaluate this material as a temperature sensor media. Reactions involved in this synthesis included the ZnSe QDs formation and the hydrolysis of TEOS, and the nucleation of the hydrolyzed silica species in the presence of a base catalyst, ammonia. In addition, the silica-encapsulated ZnSe particles were characterized by TEM and XRD.

2. Experiments

2.1. Chemicals

All chemicals used were purchased from Sigma-Aldrich. AOT, $ZnSO_4 \cdot 7H_2O$, selenium powder (100 mesh), $NaBH_4$, cyclohexane anhydrous, $NH_3 \cdot H_2O$ (28 wt%), TEOS, NP5 were used as received without further purification. The water used in all experiments was prepared by distillation and reverse osmosis.

2.2. Synthesis of Silica-Encapsulated ZnSe NPs

The schematic of synthetic method for silica encapsulated ZnSe quantum dots is given in Figure 1. First, NaHSe aqueous solution was freshly prepared by dissolving Se powder in $NaBH_4$ solution at a high pH. This reducing selenium solution was kept under nitrogen atmosphere. Then, 50 mL solutions of 0.1 M AOT in cyclohexane were poured into a reaction flask to form reverse micelles. The obtained microemulsion solution was stirred using a magnetic stirrer. Subsequently, an aqueous solution of 0.15 mL $ZnSO_4$ (0.2 mol/L) and 0.15 mL Se^{2-} (0.1 mol/L) solutions were successively injected into the reaction flask using a syringe under vigorous stirring. In the meantime, silica microemulsions were prepared with similar method, where the molar ratio of ammonia water (28 wt%) to surfactant molecules W = $[H_2O]$/[surfactant] was 5. Then, 0.694 mL of TEOS was added into 50 mL solution of NP5 (0.1 M)/water/cyclohexane microemulsions and the microemulsions of TEOS were poured into reversed micellar solutions containing ZnSe QDs and kept stirring for 24 h. All solutions were degassed by nitrogen purge for more than 20 min. All experiments were carried out at room temperature.

2.3. PL measurements and characterizations of the silica-encapsulated ZnSe NPs

Steady-state fluorescence spectra were obtained with photofluorometer (PTI QuantaMasterTM, USA). The excitation wavelength was set at 310 nm. For measuring the PL emission spectra of silica-encapsulated ZnSe NPs as a function of temperature, the ambient temperature of fluorometer cell was controlled with an oil-circulating bath with a temperature controller (JeioTech Co., Korea) from 30 ℃ to 60 ℃. XRD data were obtained with a D/MAX-2000/PC using Cu Kα radiation (λ is 1.5418 A) for the dried powder sample of synthesized silica-encapsulated ZnSe nanocrystals after collecting from microemulsions. FT-IR spectra were obtained from FT-IR spectrometer (Bruker Vertex 70, USA). For obtaining the image of nanoparticles, transmission electron microscope (TEM, FEI, Tecnai, F30S-Twin, Netherlands) was utilized. For preparing a TEM specimen, the NPs were first precipitated by acetone from the microemulsion, ultrasonicated 20 min and centrifuged at 9,800 rpm for 25 min successively. Then the solution was washed with ethanol, acetone and ethanol using the same process mentioned above. Finally, the nanoparticles were resuspended in ethanol solution, and then a drop of this solution was placed onto a carbon-coated TEM grid and allowed to evaporate.

3. Results and Discussion

3.1. Characterization of silica-encapsulated ZnSe NPs

Figure 2 shows the TEM images of silica-encapsulated ZnSe QDs. It can be seen that ZnSe NPs with well-defined spherical shapes were formed and the image shows that the average size of ZnSe NPs was about 3 nm. Indeed, by using two microemulsions method, silica-encapsulated ZnSe QDs were successfully prepared without employing a hot reaction temperature or extremely toxic H_2Se gas as a Se precursor. In addition, the figure shows that the ZnSe NPs are encapsu

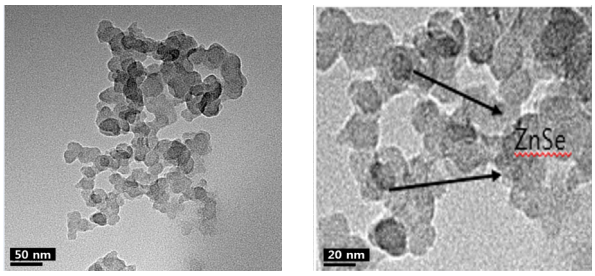

Figure 2. TEM images of silica encapsulated ZnSe QDs.

