

Preparation and Characterization of CdSe QDs via Pyrolysis of Organometallic Reagent

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Abstract- Reproducible synthetic approach for cadmium selenide quantum dot based on the pyrolysis of organometallic reagents injection into a hot non-coordinating solvent is reported. The synthesis of highly crystalline and monodisperse cadmium selenide quantum dots using inexpensive trioctylphosphine-coordinated selenium as precursor produce a discrete homogeneous nucleation under slow growth. The difference in the temperature of the precursor injection spurred the dissimilarity in the nanocrystal growth, crystallinity, shape and particle sizes. Oleic acid was used to protect the cadmium selenide quantum dots against oxidation and photon emission loss while an organic ligand layer trioctylphosphine was used to overcome predominant influences associated with agglomeration. The optical properties, morphological and structural characterization confirmed the formation of monodisperse cadmium selenide quantum dots with 2.09 to 4.90 nanometres size range which was characterized using transmission electron microscopy, field emission scanning electron microscopy, scanning electron microscopy, atomic force microscopy, optical photoluminescence and absorption spectroscopy. The peak-to-peak values, irregularities in the surface texture and the root-mean-square values of the surface roughness of the prepared cadmium selenide quantum dots were determined.

Index Terms- Synthesis, Cadmium selenide, Quantum dots, optical spectroscopy, surface texture.

I. INTRODUCTION

Quantum dots (QDs) are semiconductor nanoparticles that exhibit size and compositionally tunable band gaps that can be engineered to match the absorption of the solar spectrum. The uniqueness of cadmium selenide (CdSe) QDs lies on the tunable band gap over the entire visible spectra by varying the particle sizes. Being size dependent, the nanoparticles respond differently to solar spectrum. This property is visible from the peak emission frequency's extreme sensitivity to both the dot's size and composition. A strong stimulus could cause a valence band electron to take residence in the conduction band resulting in the creation of a positively charged hole in the valence band. The minimum photon energy absorbed by quantum dot particles into the conduction band corresponds to the energy of the band gap. The percentage of absorbed photons that result in emitted photons commonly referred to as quantum yield (QY) is important for QDs and is influenced by nonradiative transition of electrons and holes between energy levels that produce no electromagnetic radiation.

Owing to the photoelectric potential of nanoparticles their incorporation into solar cell fabrication has been intensively investigated [1-3]. Various approaches to CdSe QDs synthesis have also shown notable potential in light emitting devices, bio-tagging, and lasers. Increased interest in the use of QDs is partly due to the progress in chemical synthesis of these particles and their respective surface modification strategies [4-5]. Another feature of QD is their electronic structure which facilitates the generation of electron-hole pairs during photoexcitation. This provides the basis for their use with electrodes [6, 7].

Long-lived electron/hole pair generation allows the ejection of conduction band electrons to the electrode or the injection of electrons from the electrode into the valence band of the particle. Thus, a photo current can be detected which is much enhanced when electron donors or acceptors are present in solution. The specific detail of the QD electronic structure and the excitonic nature of the photoexcited states solely depend on the semiconductor properties and differ significantly across different materials as shown by for example lead selenide (PbSe) and CdSe [8]. The structure of the cadmium selenide - trioctylphosphine (CdSe-TOPO) QDs encompasses three parts; the core is the CdSe, the outside is the vacuum barriers and the TOPO passivation layer is located between them. Experimental results show that the decrease of passivation increases the effective barrier around the CdSe core causing remarkable blue shift [9].

CdSe QDs synthetic approach that relies on the injection of selenium (Se) precursor into a mixture of solvent and ligands has been successful. This strategy entails precise temperature control to separate the nucleation and growth of the QDs which solely depend on the temperature of the mixture, injection process utilized as well as the concentration gradient under control [10]. It has been reported that room temperature injection of cadmium acetate and sodium seleno-sulphite (Na_2SeSO_3) in oleic acid showed controlled fluorescence of CdSe QDs [11]. Murcia et al. [12] reported sono-chemical synthesis of CdSe quantum dots using TOPO, cadmium acetate and hexadecylamine. Mono-disperse zinc blende CdSe QDs ranging from 2.5 nm to 4.3 nm have been synthesized in an open-

air microfluidic reactor with polytetrafluoroethylene (PTFE) capillaries as the reaction channels [13] which is comparable to the synthesis reported here (2.09 nm to 4.90 nm).

In this paper, we present the synthesis of CdSe via pyrolysis of organometallic reagents injected into a hot non-coordinating solvent and the characterization of the optical and microstructural properties. Octadecene (ODE) is used as the non-coordinating solvent while oleic acid (OA) is used to protect the CdSe QDs against oxidation and emission loss. ODE as a solvent for the CdSe QDs possesses excellent properties. ODE is stable in air and has a low melting point (below 20 °C) and this makes it easier to be handled at room temperature. Besides, it has a high boiling point (about 360 °C) coupled with its inert nature to the Se precursor, less toxicity, low cost and good dissolving power makes it an ideal solvent for the growth of high quality QDs [14].

