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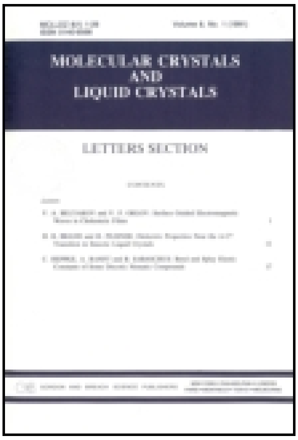

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CdSe Quantum Dots Synthesized by Tuning the Stearic Acid Concentrations via Paraffin

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CdSe Quantum Dots Synthesized by Tuning the Stearic Acid Concentrations via Paraffin

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To produce safe, stable, and cost-effective quantum dots (QDs), the experiments were conducted with paraffin liquid as a solvent. CdSe QDs are synthesized by using a pyrolysis based on the chemical colloidal method. When the cadmium precursor was prepared, the tuning of stearic acid concentrations was implemented. The investigations of crystallographic, morphological, optical properties tell that the CdSe QDs with smaller amount of impurities, smaller particles in size and larger energy gap are synthesized at relatively low stearic acid concentration, implying that the stearic acid concentration is a crucial parameter in controlling the size of QDs.

Keywords Cadmium selenide (CdSe); nanocrystals; nanoparticles; paraffin liquid; quantum dots; stearic acid concentration

Introduction

Recently, semiconductor QDs have attracted a great deal of interest because of their size-dependent optical properties and they can be engineered to suit various applications such as light emitted diodes and solar cells [1–4]. The development of nanotechnology applications using QDs has been actively studied. In the case of the QDs, they can emit most visible spectrum ranging from blue to red by tuning the particle size. Especially, QDs prepared by chemical colloidal methods can be obtaind the focusing QDs less than ~10 nm in size by choosing the suitable precursor and by controlling the growth temperature, the growth time and the surfactant concentration. Until now, the synthesis of the II-VI semiconductor QDs have been progressed. Many works have been reported on CdSe QDs fabricated by a high-temperature organometallic precursor route [5–7]. QDs fabricated by this synthesis route have a wide fluorescent emission spectra ranging from blue to red. This synthesis route includes a traditional trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP). However, it is difficult to relatively easily and rapidly produce CdSe QDs because these solvents are environmentally unfriendly, toxic, pyrophoric, explosive and expensive for a large-scale production. To solve these problems, TOPO and TOP have been substituted with a paraffin liquid as a solvent [8–9].

In this study, Cd precursor was prepared using cadmium oxide (CdO), stearic acid and paraffin liquid. Se precursor was prepared using Se powder and paraffin liquid. Stearic acid acts a surfactant. However, using a large amount of stearic acid can cause a lot of

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impurities such as cadmium stearate and reminder of stearic acid [10]. To get rid of these impurities easily, CdSe QDs are synthesized as a function of the stearic acid concentrations by using a pyrolysis based on the chemical colloidal method and their physical properties are investigated.

Experimental

Synthesis

The precursors CdO (99.99%, Aldrich), stearic acid (99.5%, Aldrich), Se powder (99.99%, Aldrich), and paraffin liquid (extrapure grade, Duksan Pure Chemicals) were used as supplied to prepare CdSe QDs. All of the reagents were used as received without further purification. CdSe QDs are synthesized by tuning the stearic acid concentrations in the paraffin-route. The stearic acid concentrations were adjusted to 2.5, 5, 7.5, 10, and 12.5 mmol. The remaining variables such as the concentrations of CdO and the paraffin liquid were fixed. To prepare the Cd precursor solution, CdO (2 mmol), paraffin liquid (15 ml) and stearic acid (2.5 ∼ 12.5 mmol) were injected into a two-neck flask and heated to 150°C with stirring to obtain a clear solution of cadmium stearate. Se powder (1 mmol) and paraffin liquid (50 ml) were added into the other three-neck flask and heated to 230°C with stirring to prepare Se precursor. Because Se powder has a melting point at 221°C [11], we fixed 230°C as the growth temperature. When the color of Se precursor changed to the dark red, Cd precursor solution was rapidly injected into the Se precursor solution. The temperature was maintained at 230°C with continuously stirring for the nucleation and the growth process. The reaction solution was cooled to the room temperature to prevent further growth. To obtain the pure CdSe QDs, the precipitated CdSe QDs were separated by centrifugation. The purification using chloroform and methanol was carried out, followed by further washing with methanol.

