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RESEARCH ARTICLE

OPTICAL DETECTION of CADMIUM SELENIDE QUANTUM DOTS via ABSORPTION SPECTROSCOPY and TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT

Quantum dots are tiny semiconductor nanocrystals. Their dimensions are between about 2 and 10 nm. They have attracted much attention due to their unique electronic and optical properties. These particles can be synthesized in a variety of ways. Synthesis methods of quantum dots can be classified into top-down and bottom-up. Top-down approach is a fragmentation process of bulk material. In contrast to top-down, quantum dots are constructed from atoms and molecules of the material at bottom-up procedure. Ball milling, optical lithography, laser ablation and arc-discharge are some top-down methods. However, chemical reduction, thermal decomposition, sol-gel and ultrasonic spray pyrolysis are bottom-up methods. In this study, chemical hot-injection synthesis method of cadmium selenide quantum dots which is a kind of bottom-up procedure will be explained. Cadmium selenide quantum dots have been grown in hot solvent at 259ºC. Concentration of cadmium selenide quantum dots dispersed in toluene has been adjusted by observing their first exciton peak. First excitonic absorbance peak of cadmium selenide quantum dots has been measured at around 2.18 eV. Transmission electron microscope photo of these growth quantum dots has been shown. The average diameter of cadmium selenide quantum dots has been found to be approximately 3.48 nm. Lattice fringe spacing of cadmium selenide quantum dots has been measured as ~0.35 nm.

Keywords: Quantum dots, Cadmium selenide, Optical absorbance, First exciton peak, Lattice fringe spacing

1. INTRODUCTION

Quantum dots are an important class of the nanostructures. Sizes of quantum dots range from about 2 nm to 10 nm. They are made of semiconducting material [1, 2]. Top-down and bottom-up approaches have been utilized to synthesize different types of quantum dots [3, 4]. Quantum dots can be constructed from their atoms by using bottom-up synthesis techniques such as melt-quenching and heat-treatment, chemical reduction, microwave, etc [5-7]. Cadmium selenide (CdSe) quantum dots were nucleated and grown in glass via melt-quenching and heat-treatment technique by M. H. Yükselici [8]. Quantum dots have been studied much because of their unique properties. Optical absorption and photoluminescence properties of quantum dots are different from those of bulk counterparts since quantum confinement effects arise at these sizes [9, 10]. C. B. Murray et al. synthesized trioctylphosphine/trioctylphosphine oxide capped CdSe quantum dots. The average sizes of these CdSe quantum dots were below 12 nm. They showed that optical absorption energy of CdSe quantum dots could be increased by around 750 meV when the average size was reduced from 11.5 nm to near 2.0 nm [11]. Thus, new white light emission diodes (LEDs) and fluorescent probes have been made by means of tailoring these optical properties [10-14]. S. Nizamoglu et al. integrated zinc sulfide covered CdSe (CdSe/ZnS) quantum dots with indium gallium nitride/gallium nitride LEDs. Average sizes of CdSe/ZnS quantum dots were selected between 1.9-5.2 nm due to their cyan, green, yellow and red photoluminescence colors. They achieved to produce white light from the blue emitting gallium nitride based LEDs by using these capped quantum dots [15].

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In this study, CdSe quantum dots were grown in hot solution, precipitated by centrifugation and then dispersed in toluene solvent. The first excitonic absorption peak of CdSe quantum dots was revealed in their optical absorbance spectra by diluting these quantum dots successively. Gaussian shape of this first excitonic absorption peak was observed. Energetic shifting and narrowing/broadening at the first excitonic absorption peak were determined at each dilution. The effect of the dilution procedure on absorbance was examined. CdSe quantum dots were shown by taking their transmission electron microscopy (TEM) photo.

2. SAMPLE PREPARATION and OPTICAL CHARACTERIZATION

0.1344 g cadmium oxide (≥99.99%), 0.8791 g stearic acid and 25.9791 g 1-octadecene were mixed and stirred (500 rpm) in a flask under pure argon gas flow. Then, this mixture was heated to 305ºC. 0.5133 g selenium (99.99%) and 4.8130 g trioctylphosphine were mixed and stirred in another flask under pure argon gas. Then, this mixture was heated to 159ºC and cooled to room temperature. 2 mL was taken from selenium and trioctylphosphine mixture and injected rapidly into cadmium oxide, stearic acid and 1-octadecene mixture being at 305ºC. Temperature was decreased to 259ºC after the injection and waited for 12 minutes at this temperature. Clear solution turned to red during this period. This hot solution was poured into a teflon beaker and frozen swiftly via liquid nitrogen. After liquefying again, it was mixed with methanol and centrifuged at 3000 rpm. Thus, CdSe quantum dots were precipitated from the solution. Washing and precipitation process was repeated 3 times. Finally, CdSe quantum dots were dispersed in toluene. Here, volume ratio of toluene to CdSe quantum dots is 2. This sample was named as sample 1. Different amounts of toluene were added to dilute sample 1. The volume ratios for sample 2, sample 3, sample 4, sample 5 and sample 6 are 8, 14, 20, 41 and 62, respectively.