To improve the optical properties of CdSe QDs, they are covered with TOPO so as to overcome the predominant defects associated with QDs such as agglomeration. The synthetic route employed was compatible with ODE as solvent which is cheap and environmentally friendly. Oleic acid is used instead of the costlier heteropolyacid (HPA) or thiodipropionic acid TDPA [15] to dissolve CdO powder to form homogeneous cadmium oleate solution and also as capping ligand for the CdSe QDs which is also compatible with ODE.

II. EXPERIMENT

A. Material

Organometallic selenium (Se, SCR, 99.5+%, Sigma-Aldrich), with trioctylphosphine (TOPO, Fluka, 90%) and octadecene (ODE, Fisher, 90%) were used to prepare the precursor. The pyrolytic solution comprises metal base cadmium oxide (CdO, SCR, 99.9+%, Sigma-Aldrich), oleic acid (OA, SCR, 90%, Sigma-Aldrich) and octadecene. All the materials were not subjected to further purification or treatment and were stored at 23 °C.

B. Methodology

The CdSe QDs synthesis follows two different steps; firstly, the preparation of the selenium (Se) precursor and secondly, the preparation of CdSe QDs. Different reaction times were chosen to obtain different sizes of the CdSe QDs.

C. Selenium solution

30mg of Se powder and 5 ml ODE were added to a 10 ml flat bottom flask over a stirrer hot plate at a temperature of 90 °C in a fume hood. Using a syringe, 0.4 ml TOPO from its sure-seal bottle was added to the flask. A magnetic stirrer bar was added to stir-heat the solution to completely dissolve the Se after which the mixture was cooled to room temperature. The solution was stored in a sealed container for one week to allow the precursor to form.

D. Synthesis of CdSe QDs

13 mg of CdO was added to 25 ml round bottom flask clamped onto a heating mantle. This operation was done in a fume hood to avoid inhalation hazard associated with cadmium compound. To the same flask, pipette was used to add 0.6 ml OA and 10 ml ODE. The cadmium solution was heated until its temperature reached 195 °C. A clean dry Pasteur pipette was used to quickly transfer 1 ml of the one week old room temperature selenium solution into the hot cadmium solution. The introduction of selenium precursor into the heated solution evolved smoke as the CdSe QDs were rapidly formed. The samples were removed at 10 seconds intervals using a 9 inch glass Pasteur pipette as the CdSe particles grew in size. The samples were synonymous with colour transition from light red to dark brown corresponding to different reaction time. We noted the observable property transitions before and after the formation of CdSe QDs as listed in Table 1.

Table 1: Observational changes in visible transition to CdSe QDs formation

	Properties	Before	After
Selenium solution	Colour	Black	Transparent after one week
	Appearance	Colloidal	Homogenous
	Solution	Heterogeneous	Sticky transparent liquid
CdO	Colour	Dark brown	Orange at 195 °C
	Appearance	Viscous colloidal	Homogenous at 195 °C
	In Solution	Heterogeneous	Oily at 195 °C
CdSe	Colour	_____	Light red to dark brown
	Texture	_____	Oily jelly-like

E. Sample Characterization

A one-cm path length quartz cuvette was used for the spectral study. Perkin Elmer Lambda-20 UV-vis spectrometer was used to carry out the optical measurement in the range of 200 – 800nm wavelength at room temperature. The absorption peaks were signatory of CdSe QDs. The photoluminescence spectra were recorded on Perkin Elmer Ls-55 Luminescence Spectrometer with xenon lamp over 350 – 700 nm range. For scanning electron microscopy and atomic force microscopy samples, transparent glass measuring 25.2 x 22.2mm having thickness of 1mm to 1.2mm was ultrasonically cleaned with distilled water for 10 minutes. The cleaning process was continued with methanol. The ultrasonically cleaned glass was dried in nitrogen gas to keep moisture away from the glass.

The atomic force microscopy technique shows three-dimensional images including surface roughness, grain size, step height and pitch of CdSe QDs sample surface topography and allows us to view the QDs distributions with a resolution similar to that obtained with scanning electron microscopy. Using the technique, surface parameters such as the peak-to-peak value, average surface roughness and surface root-mean-square values were determined. The technique was used for CdSe nanoparticles samples at room temperature and atmospheric pressure. The transmission electron microscopy and field emission scanning electron microscopy were used to study the micro-structure of the CdSe QDs. The transmission electron microscopy analysis was carried out using CdSe QDs solution. For field emission scanning electron microscopy analysis, a drop of CdSe QDs was dried at room temperature using carbon-copper grid in ODE dispersed solution.

III. RESULTS AND DISCUSSIONS

The UV-vis absorption and photoluminescence emission spectra of CdSe nanocrystals with diameter in the range of 2.09 to 4.90 nm are shown in Figs. (1a), (1b) and the mismatch in the optical absorption peak and PL emission of sample withdrawn at the same time shown in (1c) respectively. The illustration in Fig. (1a) shows that the absorption spectrum of CdSe QDs is a function of the growth time. The numbering shown on the absorption peaks (Fig. 1a) illustrates the transition in size range (1 represent the smallest and 6 the largest) as the temperature of the CdSe QDs increases. The colour of the CdSe QDs changes from light red to dark-brown in 1 min with respect to the discharge time. The fast colour transition in the CdSe QDs indicated rapid nuclei growth and this was verified by the corresponding absorption peak shift. The small CdSe QDs with an absorption peak at 482 nm was formed in 10 s and grew bigger QDs with an absorption peak at 542 nm in 1 min. The increase in size with respect to time as the peak shifts to longer wavelength was a result of transition in the interband of the CdSe QDs [16]. It became obvious that the particle size of CdSe QDs can be tuned by varying the reaction time.

