

Yüksek Sıcaklıkta Uzun Bir Süre Çekirdekletirilen Kolloidal CdSe Kuantum Noktalarının Sentezi ve Optik Karakterizasyonu

*¹Çağdaş Allahverdi

¹Toros Üniversitesi, 45 Evler Kampüsü, Mühendislik Fakültesi, Bilgisayar ve Yazılım Mühendisliği Bölümü, Nanomalzeme Üretim Laboratuvarı, Bahçelievler Mahallesi 16. Cadde No: 77, 33140 Yenışehir/Mersin, Türkiye, cagdas.allahverdi@toros.edu.tr, 

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Öz

Kolloidal CdSe kuantum noktaları, koordine olmayan oktadesen çözücü içerisinde sıcak-enjeksiyon tekniği kullanılarak yaklaşık 300°C'de 15 s çekirdekletirildi ve 272°C'de 245 dakikaya kadar büyütüldü. CdSe kuantum noktalarının sentezinde stearik asit bir kaplama ajanı olarak kullanıldı. Bu çalışmada kullanılan çekirdekletme zamanı literatürdekilere göre oldukça uzundu ve optik özelliklere olan etkisi incelendi. Birinci eksiton soğurma ve karşılık gelen rekombinasyon tepeleri, sırasıyla, optik soğurma ve fotoluminesans spektrumlarında gözlemlendi. Stokes kayma değeri 70 meV'ye kadar değişti. 20 dakika için büyütülen numunenin optik soğurma ve fotoluminesans spektrumlarında bir tepe ve omuz yapısı elde edildi. Yüksek sıcaklık altında yeterince uzun bir sürede çekirdekletirilen bu kuantum noktalarının çift büyüklük dağılımına sahip olabileceği gösterildi. CdSe kuantum noktalarının görüntüleri geçirgenlik elektron mikroskopi vasıtasıyla elde edildi. Resimleri, ImageJ görüntü işleme programı ile işlendi. 12 dakika büyütülen CdSe kuantum noktalarının ortalama büyüklüğü 2.63 nm olarak bulundu. Büyüklük dağılımı tekil dağılımlı kuantum noktalarına nazaran 4.6 kat arttı. Cd ve Se elementlerine ait X-ışınları enerji geçiş tepeleri enerji dağılımlı X-ışınları spektrumlarında gözlemlendi. Bu kuantum noktalarını saran stearik asit moleküllerinin simetrik ve asimetrik titreşim modları Fourier dönüşümlü kızıl ötesi spektroskopisi kullanılarak, sırasıyla, 2848 cm⁻¹ ve 2914 cm⁻¹ civarında belirlendi.

Anahtar Kelimeler: CdSe kuantum noktaları, optik soğurma, fotoluminesans, Fourier dönüşümlü kızıl ötesi spektroskopisi, geçirgenlik elektron mikroskopi

Synthesis and Optical Characterization of Colloidal CdSe Quantum Dots Nucleated for A Long Time at High Temperature

*¹Çağdaş Allahverdi

¹Toros University, 45 Evler Campus, Faculty of Engineering, Department of Computer and Software Engineering, Nanomaterial Production Laboratory, Bahçelievler Mahallesi 16. Cadde No: 77, 33140 Yenisehir/Mersin, Turkey, cagdas.allahverdi@toros.edu.tr

Abstract

Colloidal CdSe quantum dots were nucleated at about 300°C for 15 s and growth at 272°C up to 245 min in non-coordinating solvent octadecene by using hot-injection technique. Stearic acid was used as a capping agent in the synthesis of CdSe quantum dots. The nucleation time used in this study was considerably longer than those in the literature and its effect on the optical properties was examined. The first excitonic absorption and corresponding recombination peaks were observed in their optical absorption and photoluminescence spectra, respectively. The value of Stokes shift changed up to 70 meV. A peak and shoulder structure was obtained in the optical absorption and photoluminescence spectra of the sample growth for 20 min. It was indicated that CdSe quantum dots which are nucleated at high temperature for a sufficiently long period may have double size distribution. The images of CdSe quantum dots were obtained via transmission electron microscopy. Their images were processed with the image processing program ImageJ. The average size of CdSe quantum dots growth for 12 min was found as 2.63 nm. The size dispersion increased 4.6 times with respect to that of the monodisperse quantum dots. The X-ray energy transition peaks belong

