Microwave-assisted hydrothermal synthesis of highly luminescent ZnSe-based quantum dots with a quantum yield higher than 90%

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Microwave-assisted hydrothermal synthesis of highly luminescent ZnSe-based quantum

dots with a quantum yield higher than 90%

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Highly luminescent ZnSe-based quantum dots (QDs) were synthesized by a microwave-assisted hydrothermal method. The characteristics of the ZnSe precursor solution strongly influenced the photoluminescence (PL) quantum yields (QYs) of the QDs. The PL QY of ZnSe-core QDs synthesized under the optimum conditions reached 60%. Furthermore, the PL QY further increased to higher than 90% when a ZnS shell was applied to prepare ZnSe/ZnS-core/shell QDs.

In semiconductor quantum dots (QDs), the quantum nature of electrons and/or excitons that cannot be observed in bulk crystals becomes apparent because of QD's finite size.[1-3] A well-known example is quantum size effects.[1-3] When an electron is confined to small spaces with dimensions of the order of several nanometers, the eigenstate of excitons is discretized and the exciton energy changes in accordance with a change in the QD size.[1,4] Thus, absorption and photoluminescence (PL) energies can be controlled by manipulating QD's size. Because the optical properties of semiconductor QDs strongly depend on their size, they have been intensively investigated from the viewpoint of basic science to elucidate the size dependence of their physical and/or chemical properties.[5-8]

In addition, numerous efforts have been made to apply these characteristics of QDs to devices such as light-emitting diodes (LEDs)[9,10] and QD lasers.[11] Furthermore, because semiconductor QDs exhibit less photodegradation than organic molecules, QDs have potential applications as fluorescent markers.[7,12] Therefore, semiconductor QDs with a high PL quantum yield (QY) are essential with respect to the application of semiconductor QDs in optoelectronic devices.

Colloidal semiconductor QDs have been synthesized using various methods.[13-19] The representative method is hot-injection method of promoting crystal growth via high-temperature heating in an organic solvent.[13-15] Using this method, researchers have prepared numerous II-VI semiconductor QDs, e. g., CdSe with a high PL QY (higher than 50%).[14,15] However, from an environment and application viewpoint, the hot-injection method, which uses organic solvents, and the presence of Cd, which is toxic, have raised concerns.

ZnSe QDs have attracted significant attention in recent years.[16-20] However,

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compared with the number of reports related to the synthesis and characterization of CdSe, the number of reports related to ZnSe QDs is small. ZnSe is a wide-gap semiconductor with a 2.7-eV band-gap in bulk crystals. Thus far, ZnSe QDs have been synthesized in both organic solvents[16,17] and aqueous solutions.[18-20] Qian et al. proposed a simple and easy method of preparing ZnSe QDs through microwave irradiation of aqueous solutions[18]; they prepared alloyed ZnSe-ZnS QDs with a QY of 17% using mercaptopropionic acid (MPA) as a ligand. This method has the advantage of enabling the rapid synthesis of QDs; however, the reported QY of the obtained QDs is low. Fang et al. reported the preparation of ZnSe/ZnS-core/shell QDs with a QY of 64% using a two-step process in which the researchers prepared the core and subsequently added a shell precursor in which glutathione (γ-glutamyl-cysteinyl-glycine; GSH) was used as a ligand.[19] Zhao et al. prepared ZnSe/ZnS-core/shell QDs with a QY of 39% in a single step through thermal decomposition of the ligand N-acetyl-L-cysteine (NAC).[20] However, the PLQY was lower than that of CdSe and CdTe QDs, thus, scope for further improvements in the preparation condition exists.

In ref. 20, a study of pH conditions of precursor solutions was conducted for pH levels between 9.0 and 10.5. Recently, we reported the hydrothermal synthesis of NAC-capped ZnSe QDs without shell structure.[21] We found that the PL intensity of the ZnSe QDs was strongly dependent on the pH of the precursor solutions and that the optimum pH value was ~6.[21] According to the aforementioned reports, high-quality ZnSe QDs can be prepared through a systematic investigation of the preparation conditions of the precursor solutions, such as their pH value and the molar ratio among the Zn-ion source, Se-ion source, and the ligand.

In the present work, we report the synthesis of highly luminescent ZnSe-core and ZnSe/ZnS-core/shell QDs. By optimizing the preparation conditions, we synthesized ZnSe-core QDs with a high QY of 60%. Moreover, after the ZnS-shell coating was applied, the QY was further increased to higher than 90%, which, to our knowledge, is the highest QY reported thus far for ZnSe-based QDs.