Measurements

All measurements were carried out at the room temperature under ambient conditions. X-ray diffraction (XRD) spectra were recorded with a powder diffractometer (PANalytical, X'pert PRO MPD) operating in the Bragg configuration using Cu Kα radiation. The morphological images of QDs in samples were taken from transmission electron microscopy (TEM, Hitach, H-7100). UV-Visible (UV-Vis) absorption spectra were recorded on a optical spectrometer (M1461 OMA system, Cary 5G). Quartz cuvettes with a 10mm path length were used in this measurement. Fluorescence spectra were recorded by using a photoluminescence (PL) spectrometer (Coherent, Innova 90) with a Ar-ion laser ($\lambda = 488$ nm) as the excitation source.

Results and Discussion

Figures 1(a) to (e) represent the XRD date for CdSe QDs synthesized as a function of the stearic acid concentrations. The XRD peaks indicate that the broad peaks are in accordance with those of cubic CdSe with zinc-blende structure. These peaks seen at 25.3, 42, 49.7, 60.9, 67 and 76.8° correspond to the (111), (220), (311), (400), (331) and (422) planes of cubic CdSe crystal, respectively. The crystal structure is determined decisively by the growth temperature, and tends to form zinc-blende structure in the paraffin route at below 300°C [12–13]. The sharp peaks also observed at 22, 24 and 37° for CdSe QDs synthesized

