

Colloidal Synthesis And Characterization Of Cdse Quantum Dots: Role Of Cd:Se Molar Ratio And Temperature

Hakan Aydın, M. R. Karim, Mesut Balaban, Hilmi Ünlu

Abstract: Semiconductor Cadmium selenide (CdSe) Quantum Dots (QDs) were synthesized via colloidal chemistry method at moderately lower growth temperatures. Optical absorption and photoluminescence (PL) spectroscopy techniques were used to characterize the optical properties of CdSe QDs. Optical properties of colloidal CdSe QDs were successfully controlled by changing the initial Cd:Se molar ratios and temperature. Optical absorption and PL spectrum both showed gradual red shift with increasing Cd:Se molar ratio and temperature. High-resolution transmission electron microscopy (HRTEM) technique were used to study the structural properties of CdSe QDs. Full width at half maximum (FWHM) values obtained from the emission spectrums were helped to prove the narrow size distribution, which coincides with the matching results of HRTEM images and theoretical calculations.

Index Terms: Absorbance, HRTEM, Molar ratio, Photoluminescence, Particle size, Quantum dots, Temperature

1 INTRODUCTION

The current demand of the world for energy supply and consuming habits of people in the frame of “always having the better one” push the scientists and engineers to search for effective routes to fabricate devices that are smaller, faster, compatible and can meet the demands of sustainable energy. To relieve the energy crisis and utilize the devices based on energy conversion/storage (solar cells, batteries, thermoelectrics etc.), sensors (gas sensors, photovoltaics etc.) and catalysis covering photodegradation of toxic dyes and catalytic oxidation of carbon monoxide in the atomic scale, researchers have focused on semiconductor nanocrystal-based applications. Nanocrystals synthesized by a chemical route allow us to control their sizes and distribution. These routes include single molecule precursor [1,2], sonochemistry [3,4], solvothermal synthesis [5,6], microwave irradiation [7,8], organometallic precursor route [9] and green chemical applications [10]. Owing to increasing demands for high quality (monodispersity, high crystallinity, narrow emission spectrum and high quantum yield) QDs, it is important to develop low-cost, green and mass producible synthesis routes. Colloidal semiconductor QDs (also known as quantum dots) with their diameters range between 2-10 nm have gained a huge interest for both optical and electrical applications such as solar cells [1- 4], light emitting diodes (LEDs) [11-13], lasers [14, 15] and for fundamental studies [16-20] over the last few decades due to their size-dependent optical, physical and chemical properties.

These small-sized nanostructures have a large surface-to-volume ratio and constitute a class of materials intermediate between molecular and bulk forms of matter. QDs can be synthesized in core (bare) or core-shell forms due to interest. In this work, we present a simple and convenient colloidal synthesis method for the preparation of CdSe QDs at relatively low temperatures in order to manipulate the QDs optical properties by altering the temperature, time and initial Cd:Se precursor ratios. In the present work, the structural, morphological and optical properties of prepared CdSe QDs are studied. Our attention focused on the size of CdSe QDs at different precursor ratios and temperatures. The effects of precursor ratios on the structure of CdSe QDs are discussed by High- resolution transmission electron microscopy (HRTEM) and optical absorption and fluorescence analysis.

2 EXPERIMENTAL

2.1 Synthesis of CdSe Core QDs

For the synthesis of CdSe core QDs, the synthesis method developed by Zhu et al. [21] has been modified to use it in our laboratory. Firstly, cadmium stearate, the Cd precursor, is prepared by heating the mixture of CdO (0.01 mol, 1.284 g) and stearic acid (0.02 mol, 5.68 g) at 170°C for 15 minutes in order to use in further reactions. For a typical synthesis of CdSe core QDs, cadmium stearate (0.1358 g, 0.2 mmol) is added into a three-neck flask with 16 mL paraffin liquid without Se precursor as the Se cannot be dissolved without any phosphine-based material at relatively lower temperatures than used in original method. To overcome this situation, 2 mL TOP and Se powder (0.0078 g, 0.1 mmol) are added into a flask and are mixed in an ultrasonic cleaner at the room temperature for several seconds. The cadmium stearate-paraffin mixture is degassed in vacuum at room temperature and then is heated to a desired temperature (160-180°C) with oil-bath heating for reaction under N₂ flow. When the heat is reached to aimed temperature, TOP-Se solution is rapidly injected into the reaction flask for the nucleation and growth of CdSe QDs. Aliquots are taken at different time intervals via a syringe to monitor the growth of CdSe core QDs. After cooling down to room temperature, aliquots are centrifuged by addition of

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acetone at least three times to purify core solution. The end products are heated up to 60°C under vacuum to get rid of remaining solvents.