The ZnSe QDs were synthesized using a microwave-assisted hydrothermal method. A precursor solution was prepared according to the procedure reported by ref. 21. Briefly, $ZnCl_2$ (2.0 mmol) and NAC (4.8 mmol) were dissolved in 100 mL of deionized (DI) water followed by adjustment to pH 8.5. A freshly prepared NaHSe solution was then added. Finally, the precursor solution was adjusted to pH 6.0. To deduce the optimum conditions, we prepared various precursor solutions with different molar ratios of Zn^{2+}, Se^{2-}, and NAC. The influence of the pH shortly before the addition of the NaHSe solution on the PL intensity was also investigated. ZnSe QDs were synthesized under microwave irradiation for 4 min at 180°C using a single mode CEM Discover system.

Absorption and PL spectra were recorded using a JASCO V-650 UV/Vis spectrophotometer and a JASCO FP-8300 spectrofluorometer, respectively. PL QYs were measured with an absolute PL measurement system (Hamamatsu, CQQ20). X-ray diffraction (XRD) measurements were performed on a Rigaku SmartLab equipped with a Cu Kα radiation source ($\lambda = 0.154$ nm).

Figure 1 shows the PL spectra of ZnSe QDs synthesized with Zn^{2+}: Se^{2-}: NAC = 1.0: 0.3: 2.4. The pH value shortly before the addition of the NaHSe solution was 8.5. The band-edge PL is clearly observed in the spectra of all of the samples. With an increase in the heating time, the intensity ratio of the defect-related PL to the band-edge PL

decreased; the ZnSe QDs synthesized with a reaction time of 3 min exhibited the highest PL intensity.

Wei *et al*. reported that in the synthesis of CdSe QDs through a hydrothermal method, the Cd^{2+}: Se^{2-}: NAC molar ratio strongly affected the PL intensity of the CdSe QDs.[22] Thus, we synthesized ZnSe QDs under various conditions by changing the molar ratio of Zn^{2+} to Se^{2-} (Zn^{2+}: Se^{2-} = 1.0: *X*, where *X* = 0.1, 0.2, 0.3, 0.4) and that of Zn^{2+} to NAC (Zn^{2+}: NAC = 1.0: *Y*, where 1.2≤ *Y* ≤6.0). Figure 2 shows the experimental results for the dependence of the PL QY on the Zn^{2+}: Se^{2-}: NAC molar ratio. The results reveal that the ZnSe QDs synthesized with Zn^{2+}: Se^{2-}: NAC = 1.0: 0.2: 2.4 exhibited the highest PL intensity.

Next, we focused on the dependence of the PL intensity of ZnSe QDs on the pH shortly before the addition of the NaHSe solutions. The pH before the addition of the NaHSe solutions was changed from 6.0 to 12.0. The Zn^{2+}: Se^{2-}: NAC molar ratio and the final pH of the ZnSe precursor solution were fixed at 1.0: 0.2: 2.4 and 6.0, respectively. According to the theory for the quantum confinement effect in QDs,[23] the lowest exciton energy in a spherical QD with a radius *R* is given by

$$E(R) = E_g + \frac{\eta^2}{2\mu}\left(\frac{\pi}{R}\right)^2 - 1.8\frac{e^2}{\varepsilon R} \quad , \qquad (1)$$

where E_g, μ, and ε are the band-gap energy, reduced mass, and dielectric constant, respectively. By substituting the values in a ZnSe bulk crystal for each parameter, eq. (1) can be transformed as follows, which corresponds to eq. (4) in ref. 24,

$$E(d) = 2.67 + \frac{11.9}{d^2} - \frac{0.596}{d} \quad (\text{eV}) \qquad (2)$$

where diameter (*d*) is in nanometers. The average diameter of ZnSe QDs was calculated from the absorption peak energy based on eq. (2). As shown in Fig. 3, the PL QYs of

ZnSe QDs were strongly dependent on the pH before the addition of the NaHSe solution. The experimental results clearly indicate that the pH value before the addition of the NaHSe solutions is an important factor and that its optimum value is 8.5. Thus, we concluded that the optimum conditions for the synthesis of ZnSe QDs are a Zn^{2+}: Se^{2-}: NAC molar ratio of 1.0: 0.2: 2.4, a pH value of 8.5 shortly before the addition of the NaHSe solution, and a final pH of the precursor solution is 6.0. The highest obtained QY was 60%, as far as we know, this QY is the highest value reported thus far for water-soluble ZnSe QDs.