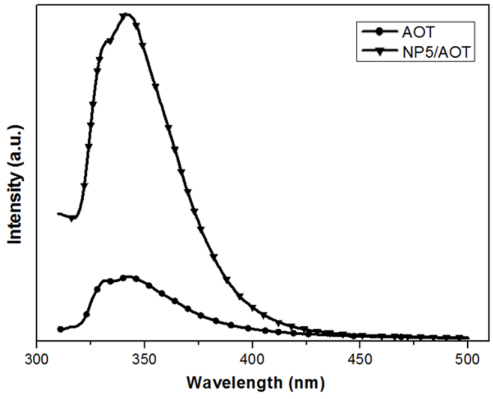

Figure 3. Fluorescence emission spectra of Silica encapsulated ZnSe NPs in reverse micelle when two AOT microemulsions were employed and AOT/NP5 microemulsion was utilized. Excitation wavelength was 300 nm.

lated within a rigid silica matrix. In fact, from our preliminary study in our lab, it was found that the silica coating for ZnSe provides photostability in PL intensity because the PL intensity of silica-encapsulated ZnSe QDs was essentially unaltered even after 8 weeks (the data are not shown). On the other hand, the pure ZnSe QDs showed the drastic reduction of PL intensity after 2 days[15,16]. Accordingly, the silica coating of ZnSe QDs is necessary for utilizing the QDs as a temperature sensor media. Moreover, it was found that the present AOT/NP5 microemulsion method provided the higher PL intensity than that for AOT/AOT microemulsion method. For comparison, we also prepared silica-encapsulated ZnSe QDs with the similar method by using AOT/AOT two microemulsions. In Figure 3, the fluorescence emission spectra of silica encapsulated ZnSe NPs are given when two different methods were employed: AOT/NP5 microemulsion method and AOT/AOT microemulsion method. As shown in the figure, the PL intensity for AOT/NP5 microemulsion method is much higher than the PL intensity for AOT/AOT microemulsion method. This result revealed that the present AOT/NP5 microemulsions provided the more complete encapsulation of ZnSe QDs probably due to the difference in the intermicellar exchange rate of microemulsions during the NP synthesis. In Figure 4, the powder XRD patterns of the silica-encapsulated ZnSe NCs are shown. The figure shows that three peaks attribute to the (111), (220) and (311) lattice planes of zinc blende ZnSe which confirms that the present synthetic method provided crystalline ZnSe NPs encapsulated by silica.

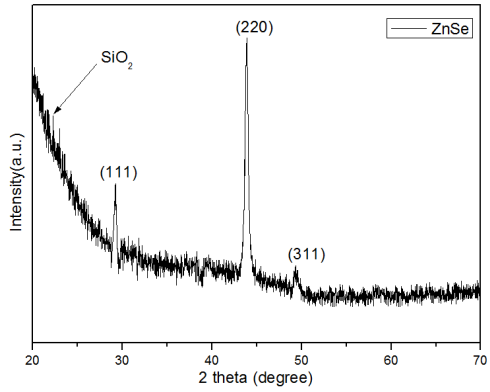

Figure 4. XRD patterns of silica-encapsulated ZnSe NCs obtained with AOT and NP5 mixed reverse microemulsion.