2.2 Optical Characterization

The optical absorption spectra of CdSe QDs in air under room temperature were obtained by using the UV-VIS-NIR Spectrophotometer (Shimadzu UV-3600). Analysis of photoluminescence features of QDs was done via Varian Cary Eclipse Fluorescence Spectrophotometer. The aliquots were diluted with n-hexane directly for characterization. High-resolution transmission electron microscopy (HRTEM) analysis of QDs was performed by using FEI Tecnai G2 F30 in National Nanotechnology Research Center (UNAM) located at Bilkent University, Ankara, Turkey.

3 RESULTS AND DISCUSSION

3.1 Optical Analysis

It is known that UV-VIS absorption spectroscopy is one of the common analytical tool used in the characterization of CdSe QDs as the lowest energy absorption feature (the first exciton) can yield information on the band gap, particle size and size distribution [22]. The size-dependent optical properties of CdSe QDs were investigated by changing the temperature and initial precursor ratio throughout the experimental studies. Increasing absorption peak values (wavelength in nm) with temperature and elapsed time, named as red shift, state the growth of QDs and quantization effect which is an expected behavior and well-matched with common studies [23, 24]. Figure 1.a and b shows absorption and normalized PL spectra of CdSe QDs synthesized at 160°C with Cd:Se molar ratio of 1:1.25 for different time. FWHM of an emission peak is the measure of color purity of the emission where the smaller values indicate more pure emission and narrow size distributions without Ostwald ripening. Table 1 shows the average FWHM values obtained from PL spectras with respect to various conditions. It is noticeable that, the average FWHM value increase as the initial Cd:Se precursor ratio decreases.

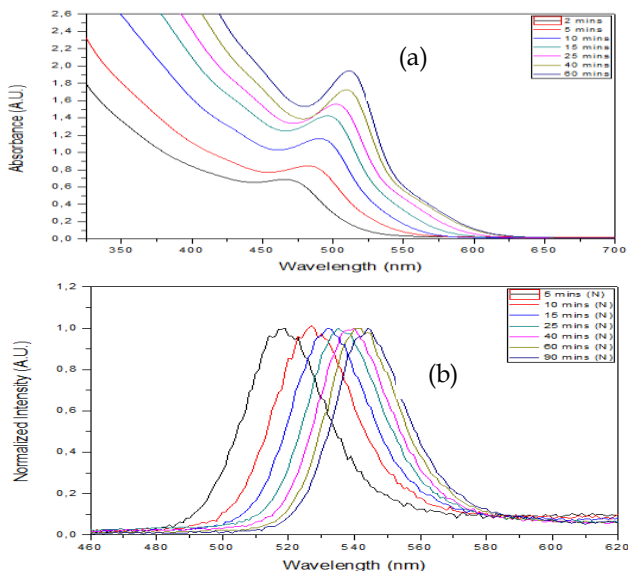


Fig. 1 (a) Absorption and **(b)** Normalized PL spectra of the CdSe QDs synthesized at 160°C with Cd:Se ratio of 1:1.25.

Table 1 Effect of Cd:Se initial precursor ratio on the average FWHM values of CdSe QDs.

Sample	Molar Ratio	Temperature	Average FWHM
CdSe	1:1.25	170°C	29.86 nm
CdSe	1:5	170°C	30.16 nm
CdSe	1:10	170°C	30.96 nm

3.2 Morphological Analysis

The diameter (or size) of CdSe QDs were estimated by using datas converted from absorption peak values to photon excitation energy values in the below equation obtained as a result of effective mass approximation (EMA):

$$E_{QD}^* \cong E_{gap} + \frac{\hbar^2 \pi^2}{2d^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.786e^2}{4\pi\epsilon\epsilon_0 d} - 0.248E_{RY}^* \quad (1)$$

where, E_{gap} is the bulk CdSe band gap energy, d is the diameter (size) of CdSe QDs, ϵ is the optical dielectric constant, m_e and m_h are the effective masses of electron and hole, respectively, in bulk CdSe, e is electronic charge and E_{RY}^* is the effective Rydberg energy. The Rydberg energy term is size independent and is usually negligible, except for semiconductors with small dielectric constant. To verify the correction of calculated QDs diameter values of different synthesis routes, HRTEM analysis was performed and shown in Figure 2. The average diameter values obtained from HRTEM images are 3.1 ± 0.2 nm for both CdSe QDs synthesized at 170°C with Cd:Se ratio of 1:5 and CdSe QDs synthesized at 160°C with Cd:Se ratio of 1:2.5. The average diameter values obtained from HRTEM images are well-matched with theoretically calculated values.