*¹Corresponding author Toros University, 45 Evler Campus, Faculty of Engineering, Department of Computer and Software Engineering, Nanomaterial Production Laboratory, Bahçelievler Mahallesi 16. Cadde No:77, 33140, Yenisehir/Mersin, Turkey. Ecagdas.allahverdi@toros.edu.tr, (+90)-542-786-4562.

to Cd and Se elements were observed in their energy dispersive X-ray spectra. Symmetric and asymmetric vibrational modes of stearic acid molecules capping these quantum dots were determined at about 2848 cm^{-1} and 2914 cm^{-1} , respectively, by using Fourier transform infrared spectroscopy.

Keywords: CdSe quantum dots, optical absorption, photoluminescence, Fourier transform infrared spectroscopy, transmission electron microscopy

1. INTRODUCTION

Since the early 1980s, colloidal quantum dots, also known as semiconductor nanocrystals, have attracted more attention because of their zero-dimensional quantum size effect [1]. As a consequence of the quantum size effect, the optical band gap of the quantum dots can be precisely adjusted by changing their size and size distribution [2]. By this way, monochromatic and efficient light emission can be obtained at a desired wavelength dependent on composition, crystallinity and surface properties of the quantum dots. This kind of light emission has high importance for light emitting diode (LED) based devices [3]. Therefore, synthesis techniques to be used and determination of optical, morphological and crystallographic properties of quantum dots are very significant. Synthesis and characterization of cadmium selenide (CdSe) quantum dots are highly worked owing to the fact that it is a model system for many-body physics and its commercial importance for the LED industry [4-6]. G. G. Yordanov et al. reported that the average size and concentration of CdSe quantum dots synthesized in non-coordinating solvent are closely related to the coordinating ligand concentration [7]. In their different study, the effect of solvent matrix on growth process was examined and stated that the nucleation and growth of CdSe quantum dots were slower when coordinating solvent was used instead of non-coordinating one [8]. Q. Dai et al. showed that the ligand of selenium (Se) such as trioctylphosphine (TOP) is required for the synthesis of CdSe quantum dots in contrary to CdS quantum dots [9]. The temperature is an other valuable parameter to be able to control the growth kinetics. Higher temperature provides faster growth rate and better crystallinity. For this reason, the quantum dots synthesized in nonaqueous solvents are more crystalline than those in aqueous solvents. However, new approaches to synthesize CdSe quantum dots in aqueous medium are developed due to decrease toxicity and synthesis cost [10, 11]. L. Qu et al. made in situ observation of the nucleation and growth process of CdSe quantum dots [12]. They classified the crystallization process of the quantum dots into four steps monitoring their photoluminescence (PL) spectrum. These are i) continuous nucleation: obvious tail occurs on the short wavelength side of the PL spectrum, ii) growth and focusing of size distribution: the PL spectrum narrows, iii) stable stage: gradually broadening of the PL and no notable shift in the peak position, and iv) Ostwald ripening: the PL spectrum broadens significantly and becomes asymmetric.

In this work, stearic acid coated CdSe quantum dots in a non-coordinating solvent octadecene were synthesized by using hot-injection method [13]. The nucleation process of the quantum dots was not minimized by reducing the solvent

temperature rapidly after the injection as in the hot-injection methods used in the literature [14, 15]. On the contrary, this process was extended to be able to induce a polydispersity. For this reason, CdSe quantum dots were initially nucleated at 302°C and then exposed to 300°C for 15 s. The average diameter of the CdSe quantum dots was found to be about 2.63 nm by using transmission electron microscopy (TEM) and image processing. The double size distribution was determined in the optical absorption (OA) and photoluminescence (PL) spectra of 20 min heat treated sample. Their compositional and surface molecules were investigated via energy dispersive X-ray (EDX) and Fourier transform infrared (FTIR) spectroscopies.