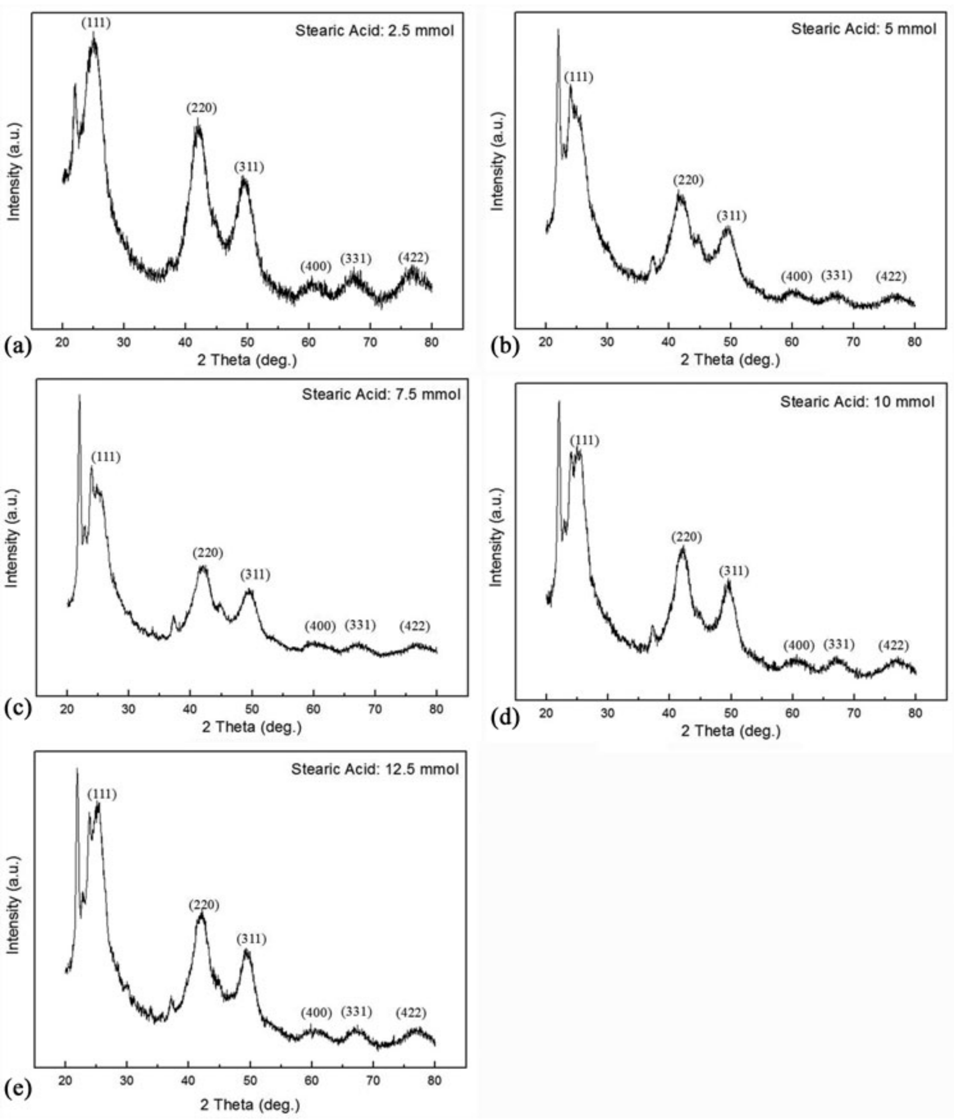

Figure 1. XRD patterns of the CdSe QDs synthesized as a function of the stearic acid concentrations. ((a) 2.5, (b) 5, (c) 7.5, (d) 10, and (e) 12.5 mmol).

as a function of the stearic acid concentrations. These peaks seem to be due to the cadmium stearate and the stearic acid, being organic components in the precipitate of the CdSe QDs [13]. Because two organic components act as impurities in the CdSe QDs, removal of these impurities is prerequisite to obtain good QDs. One can find that these peaks are observed weakly in the CdSe QDs fabricated in the precursor solutions with stearic acid concentration of 2.5 mmol, compared to that of the others as shown in Figs. 1(a) to (e). Experimental results suggest that reducing the stearic acid concentrations causes a decrease of the peaks due to the impurities in CdSe samples. The grain size was estimated using full width at half maximum (FWHM) of (311) plane by Scherrer equation. From the estimation, we