As pointed out in ref. 20, microwave-assisted hydrothermal synthesis requires professional and expensive microwave equipment. To verify whether the optimum conditions deduced in the present work are also applicable in a conventional hydrothermal synthesis, we attempted to synthesize ZnSe QDs using a hydrothermal method without microwave irradiation. Notably, ZnSe QDs obtained by heating the precursor solution at 200°C for 60 min using an autoclave also exhibited a high PL QY of 60%, which matches that of the QDs synthesized using microwave irradiation. Thus, the preparation conditions of the ZnSe precursor solution strongly influence the quality of the obtained ZnSe QDs, whereas the heating method (i.e., with/without microwave irradiation) does not.

In the next step, to further improve the QY, we synthesized ZnSe/ZnS-core/shell QDs. When ZnS is used as a shell, ZnSe/ZnS forms a type-I potential structure in which electrons and holes are confined in the ZnSe core.[25] Furthermore, because the non-radiative recombination process caused by the surface state of ZnSe QDs is suppressed, an increase in the PL intensity is expected. ZnSe/ZnS-core/shell QDs were prepared as follows. First, 490 mg of $Na_2S \cdot 9H_2O$ was added to 20 mL of DI water to

prepare the S^{2-}-ion source. NAC (1.96 g) was then dissolved in 100 mL of DI water, and

745 mg of $Zn(ClO_4)_2 \cdot 6H_2O$ was added as a Zn^{2+}-ion source. NaOH was added to this

solution to adjust the pH to 5.0, and then 6 mL of the S^{2-}-ion source was added. Finally,

the ZnS precursor solution was prepared by adding diluted HCl to adjust the pH to 6.0.

The Zn^{2+}:S^{2-} : NAC molar ratio was 1.0: 0.3: 4.8. The ZnS precursor solution was added

to the already prepared ZnSe QD solution, and ZnSe/ZnS-core/shell QDs were

synthesized by microwave irradiation.

Figure 4 shows the absorption spectra of ZnSe-core and ZnSe/ZnS-core/shell QDs.

A new absorption feature was confirmed at 4.4 eV, which is a higher-energy region than

the band-gap energy of ~3.7 eV in a ZnS bulk crystal; this feature was not observed in

the spectra of the ZnSe-core QDs. It is well known that an additional absorption

structure is observed on the high energy side than the band-gap energy of shell material

when core/shell-QDs are formed.[26] This transition originates from the higher excited

states of electrons and holes spreading over entire core/shell-QDs. Furthermore, the

absorption peak the ZnSe/ZnS-core/shell QDs shifted toward lower energies compared

to the absorption peak of the ZnSe-core QDs. Conceivably, the effective confinement

energy of the wave function may have been decreased when the ZnSe QDs were

covered with ZnS.[25] Thus, these observations suggest that the ZnSe/ZnS-core/shell QDs

were successfully synthesized.

To confirm the formation of the core/shell structure, X-ray structural analyses of

both the ZnSe-core and the ZnSe/ZnS-core/shell QDs were carried out; the

corresponding XRD patterns are shown in Fig. 5. The three broad diffraction peaks in

the pattern of the ZnSe-core QDs correspond to the (111), (220), and (311) planes of the

cubic zinc-blende ZnSe lattice structure (JCPDS Card No. 80-0021). Compared with the

peaks in the XRD pattern of the ZnSe-core QDs, those of the ZnSe/ZnS-core/shell QDs were shifted to higher 2θ angles. Usually, when core/shell-QDs are formed, the diffraction peak is shifted to that of the shell material.[19,20] Since the lattice constant of ZnS is 5.40 Å, which is smaller than 5.67 Å in ZnSe, the diffraction peak of ZnS appears higher 2θ angles than those of ZnSe. On the basis of the experimental results in Figs. 4 and 5, we concluded that ZnSe/ZnS-core/shell QDs were synthesized successfully.

Finally, we investigated the PL QY of the ZnSe/ZnS-core/shell QDs. Figure 6 shows the PL spectra of the ZnSe-core and the ZnSe/ZnS-core/shell QDs. Compared with the PL intensity of the ZnSe-core QDs, that of ZnSe/ZnS-core/shell QDs is higher. Notably, ZnSe/ZnS-core/shell QDs exhibit a PL QY higher than 90%.To the best of our knowledge, this PL QY is the highest reported thus far for ZnSe-based QDs.

In summary, we have investigated the optimum conditions for the synthesis of highly luminescent ZnSe QDs. The characteristics of the ZnSe precursor solution strongly influenced PL QYs of the ZnSe QDs. The optimum conditions for the synthesis of ZnSe QDs were found to be (a) a Zn^{2+}: Se^{2-}: NAC molar ratio of 1.0: 0.2: 2.4, (b) a pH shortly before the addition of the NaHSe solution of 8.5, and (c) a final pH of the precursor solution of 6.0. The PL QY of the ZnSe-core QDs synthesized under the optimum conditions reached 60%. By contrast, with the synthesis of ZnSe/ZnS-core/shell QDs, the PL QY was increased to higher than 90%. The present results open the possibility of using ZnSe-based QDs as blue luminescence materials.