2. EXPERIMENTAL

2.1. Materials

Chemicals used to synthesize CdSe quantum dots were bought from Sigma-Aldrich, Inc. These chemicals are cadmium oxide (CdO; $\geq 99.99\%$), selenium (Se; 99.99%), stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$; 95%), 1-octadecene ($\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$; 90%) and trioctylphosphine ($[\text{CH}_3(\text{CH}_2)_7]_3\text{P}$; 90%). The precipitation and purification processes of CdSe quantum dots were carried out by using methanol (CH_3OH ; $\geq 99.99\%$). The quantum dots were diluted in toluene ($\text{C}_6\text{H}_5\text{CH}_3$; $\geq 99.99\%$) after the purification.

2.2. Synthesis

As shown in Figure 1, cadmium oxide (0.1334 g) was mixed with octadecene (25.9682 g) and stearic acid (0.8796 g) in a three-neck round-bottom flask equipped with an injection inlet, a reflux condenser and a glass thermocouple probe. This first step for the synthesis of quantum dots was marked with QA (Quantum dots synthesis: first step **A**) in Figure 1. The mixture was stirred vigorously for 15 min under argon atmosphere about 28°C . The temperature of the mixture was raised to 302°C . The clear solution was obtained during the temperature increase. In other flask, selenium (0.5121 g) was mixed with trioctylphosphine (4.8109 g) under argon and this mixture was heated up to 154°C (QB). Then, it was cooled down to room temperature. 2 mL of this trioctylphosphine-selenide (TOP-Se) solution was quickly loaded into the injection port (QC) and fast injected into the clear cadmium solution (QD). Upon injection, light yellow color was appeared and its color was changed from light yellow to light red (QE). The temperature was kept about 300°C for 15 s and decreased to 272°C and the reaction was maintained for different durations which are 12 min (sample

s12), 20 min (sample s20), 190 min (sample s190) and 245 min (sample s245). The quantum dot solution was poured into a Teflon beaker cooled with liquid nitrogen at the end of the reaction. The photograph of sample s12 in a glass vial is seen in Figure 2. As shown in Results and Discussion section, this sample has the highest absorption and emission

intensity among the samples. The CdSe quantum dots were washed with methanol and then precipitated from the solution at 3000 rpm for 5 min. This centrifugation process is repeated three times for each sample. Finally, the quantum dots were dispersed in toluene solvent for optical characterization.