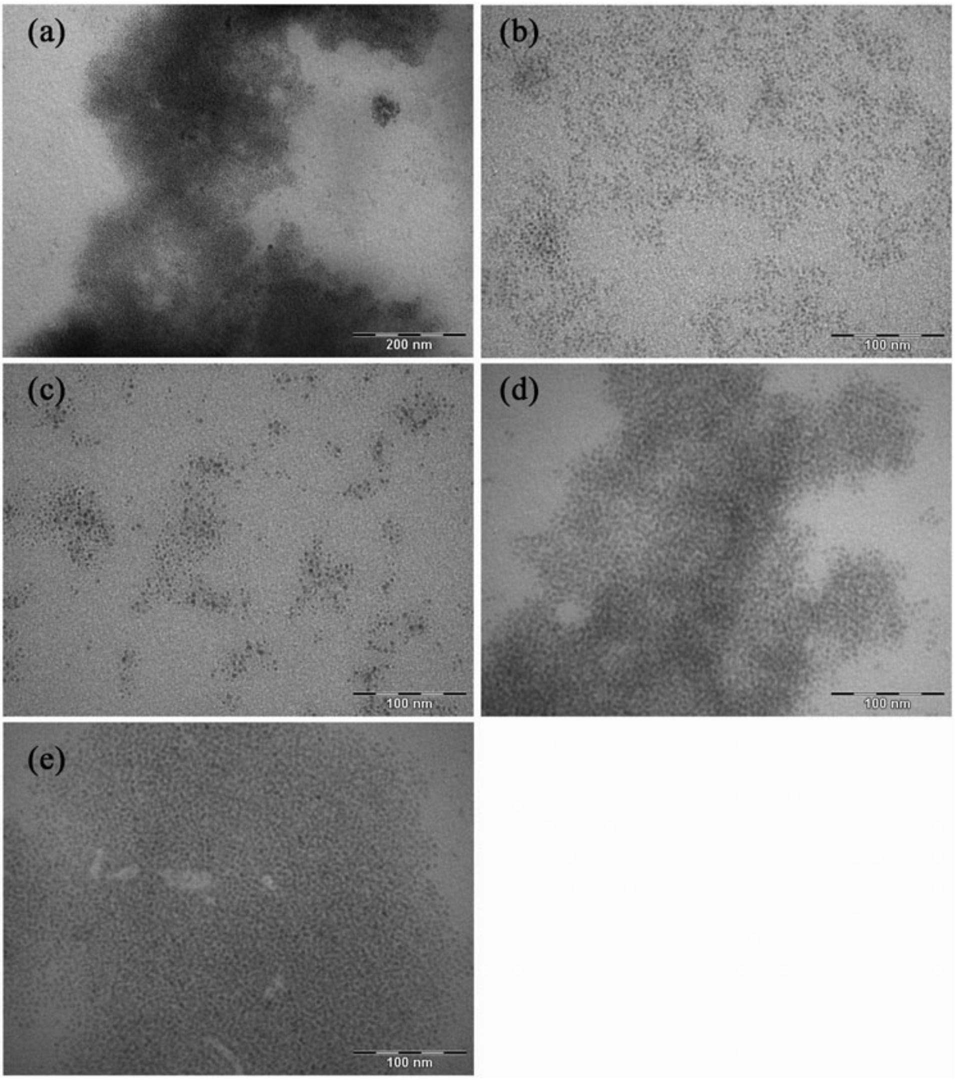

Figure 2. TEM images of the CdSe QDs synthesized as a function of the stearic acid concentrations. ((a) 2.5, (b) 5, (c) 7.5, (d) 10, and (e) 12.5 mmol).

confirmed the grain size of 3.3 nm at 2.5 mmol, 3.49 nm at 5 mmol, 4.07 nm at 7.5 mmol, 4.14 nm at 10.5 mmol and 4.3 nm at 12.5 mmol, respectively.

TEM images of the CdSe QDs synthesized as a function of the stearic acid concentration are shown in Figs. 2(a) to (e). Synthesized CdSe QDs solution was dispersed in pyridine to prevent precipitation. TEM images of the CdSe QDs show nearly spherical crystalline particles. The respective size distributions according to the concentrations of the stearic acid were measured from a statistical TEM analysis of approximate fifty particles per sample. From this analysis, we confirmed the narrow particle size distribution of 3.5 nm at 2.5 mmol, 3.6nm at 5 mmol, 4.1 nm at 7.5 mmol, 4.3 nm at 10.5 mmol, and 4.4 nm at 12.5 mmol, respectively. This data is quite consistent with the grain size calculated from