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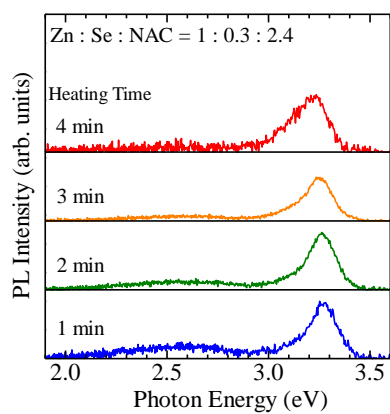
Fig. 1. PL spectra of ZnSe QDs synthesized with Zn^2: Se^{2-}: NAC = 1.0: 0.3: 2.4. The pH shortly before the addition of the NaHSe solution was 8.5.
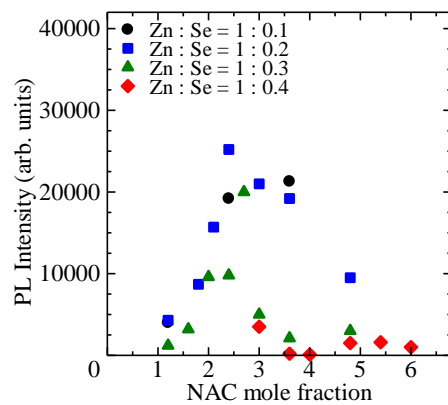
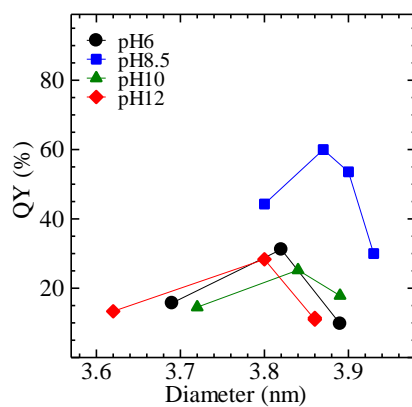Fig. 2. The dependence of PL intensity on the Zn^{2+}: Se^{2-}: NAC molar ratio.

Fig. 3. The dependence of PL QY on the pH shortly before the addition of the NaHSe solutions. The pH before the addition of the NaHSe solutions was changed from 6.0 to 12.0. The Zn^{2+}: Se^{2-}: NAC molar ratio and the final pH of the ZnSe precursor solution were fixed at 1.0: 0.2: 2.4 and 6.0, respectively.
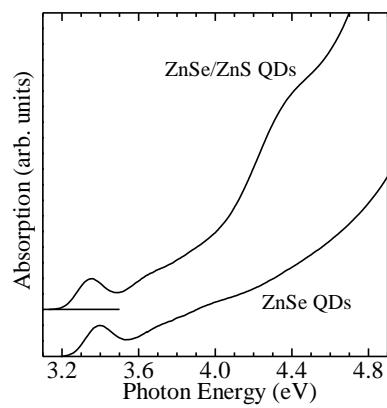
Fig. 4. Absorption spectra of ZnSe-core and ZnSe/ZnS-core/shell QDs.
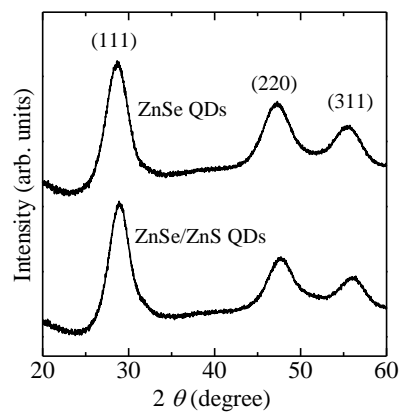
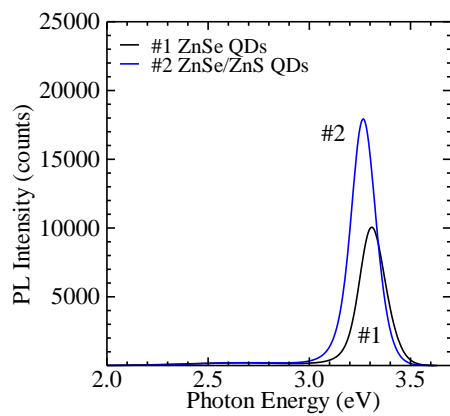Fig. 5. X-ray diffraction patterns of ZnSe-core and ZnSe/ZnS-core/shell QDs.

Fig. 6. PL spectra of ZnSe-core and ZnSe/ZnS-core/shell QDs.