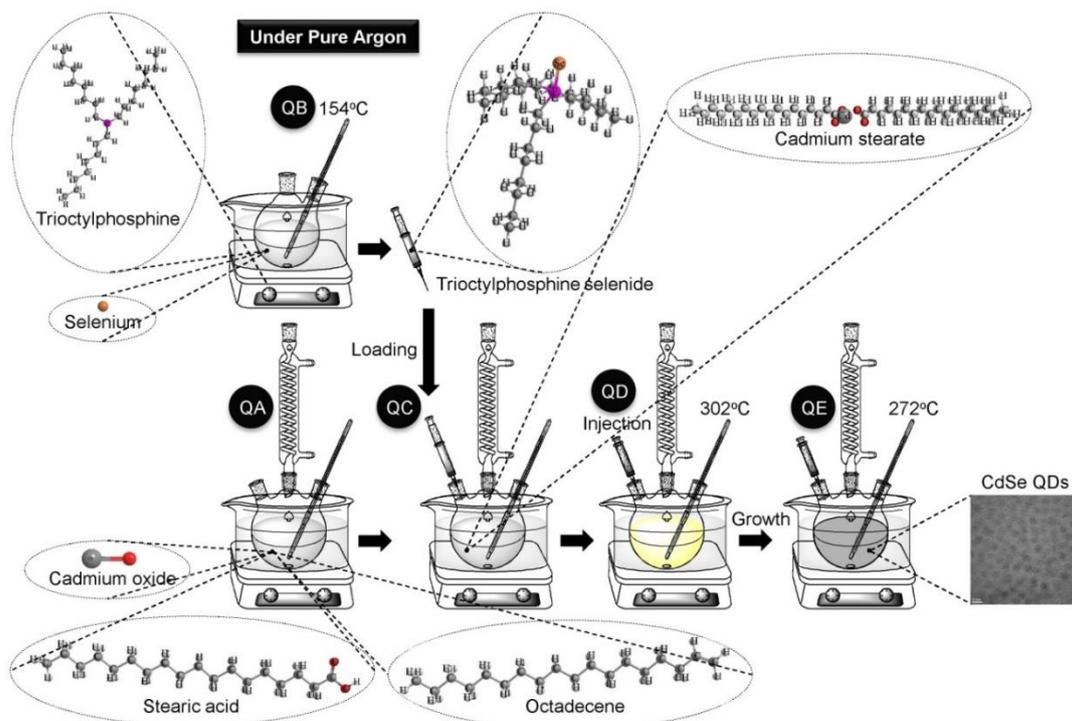


Figure 1. Synthesis of stearic acid coated CdSe quantum dots. The synthesis steps are labeled with QA, QB, QC, QD and QE, respectively.



Figure 2. The photograph of sample s12 in a glass vial under fluorescent lamp light.

2.3. Optical Characterization

The compositional, morphological and optical properties of synthesized CdSe quantum dots were investigated with

EDX, OA, PL, FTIR and TEM. The OA measurement was made using a homemade setup consisting of a tungsten halogen lamp powered with a constant current-voltage source, two optical lenses to focus light onto the sample and to collect and refocus light from the sample into the entrance slit of the Cornerstone™ 130 1/8m monochromator equipped with a silicon detector and a multifunction optical power meter.

The optical absorption spectra were recorded in the visible wavelength range from 500 nm to 700 nm. The photograph of the OA measurement setup is given in Figure 3. The PL of the samples was measured with Varian Cary Eclipse fluorescence spectrophotometer between 475-675 nm.

The surface ligands of CdSe quantum dots were determined via FTIR spectrum recorded in the range of 650-4000 cm^{-1} . Their morphology was examined using a JEOL JEM-2100F high resolution TEM with 4.2 MP Orius™ CCD camera, which is operated at 200 kV. ImageJ which is an open source image-processing program was used to precisely determine size distribution of the quantum dots observed in TEM images.

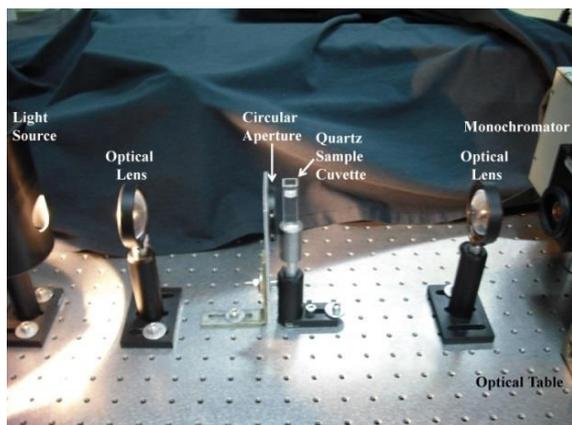


Figure 3. Homemade ultraviolet-visible (UV-Vis) OA setup constructed on an optical table.

3. RESULTS AND DISCUSSION

In Figure 4, the optical density of the samples is shown. The absorption peak of s12 appears at 566.5 nm. This peak is often called as first exciton peak [16]. The optical density of the peak decreases and one peak and one shoulder are seen in the spectrum of s20. The peak is at 567.1 nm and the shoulder is at 597.2 nm. However, the first exciton peak and a lower wavelength shoulder are occurred at 553.5 nm and 522 nm for s190, respectively. Then, this structure moves to longer wavelengths and finally turns into a shoulder at 584 nm. As a result, the first exciton peak shifts from 553.5 nm to 584 nm due to the quantum confinement effect [16, 17].