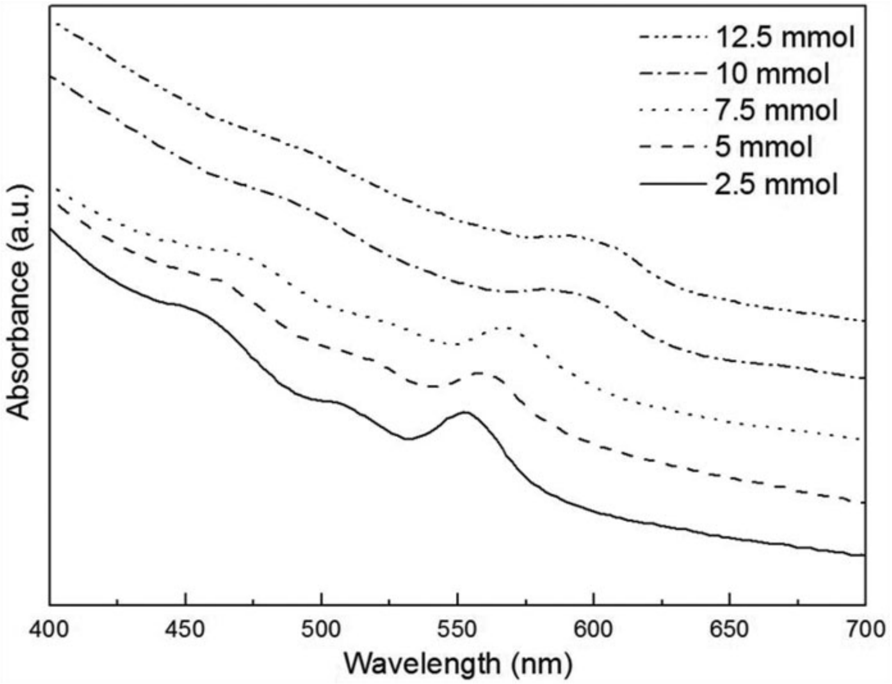

Figure 3. UV-Visible absorption spectra of the CdSe QDs synthesized as a function of the stearic acid concentrations.

the XRD peak. Experimental results suggest that reducing the stearic acid concentrations causes a decrease of the particle size distribution in CdSe samples. Thus, the stearic acid concentration is a key parameter to control the particle size distribution of CdSe QDs.

UV-Visible absorption spectra of the CdSe QDs synthesized as a function of the stearic acid concentration are shown in Fig. 3. The absorption spectra possess up to three distinct electronic transitions, indicating very narrow size distributions of the as-prepared CdSe QDs [14]. This spectra represented by the sharp absorption peaks if the growth stops in the "focusing of size distribution" regime [15]. Especially, the sharp absorption peaks for each sample was observed at around 552, 558, 566, 590, and 598 nm in cases of 2.5, 5, 7.5, 10, and 12.5 mmol of stearic acid concentration, respectively. As can be seen in Fig. 3, the most sharp absorption peak arises from the stearic acid concentration of at below 7.5 mmol while relatively weak and broad absorption peak takes place at 10 and 12.5 mmol. These results tell that the CdSe QDs synthesized at below 7.5 mmol have more focusing tendency in the size distribution, compared with those synthesized at 10 and 12.5 mmol. In addition, the apparent blue shift toward shorter wavelength was observed with decreasing the stearic acid concentrations, implying that the low stearic acid concentration condition yields smaller particle size of the QDs.

Figure 4 shows PL spectra for CdSe QDs synthesized as a function of the stearic acid concentrations. Experimental emission spectra for 488 nm excitation possess a highly pronounced and relatively narrow peak. The peaks seen at 566, 572, 598, 605, and 606 nm correspond to the 2.5, 5, 7.5, 10, and 12.5 mmol of stearic acid concentration, respectively. PL spectra for CdSe QDs synthesized at 2.5, 7.5, 10, and 12.5 mmol of the stearic acid concentration show sharp and fairly symmetric shape with FWHM of 35 nm while at