Samples were filled in a quartz cuvette and excited with a 50 W tungsten halogen lamp operated at constant voltage 12.01 V and constant current 3.92 A. Optical absorbance of the samples were recorded by means of Oriel 74000 Cornerstone 1/8 m monochromator coupled with Oriel 71580 optical power detector (silicon detector) and Oriel 70310 optical power meter. Light rays were passed through the cuvette and focused into the entrance slit of the monochromator via plano-convex glass lenses. Grating having 1200 lines per mm was used inside the monochromator. The monochromator was calibrated with Oriel 6035 Hg(Ar) spectral calibration lamp. All optical absorbance measurements were made on a TMC model scientific grade optical table to be able to align the optical elements and isolate the optical system from ambient vibrations. TEM measurement was made with JEOL JEM-2100F. Sample 5 was dropped on a TEM grid and waited for its drying. TEM photos were taken at accelerating voltage of 200 kV.

3. RESULTS and DISCUSSION

The optical absorbance spectra of the samples are shown in Figure 1. The absorbance of toluene was subtracted from those of the samples. Therefore, these absorbances result only from CdSe quantum dots. As seen from Figure 1, the absorbance decreases about 5.7 times from sample 1 to sample 6 with dilution of the sample. The absorbance diminishes due to lowering concentration of CdSe quantum dots in toluene. The absorbance peak position shifts ~29 meV from sample 1 to sample 6. This slight energy shift shows that the sample is homogeneous. The absorbance peak of the sample appears above the band gap energy of bulk CdSe which is 1.74 eV. Here, the quantum confinement effect has caused as much as 453 meV energy shift from the bulk band gap energy. This absorbance peak is known as the first excitonic peak. Gaussian shape of the absorbance peak is evident in the spectra. Thus, the intensity, energy and full width at half maximum (FWHM) of the absorbance peak can be found by placing a gaussian curve on it. For example, the curve G5 seen at Figure 1 is a gaussian function which fits the first excitonic absorbance peak of sample 5. The extracted fitting values from each sample are listed at Table 1.

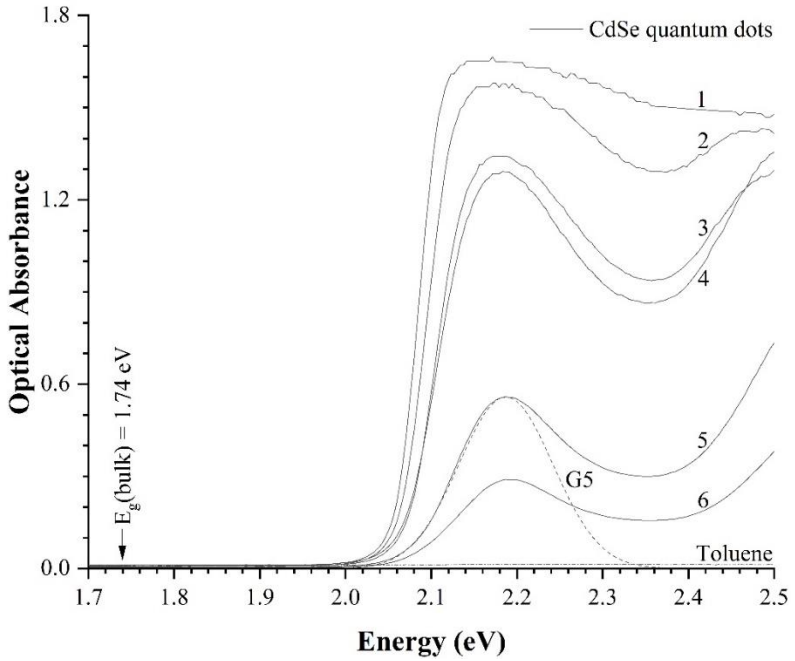

Figure 1. Optical absorbance spectra of CdSe quantum dots. Each sample spectrum is labeled with its number, e.g., label "1" for sample 1. Dashed line G5 shows gaussian curve fitting of first excitonic peak of sample 5. Absorbance of pure toluene is marked with the word of "Toluene". E_g(bulk) depicts the band gap energy of bulk CdSe.