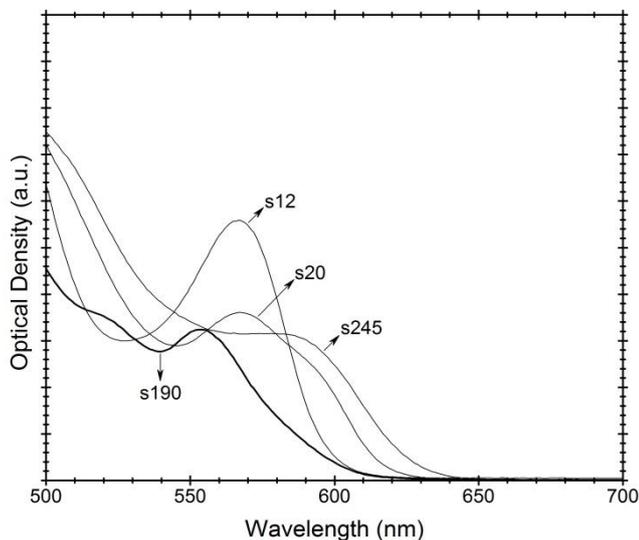


Figure 4. OA spectra of the samples. 12 min, 20 min, 190 min and 245 min samples are shown with the labels s12, s20, s190 and s245, respectively.

The PL spectra of the samples are shown in Figure 5. The

PL peaks (shown with solid curves) are curve fitted by using Gaussian curves (shown with dashed curves). According to the dashed curves, the PL peak of s12 positioned at 576.4 nm is separated into one peak and one shoulder structure for s20 and then this structure turns into one peak at 571.2 nm for s190. Two peaks are seen for s245 again. In other words, single size distribution is seen for s12 and s190 while there is a double size distribution for s20 and s245.

The PL intensity diminishes with the growth time. The increment of reaction time causes departure of the ligand from the surface of the quantum dots and it weakens the PL intensity because of deterioration in the surface passivation [18]. However, there is no a considerable shift in the PL peak position. In Figure 6, OA (shown with filled squares) and PL (shown with open circles) peak positions are plotted against the growth time. The curve fitting parameters obtained for the samples are summarized in Table 1.

The colloidal quantum dots whose size dispersion is smaller than 10% are called as monodisperse [19]. The full width at half maximum (FWHM) of photoluminescence of the monodisperse CdSe quantum dots is smaller than 45 nm and they are accepted as pure color emitters [20, 21]. As seen in Table 1, the FWHM of the sample s12 is slightly greater than 45 nm. In addition, its calculated size dispersity from image analysis is ~46% (1.20 nm/2.63 nm) and it shows that the sample is not monodisperse.

Therefore, it can be stated that the prolonged nucleation time induces considerably polydispersity in the sample. When small weights of these CdSe quantum dots are used in making of organic solar cell devices, the power conversion efficiency of the device increases due to high crystallinity and polydispersity of the quantum dots [22].

The nonresonant Stokes shift of CdSe quantum dots at room temperature is also given in Table 1. The nonresonant Stokes shift is the energy difference between the first excitonic absorption peak and its photoluminescence peak. The internal crystal field and electron-hole exchange energy of CdSe quantum dots create this shift [23, 24].

Kuno et al. reported that the nonresonant Stokes shift at room temperature for surface modified CdSe nanocrystals between 2-4 nm in diameter could take value from ~25 meV to ~115 meV [25]. Similar results were also reported by other groups [26, 27].

The Stokes shifts calculated in Table 1 are consistent with those in the literature. The photograph of sample s12 under 366 nm UV light is given in Figure 7. The strong PL emission of CdSe quantum dots can be seen with naked eye.