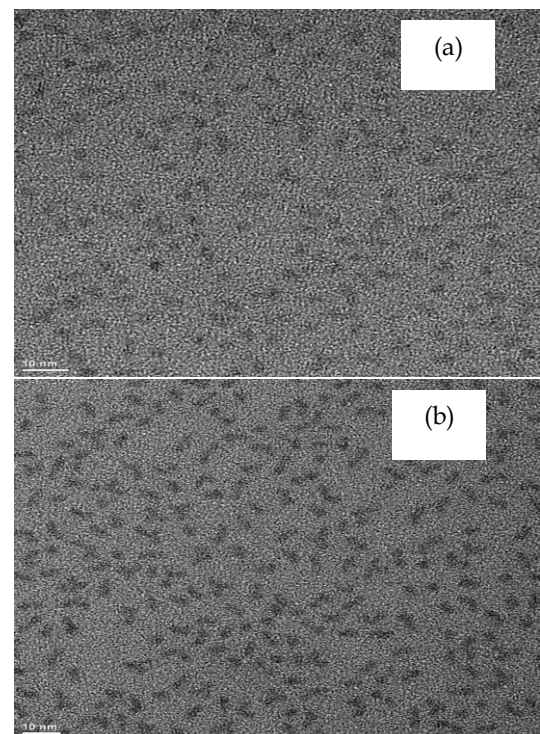


Fig 2 HRTEM images of **(a)** CdSe QDs synthesized at 170°C with Cd:Se ratio of 1:5 and **(b)** CdSe QDs synthesized at 160°C with Cd:Se ratio of 1:2.5. The label is indicator of 10 nm length.

3.3 Effect of Temperature & Precursor Ratio on the Quantum Dots Growth

Since the growth kinetics of semiconductor QDs are dependent on temperature, time and initial precursor ratio for any synthesis route, influence of changes in these variables on the final properties CdSe QDs were investigated. The most important parameter, Cd:Se molar ratio of the precursors; was found having the ability of change the average particle size, number of density and size distribution by “focusing” and “defocusing” the particle growth in the solution [16]. Figure 3 shows the diameter distribution of QDs grown with different Cd:Se molar ratios at given synthesis temperatures.

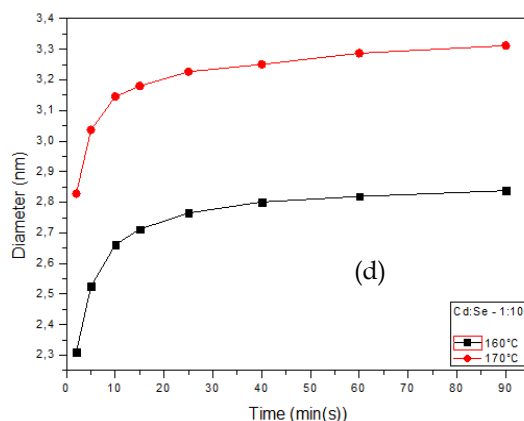
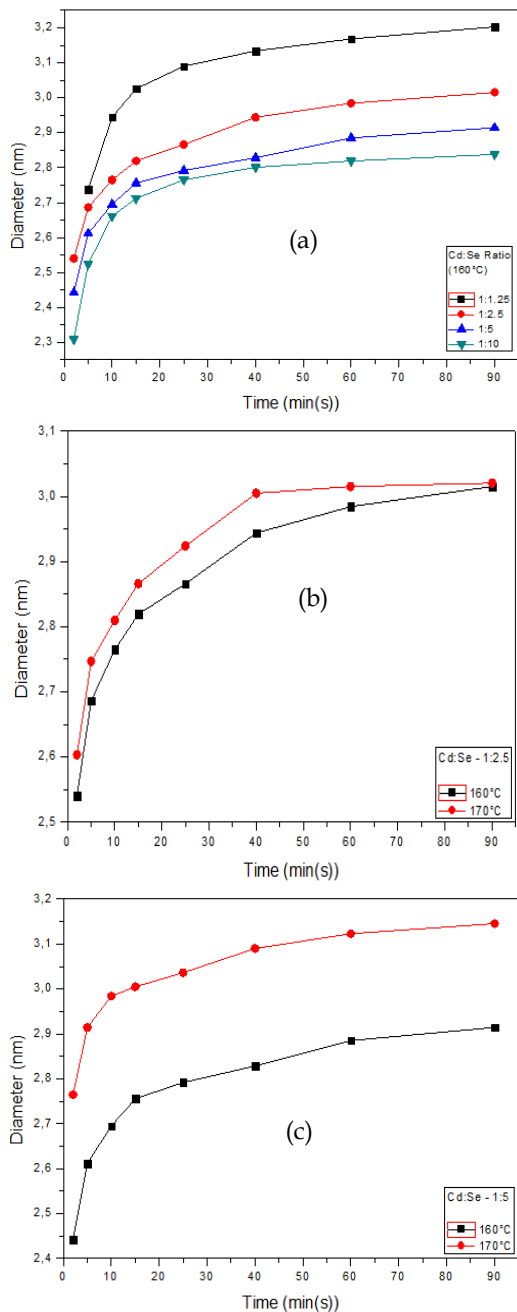