Table 1. Gaussian fitting of the absorbance peak of the samples.

Sample	Peak Intensity	Peak Position (eV)	Peak FWHM (meV)
1	1.655	2.164	117.7
2	1.575	2.175	122.5
3	1.343	2.180	122.5
4	1.291	2.183	129.5
5	0.558	2.187	129.5
6	0.290	2.193	141.3

TEM photo of sample 5 is shown at Figure 2. CdSe quantum dots have been seen almost spherical and they have exhibited a good crystalline structure according to this photo. W. William Yu et al. have obtained an empirical formula to determine average size of CdSe quantum dots from their absorption spectrum [16]. This formula is given at Equation (1).

$$D(\lambda) = 1.6122 \times 10^{-9}\lambda^4 - 2.6575 \times 10^{-6}\lambda^3 + 1.6242 \times 10^{-3}\lambda^2 - 0.4277\lambda + 41.57 \qquad (1)$$

In Equation (1), λ (nm) is the wavelength of the first absorption peak and D (nm) is the average diameter of CdSe quantum dots. Average diameter of CdSe quantum dots have been calculated as ~3.43 nm for sample 5 by using Equation (1). In addition, the diameter of CdSe quantum dot indicated by a white arrow in Figure 2 have been found to be ~3.38 nm. Average sizes have been calculated for all samples and given in Table 2.

Table 2. Average diameter of CdSe quantum dots. Average diameter has been calculated using Equation (1) for each sample.

Sample	Average Diameter (nm)
1	3.60
2	3.52
3	3.48
4	3.46
5	3.43
6	3.39

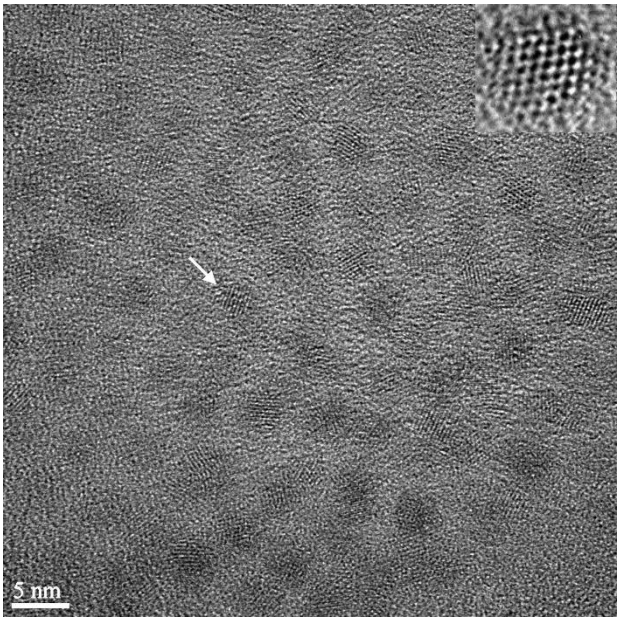

Figure 2. TEM photo of Sample 5. CdSe quantum dots are seen evidently. White arrow indicates one of them. The diameter of this pointed CdSe quantum dot is ~3.38 nm. Length of scale bar corresponds to 5 nm. The inset shows magnified image of a CdSe quantum dot.

The successive atomic planes inside CdSe quantum dots are seen in Figure 2. The relative position of these atomic planes with respect to each other is plotted at Figure 3. The average distance between two successive atomic planes has been calculated as ~0.35 nm. This distance, that is to say lattice fringe spacing, corresponds to the fringe spacing of wurtzite and/or zincblende CdSe [17, 18]. However, it is known that wurtzite type CdSe quantum dots are favored at high temperature synthesis with precursor injection such as 300^{o}C [17, 19-22]. Hence, synthesized CdSe quantum dots are most probably wurtzite type. Selected area electron diffraction (SAED) pattern of these CdSe quantum dots is shown in Figure 4. Cd and Se elements constituting core of CdSe quantum dots and furthermore phosphorus (P) element due to trioctylphosphine capping ligands of CdSe quantum dots have been detected at energy dispersive X-ray analysis (EDX) of the samples.