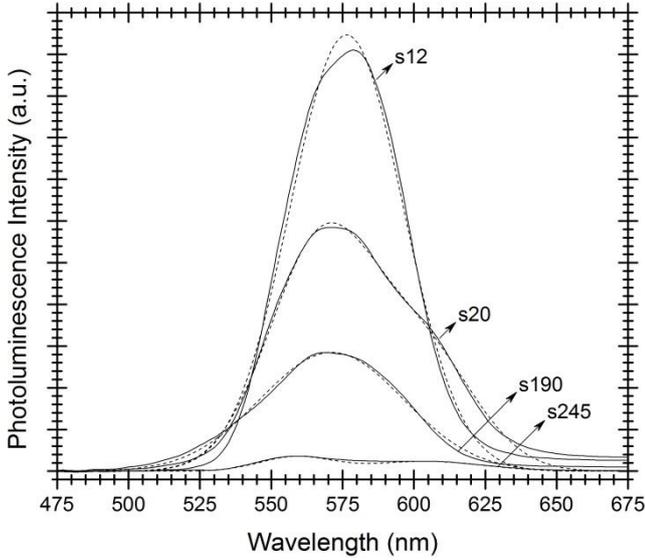


Figure 5. PL spectra of the samples. Solid curves (—) show experimental PL values for the samples. Their curve fittings are shown with dashed curves (---).

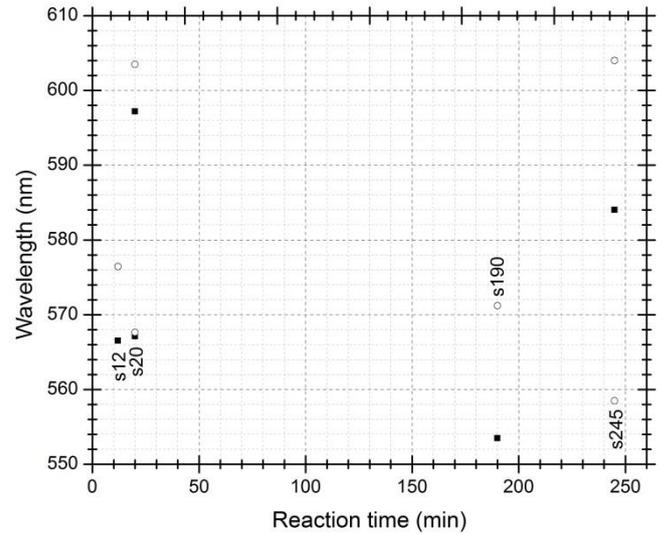


Figure 6. OA and PL peak positions of the samples against the reaction time. OA and PL peak wavelengths are shown with filled squares (■) and open circles (o), respectively.

Table 1. The physical parameters obtained via curve fitting of OA and PL peaks of the samples by using Gaussian function(s).

Sample	Optical Absorption (First Exciton Peak)		Photoluminescence		Stokes Shift	
	Gaussian curve(s)*	FWHM** (nm)	Gaussian curve(s)*	FWHM** (nm)	(nm)	(meV)
s12	a ₀ =0.558 a ₁ =566.500 a ₂ =15.050	35.440	a ₀ =523.360 a ₁ =576.439 a ₂ =19.790	46.602	9.939	-38
s20	a ₀ =0.360 a ₁ =567.100 a ₂ =19.720	46.437	a ₀ =273.314 a ₁ =567.624 a ₂ =18.474	43.504	0.524	-2
	a ₀ =0.098 a ₁ =597.200 a ₂ =9.600	22.606	a ₀ =136.014 a ₁ =603.466 a ₂ =18.474	43.504	6.266	-22
s190	a ₀ =0.324 a ₁ =553.460 a ₂ =16.840	39.655	a ₀ =142.500 a ₁ =571.187 a ₂ =25.105	59.117	17.727	-70
s245	a ₀ =0.312 a ₁ =584.000 a ₂ =21.120	49.734	a ₀ =17.075 a ₁ =558.500 a ₂ =12.543	29.537	-25.500	97
			a ₀ =11.885 a ₁ =604.000 a ₂ =19.970	47.026	20.000	-70

*Total Gaussian function is $\sum_{i=1}^{n=1,2} a_{0i} e^{-0.5 \left(\frac{x-a_{1i}}{a_{2i}} \right)^2}$. a₀, a₁ and a₂ are peak intensity, wavelength and standard deviation, respectively.
 **FWHM is full width at half maximum.