Fig. 3 (a) Growth of CdSe QDs with different Cd:Se molar ratios at 160°C and Effect of temperature on CdSe QDs growth for Cd:Se ratio of (b) 1:2.5, (c) 1:5, (d) 1:10.

As the amount of Cd precursor increases, QDs grow into larger diameters very fast and growth is the predominant process over nucleation, which reduces the number of density and increases the average particle size under same experimental conditions, coherent with the study of Bhattacharjee et al. [25]. Increase in the NC diameter is also responsible for red shift in the emission and absorption spectra of CdSe QDs. On the other hand, the operating temperature influences the growth of QDs when it compared in identical chemical compounds and elapsed time. As shown in the Figure 4, difference in the diameter of grown QDs increases with the excessive amount of initial Se precursor, therefore indicating that the effect of operating temperature is evident for the Se rich samples. However, lower temperatures are not suitable for the ideal growth of Cd rich samples.

4 CONCLUSION

For the synthesis with altering the Cd:Se initial precursor ratio at a fixed temperature, it was observed that the samples with a high Cd:Se ratios are able to nucleate and grow faster. However, it was explored that the influence of operating temperature becomes dominant on the growth of QDs as the Cd:Se initial precursor ratio decreases. It was attributed to unfavorable temperatures for the growth of Cd rich samples. For a fixed temperature, it was investigated that there is an increase for FWHM values obtained from PL spectras by reducing the Cd:Se initial precursor ratio.

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REFERENCES

- [1] P. A. Ajibade, “Synthesis and Use of [Cd(Detu)₂(OOCCH₃)₂]-H₂O as Single Molecule Precursor for Cds Nanoparticles.” The Scientific World Journal, 2013, 1-6.
- [2] B. Y. Geng, X. W. Liu, J. Z. Ma, , Q. B. Du, , & L. D. Zhang, “Size-Dependent Optical and Electrochemical Band Gaps of ZnS Nanorods Fabricated Through Single,”Molecule Precursor

