Absorption and photoluminescence properties of CdSe quantum dots prepared by hydrothermal method

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Abstract. Herein, we investigated the preparation and optical properties of water-soluble CdSe quantum dots (QDs). CdSe QDs with a narrow size distribution were hydrothermally prepared by reacting Cd^{2+} with NaHSe in the presence of N-acetyl-L-cysteine as ligand. Furthermore, photoluminescence quantum yield increased to ~47% when a ZnS shell was applied to prepare the CdSe/ZnS core/shell QDs.

1. Introduction
In semiconductor quantum dots (QDs), both the absorption and photoluminescence (PL) energies can be controlled by the size of the QD owing to the quantum size effect. Semiconductor QDs have been expected to be new fluorescent materials because they can absorb light with a wide range of wavelengths and excellent in anti-photobleaching properties as compared with organic dyes. To date, several studies have been conducted on the preparation and optical properties of semiconductor QDs [1]. In 1993, Murray et al. reported the successful preparation of CdSe QDs with a narrow size distribution and high PL efficiency using chemical reactions in an organic solvent [2]. CdSe QDs have become model materials for studying the optical properties of QDs [3, 4].

To apply QDs to bio-imaging application, water-soluble QD is necessary. QD synthesized by the hot injection method can be dispersed in water via the ligand exchange process [5, 6]. A more straightforward method is to synthesize the QDs in an aqueous solution [7]. However, such water-soluble CdSe QDs have a problem of low PL quantum yield (QY) and broad absorption and PL spectral widths. Thus, directly synthesizing water-soluble CdSe QDs with good optical properties is still a challenge.

Qian et al. successfully prepared mercaptopropionic acid (MPA)-capped CdSe QDs with a PL QY of 25% using a microwave-assisted hydrothermal method [8]. Schumacher et al. focused on CdSe/ZnS core/shell QDs that are more biocompatible than CdSe-CdS QDs, and synthesized CdSe/ZnS QDs with a PL QY of 13% [9]. In our previous work, we successfully prepared CdTe and ZnSe QDs with a narrow size distribution and high PL QY through the hydrothermal method using N-acetyl-L-cysteine (NAC) as ligand [10-13]. In the present work, we investigated the preparation and optical properties of water-soluble CdSe QDs, prepared via the hydrothermal method. Furthermore, we prepared CdSe/ZnS core/shell QDs to improve the PL properties of QDs by covering the CdSe QDs with a ZnS-shell layer.

2. Experimental
CdSe QDs were prepared using the hydrothermal method. The CdSe precursor solution was prepared by mixing NAC as ligand, Cd(ClO$_4$)$_2$·6H$_2$O as a Cd-ion source, and NaHSe as an Se-ion source. The following molar ratios and concentrations of monomers were used Cd:Se:NAC = 1.0:0.3:6.0 and [Cd$^{2+}$] = 20 mM. To prepare the QDs, 10 ml of the precursor solution was transferred into an autoclave and heated at 180°C using an oil bath for a specified period, and then cooled to room temperature. We prepared CdSe/ZnS core/shell QDs to improve the PL properties. First, ZnS precursor solution was prepared as follows. Zn(ClO$_4$)$_2$·6H$_2$O (0.53 mmol) and NAC (2.54 mmol) were dissolved in 20 mL DI water, and the pH was adjusted to 5.0. After adding Na$_2$S·9H$_2$O (0.16 mmol), the precursor solution was adjusted to pH 6.0. The ZnS precursor solution was added to the already prepared CdSe QD solution, and the CdSe/ZnS QDs were prepared by continuously adding ZnS solution while heating at 120 °C.

Absorption and PL spectra were measured using JASCO V-650 UV-Vis spectrophotometer and FP-8300 spectrofluorometer, respectively. A laser diode (375 nm, Hamamatsu PLP M10306-27) with a pulse duration of 50 ps and a repetition rate of 100 kHz was used as excitation light to measure the PL-decay profiles. The decay profiles were obtained using a time-correlated single-photon counting method. X-ray diffraction (XRD) measurements were performed using Rigaku SmartLab with Cu Kα radiation while transmission electron microscopy (TEM) images were obtained using JEOL JEM-2100.

3. Results and Discussion

Figure 1(a) shows the absorption and PL spectra of the CdSe QDs synthesized with reaction times of 3, 10, 20, 40, and 80 min. The absorption-peak energy in each sample is shifted to the higher-energy side than the band gap energy of 1.74 eV in the CdSe bulk crystal. This high-energy shift suggests the formation of CdSe QDs. Furthermore, it is noted that the synthesized CdSe QDs have a narrow size distribution since the absorption peak is clearly observed in all the samples. As the reaction time increased, the onset and peak energies of the absorption spectra were shifted to the lower-energy side. This is because the quantum confinement effect decreases with increasing QD size. Donegá et al. reported that the lowest exciton energy in CdSe QDs with a diameter $d$ is given by [14].

$$E(d) = 1.858 + \frac{1}{0.220d^2 + 0.008d + 0.373} \text{ (eV)}.$$  \hspace{1cm} (1)

![Figure 1](image-url)
e surface area to volume decreases as the QD diameter increases. This is considered to cause the suppression of the defect-related PL. Moreover, the decrease in the intensity of the PL in CdSe QDs of 2.3-nm or larger diameters is considered to be due to the thermal decomposition of the ligand [11, 15].

![Figure 2](image1.png)

**Figure 2.** (a) XRD patterns of CdSe QDs synthesized with reaction times of 20, 40, and 60 min. (b) TEM image of the CdSe QDs synthesized with a reaction time of 60 min.