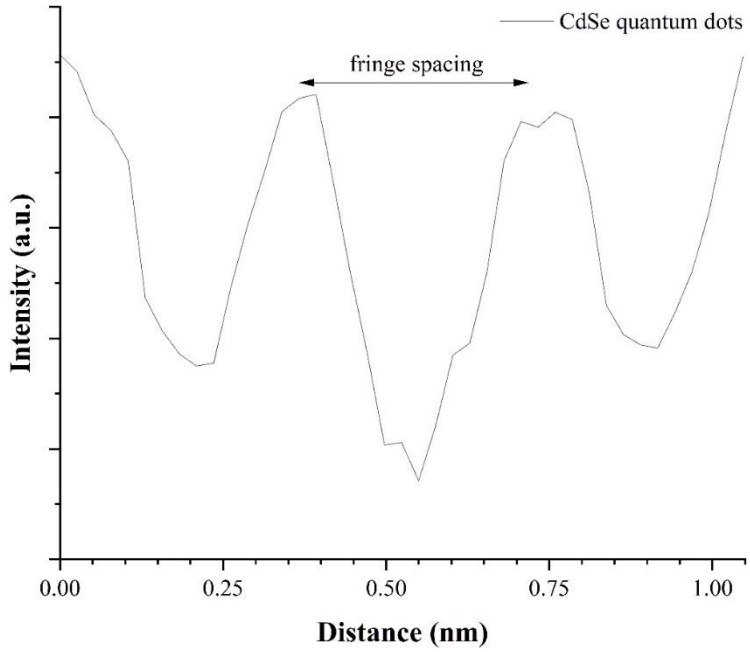

Figure 3. The distance between successive atomic layers of CdSe quantum dot. Lattice fringe spacing corresponds to a distance between the sequential peaks in this graph. Lattice fringe spacing of CdSe quantum dots is ~0.35 nm.

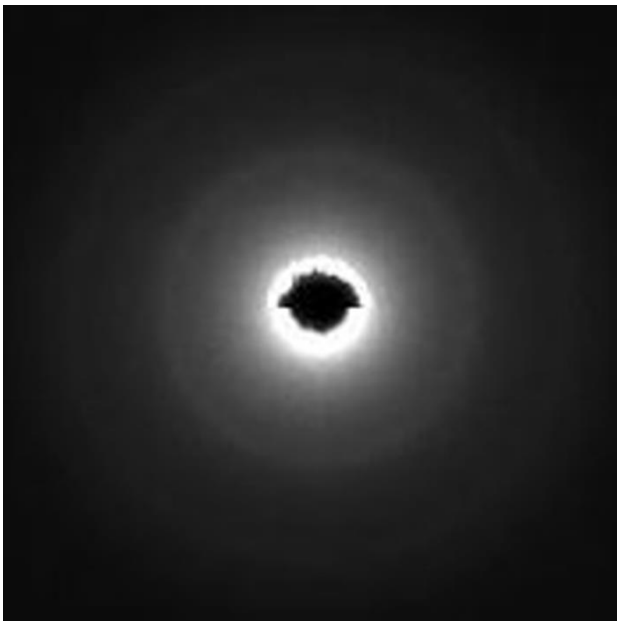

Figure 4. SAED pattern of Sample 5. Diffraction rings from CdSe quantum dots are visible.

4. CONCLUSION

CdSe quantum dots were nucleated with precursor injection at 305°C and grown at 259°C along 12 minutes in octadecene. The first excitonic absorption peak of CdSe quantum dots dispersed in toluene was measured by using Cornerstone 1/8 m monochromator with silicon detector. Gaussian shape of their

absorbance spectra was revealed, and the absorbance peak parameters were determined for the samples. The first excitonic absorbance peak was observed around 2.18 eV. Average size of CdSe quantum dots was calculated around 3.48 nm. Fringe spacing of CdSe quantum dots was measured as ~0.35 nm from their TEM photos. For undoped CdSe quantum dots, the fringe spacing has been reported between 0.33-0.36 nm in the literature [17, 18]. Therefore, the fringe spacing found in this study is consistent with that of the literature. The optical absorption energy of CdSe quantum dots with an average diameter of 3.48 nm was found to be 453 meV higher than the band gap energy of bulk CdSe. This energy shift was measured between 500-600 meV for 3.2-3.7 nm CdSe quantum dots by C. B. Murray et al [11]. The difference between these two results is probably arises from the synthesis procedure itself and different precursors used in the synthesis. This diverse result can be understandable and acceptable considering that the synthesis parameters such as temperature and time will affect the crystalline structure and quality of CdSe quantum dots and thus change the quantum confinement degree.

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CONFLICT of INTEREST

The author declares that there is no conflict of interest regarding the publication of this article.

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