Figure 7. The photograph of sample s12 in a glass vial under 366 nm UV light.

The TEM photos of s12 are seen in Figure 8(a, b, c). The quantum dots have nearly spherical-shape in these images. A selected area electron diffraction (SAED) pattern of these quantum dots is given in Figure 8d. The histogram of the

quantum dot diameter obtained from Figure 8a which includes non-overlapping 1766 particles is plotted in Figure 8e. The average quantum dot diameter of s12 is found to be approximately 2.90 nm with regard to this histogram. Gaussian size distribution of the quantum dots is evident in this sample (see red Gaussian curve in Figure 8e). Therefore, the average quantum dot diameter of s12 is given as 2.63 ± 1.20 nm by using this Gaussian size distribution. The EDX analysis of s12 indicates elemental cadmium (Cd) and selenium (Se) from the quantum dots in Figure 8(f, g). The other elements determined in the spectrum (carbon (C), oxygen (O), silicon (Si) and phosphor (P)) are owing to either ligands of the quantum dots or impurities in raw precursors. However, Copper (Cu) peaks are largely due to the used TEM grid supporting the sample. The FTIR spectrum of sample s190 is shown with that of stearic acid in Figure 9. As seen in the figure, the symmetric and asymmetric stretching vibrations of CH_2 groups of stearic acid are around 2848 cm^{-1} and 2914 cm^{-1} , respectively [28]. These vibration modes are also observed in the spectrum of s190, which means that CdSe quantum dots are coated with stearic acid.