- Route. *Applied Physics Letters*, 90(18), 183106, 2007.
- [3] Murcia, M. J., Shaw, D. L., Woodruff, H., Naumann, C. A., Young, B. A., & Long, E. C. (2006). Facile Sonochemical Synthesis of Highly Luminescent ZnS-Shelled CdSe Quantum Dots. *Chemistry of Materials*, 18(9), 2219-2225.
- [4] N. A. Dhas, C. P. Raj and A. Gedanken, "Preparation of Luminescent Silicon Nanoparticles: A Novel Sonochemical Approach," *Chemistry of Materials*, 10(11), 1998.
- [5] Nam, D., Song, W., & Yang, H. Facile, "Air-Insensitive Solvothermal Synthesis of Emission-Tunable CuInS₂/ZnS Quantum Dots with High Quantum Yields," *Journal of Materials Chemistry*, 21(45), 18220, 2011..
- [6] Wang, P., Jiang, T., Zhu, C., Zhai, Y., Wang, D., & Dong, S, "One-Step, Solvothermal Synthesis of Graphene- CdS and Graphene-ZnS Quantum Dot Nanocomposites and Their Interesting Photovoltaic Properties," *Nano Research*, 3(11), 794-799. 2010.
- [7] Qian, H., Li, L., & Ren, J, "One-Step and Rapid Synthesis of High Quality Alloyed Quantum Dots (CdSe- CdS) in Aqueous Phase by Microwave Irradiation with Controllable Temperature," *Materials Research Bulletin*, 40(10), 1726-1736, 2005.
- [8] He, Y., Lu, H., Sai, L., Su, Y., Hu, M., Fan, C., et al., "Microwave Synthesis of Water-Dispersed CdTe/CdS/ZnS Core-Shell-Shell Quantum Dots with Excellent Photostability and Biocompatibility". *Advanced*, 2008.
- [9] Danek, M., Jensen, K. F., Murray, C. B., & Bawendi, M. G. Synthesis of Luminescent Thin-Film CdSe/ZnSe Quantum Dot Composites Using CdSe Quantum Dots Passivated with an Overlayer of ZnSe. *Chemistry of Materials*, 8(1), 173-180, 1996.
- [10] Jiang, F., Wang, C., Shu, C., Gu, Y., Huang, N., Zheng, J., et al. Eco-Friendly Synthesis of Size-Controllable Amine-Functionalized Graphene Quantum Dots with Antimycoplasma Properties," *Nanoscale*, 5(3), 1137., 2013.
- [11] Huang, C., Su, Y., Wen, T., Guo, T., & Tu, M. "Single-Layered Hybrid DBPPV-CdSe-ZnS Quantum-Dot Light-Emitting Diodes," *IEEE Photonics Technology Letters*, 20(4), 282-284, 2008.
- [12] Shen, C., Li, K., Hou, Q., Feng, H., & Dong, X. "White LED Based on YAG: Ce, Gd Phosphor and CdSe- ZnS Core/Shell Quantum Dots," *IEEE Photonics Technology Letters* , 22(12), 884-886, 2010.
- [13] Chen, M., Yang, J., & Shiojiri, M., "ZnO-Based Ultra-Violet Light Emitting Diodes and Nanostructures Fabricated by Atomic Layer deposition," *Semiconductor Science and Technology*, 27(7), 074005, 2012.
- [14] Deng, L., Han, L., Xi, Y., Li, X., & Huang, W., "Design Optimization for High-Performance Self-Assembled Quantum Dot Lasers With Fabry-Perot Cavity," *IEEE Photonics Journal*, 4(5), 1600-1609, 2012.
- [15] Yan, J. H., Wang, C. G., Zhang, H., & Cheng, C, "Evaluation of Emission Cross Section of CdSe Quantum Dots for Laser Applications," *Laser Physics Letters*, 9(7), 529-531, 2012.
- [16] Peng, X., Wickham, J., & Alivisatos, A. P., "Kinetics of II-VI and III-V Colloidal Semiconductor Nanocrystal Growth: Focusing of Size Distributions," *Journal of the American Chemical Society*, 120(21), 5343-5344, 1998.
- [17] Mi, W., Tian, J., Jia, J., Tian, W., Dai, J., and Wang, X., "Characterization of Nucleation and Growth Kinetics of the Formation of Water-Soluble CdSe Quantum Dots by Their Optical Properties," *Journal of Physics D: Applied Physics*, 45(43), 435303, 2012.
- [18] Peter, A. J., & Lee, C. W. (2012). Electronic and Optical Properties of CdS/CdZnS Nanocrystals. *Chinese Physics B*, 21(8), 087302.
- [19] Buckley, S., Rivoire, K., & Vučković, J., "Engineered Quantum Dot Single-Photon Sources," *Reports on Progress in Physics*, 75(12), 126503, 2012.
- [20] Shu, L., Wu, H., Wan, Z., Cai, C., Xu, T., Lou, T., et al., "Physical Approaches to Tuning the Luminescence Color Patterns of Colloidal Quantum Dots," *New Journal of Physics*, 14(1), 013059, 2012.
- [21] Zhu, C., Wang, P., Wang, X., & Li, Y. , "Facile Phosphine-Free Synthesis of CdSe/ZnS Core/Shell Nanocrystals Without Precursor Injection," *Nanoscale Research Letters*, 3(6), 213-220, 2008.
- [22] Murray, C. B., Norris, D. J., & Bawendi, M. G., "Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites," *Journal of the American Chemical Society*, 115(19), 8706-8715, 1993.
- [23] Tian, C., Wang, E., Kang, Z., Mao, B., Zhang, C., Lan, Y., et al., "Synthesis of Ag-Coated Polystyrene Colloids by an Improved Surface Seeding and Shell Growth Technique," *Journal of Solid State Chemistry*, 179(11), 3270-3276, 2006.
- [24] Talapin, D. V., Rogach, A. L., Kornowski, A., Haase, M., & Weller, H., "Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a

Hexadecylamine-Trioctylphosphine
Oxide-Trioctylphosphine Mixture," Nano Letters, 1(4),
207-211, 2001.

- [25] Bhattacharjee, B., Hsu, C., Lu, C., & Chang, W. H.
,"Colloidal CdSe-ZnS Core-Shell Nanoparticles:
Dependence of Physical Properties on Initial Cd to Se
Concentration," Physica E: Low-dimensional Systems
and Nanostructures, 33(2), 388-393, 2006.