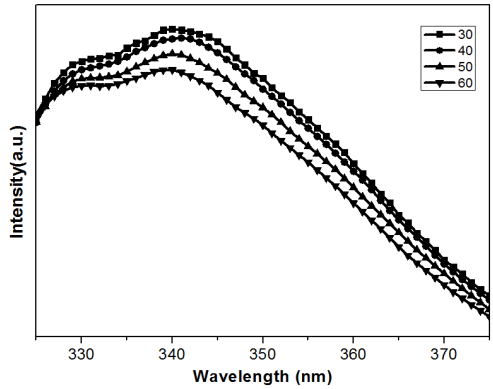

Figure 5. PL emission spectra of silica encapsulated ZnSe NPs as a function of ambient temperature.

3.2. Temperature dependence of silica-encapsulated QDs

Figure 5 shows the PL emission spectra of silica-encapsulated ZnSe NPs in microemulsions as a function of ambient temperature. The temperature was varied from 30 ℃ to 60 ℃ and the emission spectra were measured after 30 min of thermal equilibrium. The figure shows that emission intensity of silica-encapsulated ZnSe NPs QDs was gradually decreased with increase of temperature. The thermal quenching of QDs was previously explained to be due to a thermal activation of surface trap states and an increased nonradiative Augur exciton recombination[17]. Figure 6 shows the normalized variation in integrated PL emission intensity of silica-encapsulated ZnSe QDs with temperature and a least-squares linear regression analysis of the data. The normalized area (from 325 nm to 375 nm) decreased linearly with increase of temperature over the range from 30 ℃ to 60 ℃ (R^2 = 0.9979). Indeed, silica-encapsulated ZnSe showed a great linearity. More importantly, the change in PL intensity was reversible, i.e., the same linearity was observed (R^2 = 0.9941, data not shown) on decreasing ambient temperatures from 60 ℃ to 30 ℃. The reversible temperature dependence is important when the media is applied as a temperature sensor. For example, mercaptopropionic acid (MPA)-capped CdTe QDs showed the irreversible dependence in the PL intensity on temperature. The PL intensity increased when the temperature decreased from 50 ℃ to 20 ℃. However, after the temperature decreased from 50 ℃ to 20 ℃, the PL

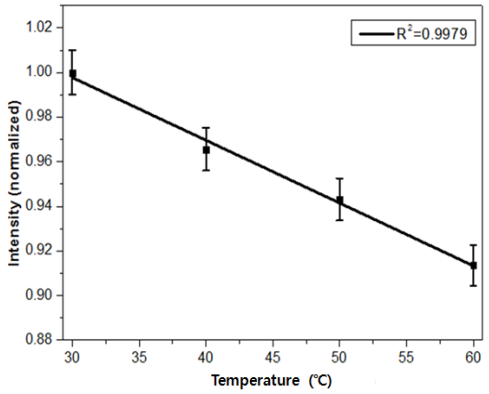

Figure 6. Normalized variation in integrated PL emission intensity with temperature and a least-squares linear regression analysis of the data.

intensity was approximately 50% of that at 20 ℃ before heating[18]. It is believed that some reactions such as oxidation may occur, which disturbed the repopulation of mobile electrons and holes leading to the irreversible PL quenching[19,20]. In the case of silica-encapsulated ZnSe NPs, it is expected that the silica shell effectively protect ZnSe QDs from oxidation. This reversible temperature dependence of the luminescence combined with its insensitivity to quenching by oxygen establishes this material as an attractive class of optical indicators for luminescence temperature sensor applications.

4. Conclusions

By mixing AOT microemulsions containing ZnSe NPs with NP5 microemulsions containing TEOS, cubic zinc blende NPs (3 nm in diameter) were synthesized and encapsulated by silica nanoparticles (20 nm in diameter). The fluorescence emission intensity of silica-encapsulated ZnSe NPs was decreased with increase of ambient temperature over the range from 30 ℃ to 60 ℃ and great linearity was observed between temperature and emission intensity. In addition, the temperature dependence of PL for silica-encapsulated ZnSe NPs showed reversible pattern on ambient temperature.

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