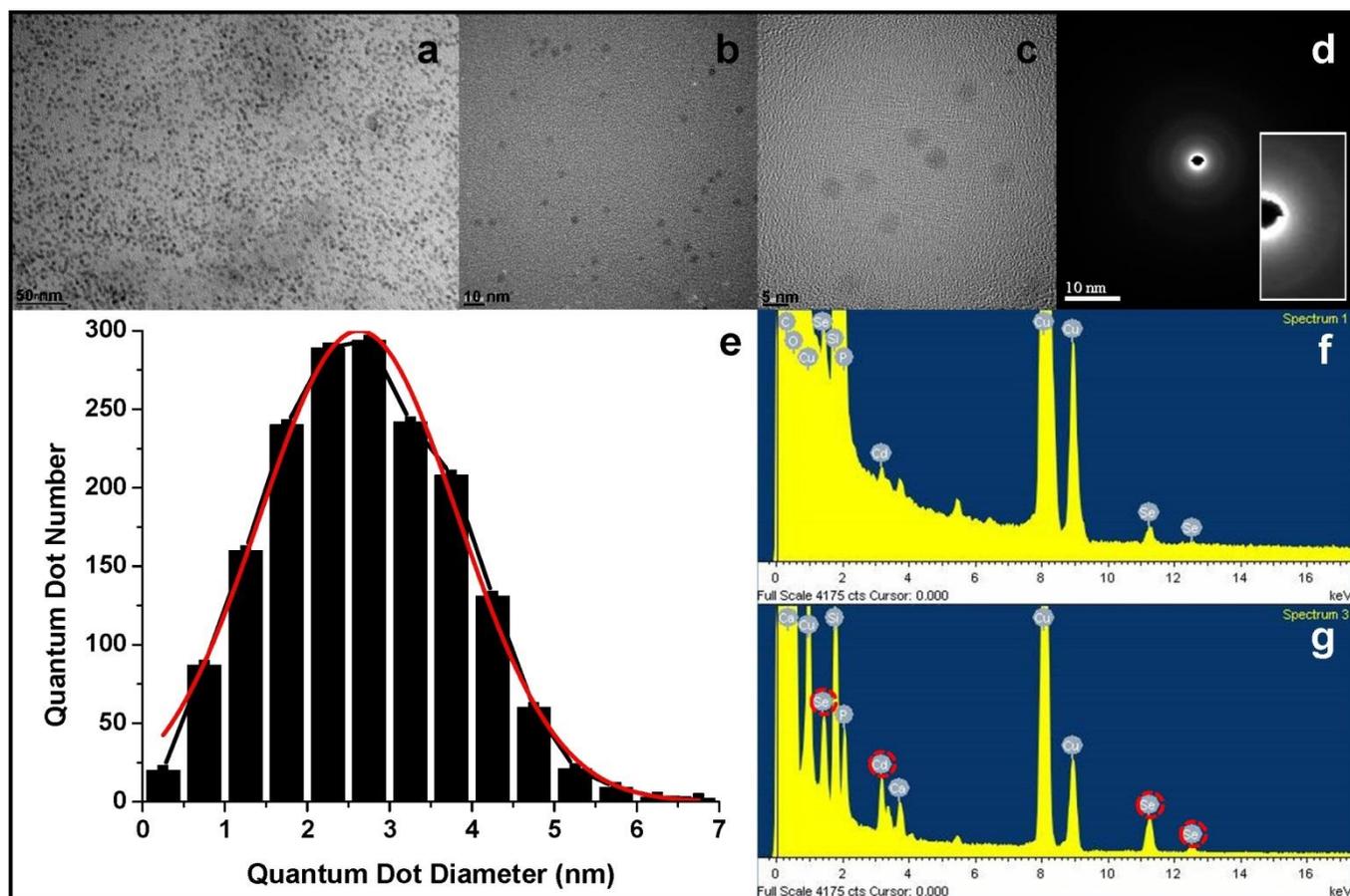


Figure 8. TEM images (a, b, c), SAED pattern (d), size distribution (e) and EDX spectra of sample s12 (f, g).

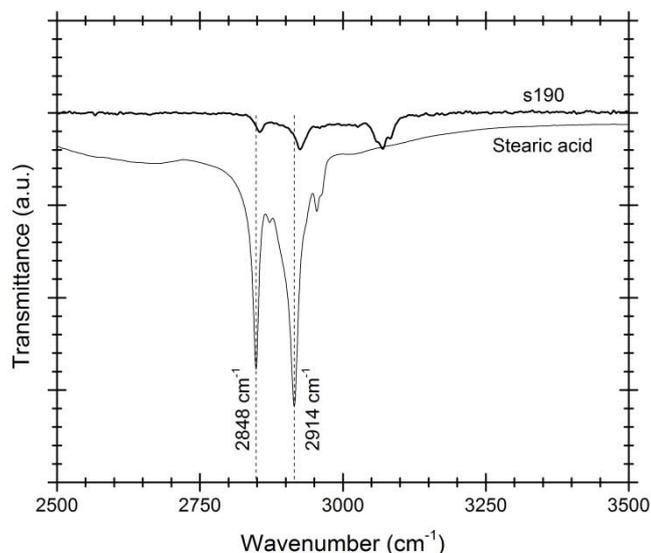


Figure 9. FTIR spectra of sample s190 and stearic acid sample.

4. CONCLUSION

Colloidal CdSe quantum dots are synthesized in a non-coordinating solvent octadecene by using hot-injection method. The spherical shape of CdSe quantum dots is observed under TEM and their average diameter and standard deviation are found to be 2.63 ± 1.20 nm. Cd and Se elements constituting the structure of these quantum dots are determined by the EDX analysis. Stearic acid molecules coating CdSe quantum dots are observed in their FTIR spectrum. The PL emission band which corresponds to electron-hole recombination is observed around 576 nm. The synthesis procedure given in this paper can be easily modified to produce CdSe quantum dots having different size, distribution and shape, which is important for the display industry. In other study, the crystal structure of CdSe quantum dots is going to be revealed by X-ray powder diffraction.

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