From the absorption-peak energy, the mean diameter can be estimated to be 1.6, 1.9, 2.1, 2.2, and 2.4 nm for CdSe QDs synthesized with reaction times of 3, 10, 20, 40, and 80 min, respectively, on the basis of equation (1).

Band-edge PL and defect-related PL were observed in the PL spectrum, wherein the intensity ratio of both PLs strongly depends on the QD size. Figure 1(b) shows the dependence of the PL intensity for the band-edge PL (solid circles) and defect-related PL (solid triangles) on the QD diameter. The band-edge PL was observed as the main PL band in samples with 2.3 nm diameter or larger, whereas the defect-related PL band was observed as the main PL band in samples with 2.2 nm diameter or smaller. The ratio of the surface area to volume decreases as the QD diameter increases. This is considered to cause the suppression of the defect-related PL. Moreover, the decrease in the intensity of the PL in CdSe QDs of 2.3-nm or larger diameters is considered to be due to the thermal decomposition of the ligand [11, 15].

![Figure 3](image2.png)

**Figure 3.** (a) Absorption and (b) PL spectra, and (c) PL-decay profiles of the band-edge PL in CdSe core and CdSe/ZnS core/shell QDs.
To confirm the formation of CdSe QDs, X-ray structural analysis and TEM measurements were performed. Figure 2(a) shows the XRD patterns of CdSe QDs synthesized with reaction times of 20, 40, and 60 min. The three diffraction peaks correspond to the (111), (220), and (311) planes of the cubic zinc-blende CdSe lattice structure. Therefore, we conclude that the synthesis of CdSe QDs with a zinc blende structure was successful. Figure 2(b) shows a TEM image of the CdSe QDs synthesized with a reaction time of 60 min. Based on the TEM image, the average diameter of the QDs was obtained as ~2.4 nm. This agrees well with the diameter estimated from the absorption-peak energy.

The CdSe/ZnS core/shell QDs were prepared by covering the surface of the CdSe QD with a ZnS layer to improve the PL characteristics. Figure 3(a) shows the absorption spectra of the CdSe-core and the CdSe/ZnS core/shell QDs. In the core/shell QDs, a new absorption structure was confirmed around 4.1 eV, which is higher than the band gap energy of 3.7 eV in the bulk ZnS crystal. This is considered to be a signal demonstrating the formation of ZnS shell. Furthermore, it can be seen that the lowest absorption-peak energy in the core/shell QDs is shifted to the low-energy side as compared with the absorption peak in the core QDs. This is due to the decrease in the effective quantum confinement energy after the ZnS shell is formed. Thus, based on the absorption characteristics, it can be concluded that the CdSe/ZnS core/shell QDs were successfully prepared.

Figure 3(b) shows the PL spectra of the CdSe core and the CdSe/ZnS core/shell QDs. It can be seen clearly that the PL characteristics were remarkably improved by the formation of the ZnS layer. The CdSe/ZnS core/shell QDs exhibit a high PL QY of ~47%. To the best of our knowledge, thus far, this PL QY is the highest reported for CdSe-based QDs synthesized in aqueous solution. Figure 3(c) shows the PL-decay profiles of the band-edge PL in the CdSe core and the CdSe/ZnS core/shell QDs. It can be seen that the decay profile in the core/shell QDs is prolonged as compared with the decay profile in core QDs. When the ZnS shell is formed, the non-radiative recombination process on the surface of the core QDs is suppressed, resulting in higher PL QY and longer decay time.

4. Conclusion
We successfully synthesized water-soluble NAC-capped CdSe QDs using the hydrothermal synthesis method. The average size of the CdSe QDs was controllable by the reaction time. In addition, by covering the surface of the core QD with a ZnS layer, the PL characteristics improved drastically. As a result, we successfully prepared CdSe/ZnS core/shell QDs with a PL QY as high as ~47%.

References
[1] Klimentov V I 2004 Semiconductor and Metal Nanocrystals (Marcel Dekker Inc.)
[2] Murray C B, Norris D J and Bawendi M G 1993 J. Am. Chem. Soc. 115 8706
[3] Donegá C M, Bode M and Meijerink A 2006 Phys. Rev. B 74 085320
[4] Klimentov V I, Ivanov S A, Nanda J, Achermann M, Bezel I, Mcguire J A and Piriyatinski A 2007 Nature 447 441
[5] Bruchez Jr M, Moronne M, Gin P, Weiss S and Alivisatos A P 1998 Science 281 2013
[6] Reiss P, Bleuse J and Pron A 2002 Nano Lett. 2 781
[7] Rogach A L, Kornowski A, Gao M, Eychmüller A and Weller H 1999 J. Phys. Chem. B 103 3065
[8] Qian H, Li L and Ren J 2005 Mater. Res. Bull. 40 1726
[9] Schumacher W, Nagy A, Waldman W J and Dutta P K 2009 J. Phys. Chem. C 113 12132
[10] Bu H, Kikunaga H, Shimura K, Takahasi K, Taniguchi T and Kim D 2013 Phys. Chem. Chem. Phys. 15 2903
[11] Watanabe T, Takahashi K, Shimura K, Bu H, Kim H D and Kim D 2017 Bull. Chem. Soc. Jpn. 90 52
[12] Lee Y S, Bu H, Taniguchi T, Takagi T, Sobue S, Yamada H, Iwaki T and Kim D 2016 Chem. Lett. 45 878
[13] Lee Y S, Nakano K, Bu H and Kim D 2017 Appl. Phys. Express 10 065001
[14] Donegá C M and Koole R 2009 J. Phys. Chem. C 113 6511
[15] Zhao D, He Z, Chan W H and Cho M M F 2009 J. Phys. Chem. C 113 1293