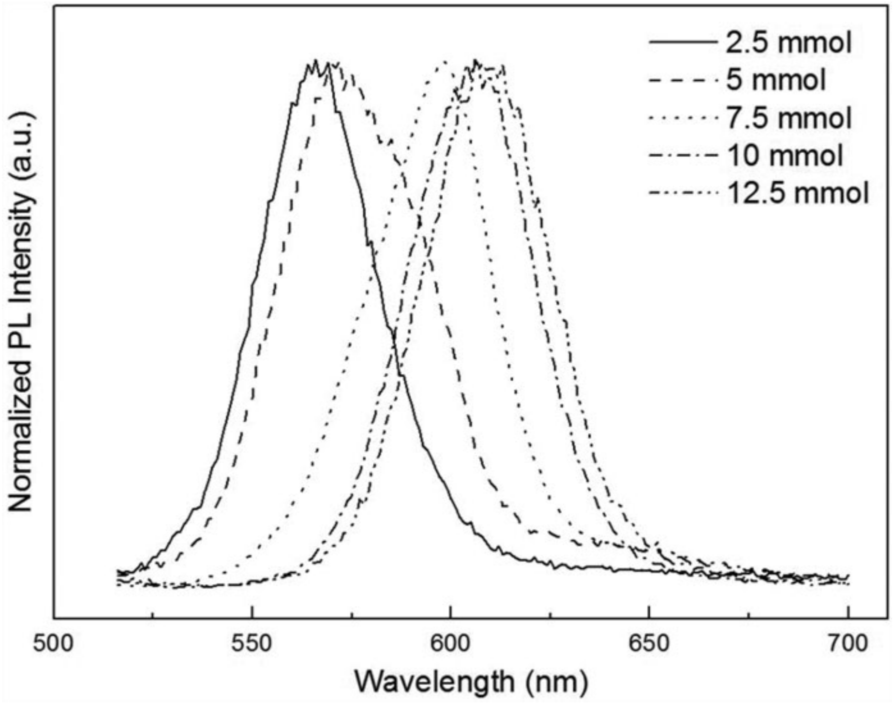

Figure 4. PL spectra of the CdSe QDs synthesized as a function of the stearic acid concentrations.

5 mmol of the stearic acid concentration shows relatively broad and anti-symmetric shape with FWHM of 45 nm, suggesting a relatively wide distribution of particle size. The PL peaks also reveal that the band gap energy was blue-shifted with decreasing the steaic acid concentration, corresponding well to the absorption peaks. In addition, as shown in Figs. 3 and 4, absorbance has shorter wavelength than emission by average 17 nm, due to the Stokes shift.

Conclusions

CdSe QDs are synthesized as a function of the stearic acid concentrations by using a pyrolysis based on the chemical colloidal method. To obtain high quality CdSe QDs, an appropriate precursor was prepared by using stearic acid and paraffin liquid, and stearic acid concentrations were tuned to control the particle size distribution. The investigations via XRD and TEM tell that the CdSe QDs with smaller amount of impurities and smaller particles in size are synthesized at relatively low stearic acid concentration. The investigations via UV-Visible and PL spectra confirm that the CdSe QDs with larger enery gap are synthesized at relatively low stearic acid concentration, implying that the stearic acid concentration is a crucial parameter in controlling the size of QDs.

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References

[1] Gosnell, J. D., Schreuder, M. A., Bowers, M. J., Rosenthal, S. J., & Weiss, S. M. (2006). *Proc. of SPIE.*, *6337*, 63370A.

[2] Kim, L. A. *et al.* (2008). *Nano Letters.*, *8*, 4513.

[3] Kongkanand, A., Tvrdy, K., Takechi, K., Kuno, M., & Kamat, P. V. (2008). *J. Am. Chem. Soc.*, *130*, 4007.

[4] Robel, I., Subramanian, V., Kuno, M., & Kamat, P. V. (2006). *J. Am. Chem. Soc.*, *128*, 2385.

[5] Hines, M. A., & G-Sionnest, P. (1996). *J. Phys. Chem.*, *100*, 468.

[6] Asokan, S. *et al.* (2005). *Nanotechnology*, *16*, 2000.

[7] Neeleshwar, S., Chen, C. L., Tsai, C. B., & Chen, Y. Y. (2005). *Phys. Rev. B*, *71*, 201307.

[8] Liao, Y. F., Li, W. J. (2008). *J. Zhejiang Univ. Sci. A*, *9*, 133.

[9] Wang, L., Sun, X., Liu, W., & Liu, B. (2010). *Mater. Chem. Phys.*, *120*, 54.

[10] Yordanov, G. G., Dushkin, C. D., & Adachi, E. (2008). *Colloids Surf. A: Physicochem. Eng. Asp.*, *316*, 37.

[11] Yang, Y. A., Wu, H., Williams, K. R., & Cao, Y. C. (2005). *Angew. Chem. Int. Ed.*, *44*, 6712.

[12] Xing, B., Li, W., & Dou, H. (2008). *J. Phys. Chem. C*, *112*, 14318.

[13] Deng, Z., Cao, L., Tang, F., & Zou, B. (2005). *J. Phys. Chem. B*, *109*, 16671.

[14] Talapin, D. V., Rogach, A. L., Kornowski, A., Haase, M., & Weller, H. (2001). *Nano Lett.*, *1*, 207.

[15] Peng, Z. A., & Peng, X. (2001). *J. Phys. Chem. Soc.*, *123*, 183.