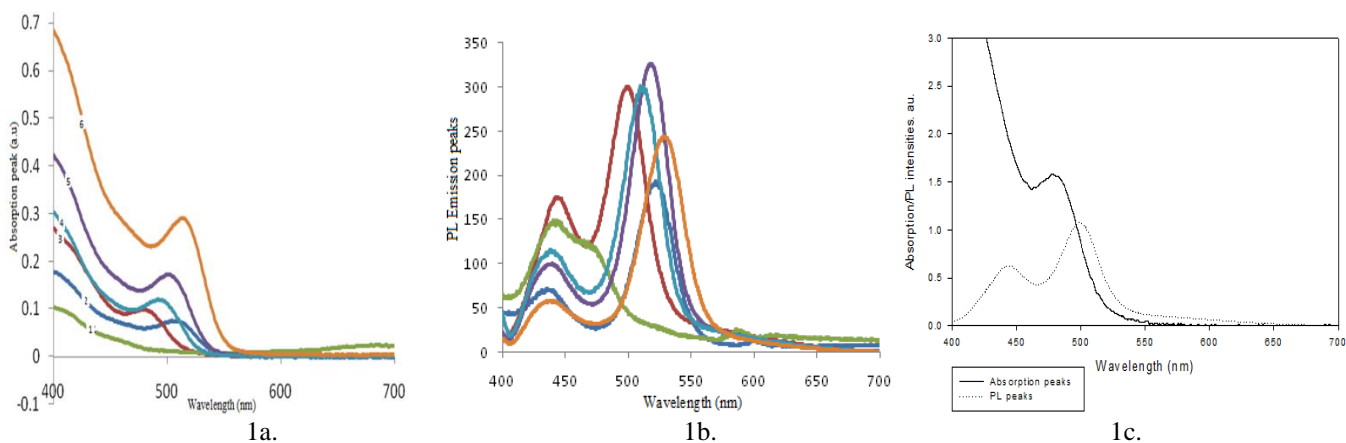


Fig. 1 a) depicts the optical absorption of the synthesized CdSe QDs; b) PL emission peaks of different particle sizes; c) Peak mismatch of the optical absorption peak and PL emission peak of CdSe QDs.

The corresponding photoluminescence spectra of the CdSe nanocrystals in Fig. (1b) show the extension time of reaction which is obvious with emission wavelength shifts from 442 nm to 533 nm. The intensity of the photoluminescence peak for the CdSe QDs increased with increase in the growth time in 1 min. In addition, the photoluminescence peak was broad and asymmetric initially and became narrower and symmetric as the reaction time increased. Similar nanocrystal size distribution was reported by Peng et al [17] where 1.5 min reaction time resulted in the increase of particle size owing to the depletion of the monomer concentration in the reaction solution. The photoluminescence properties of CdSe QDs are important because the tunability of the emission wavelength and nanocrystal size which is a signatory of the peaks could influence their applications since their optoelectronics properties are size-

related. The peak difference between the absorbed and emitted photons as illustrated in Fig. (1c) was thought to be caused by thermal losses. Spectral relationship of UV-vis and photoluminescence in Fig. 1c shows that the photoluminescence spectra are typical of CdSe QDs consisting of two peaks: one with the position closer to the absorption peak called band-edge photoluminescence and the other is red-shifted peak referred to as trap-related photoluminescence.

Scanning electron microscopy (SEM) diffraction pattern of the CdSe QDs given in Fig. (2) shows regular repeating pattern of CdSe QDs image. Each bright spot corresponds to the crystal plane and the symmetry of the spot speaks of the crystal structure.

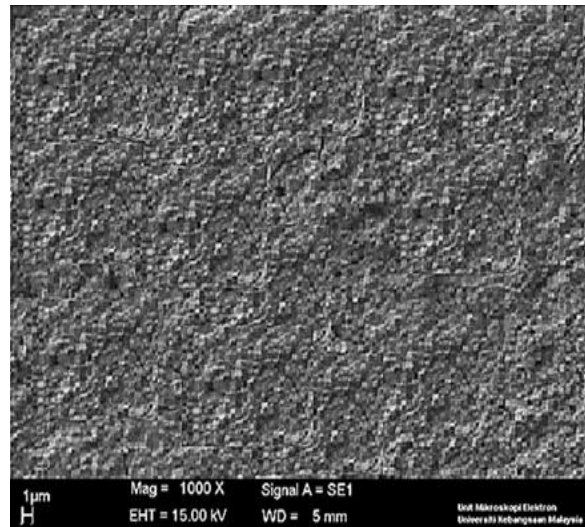
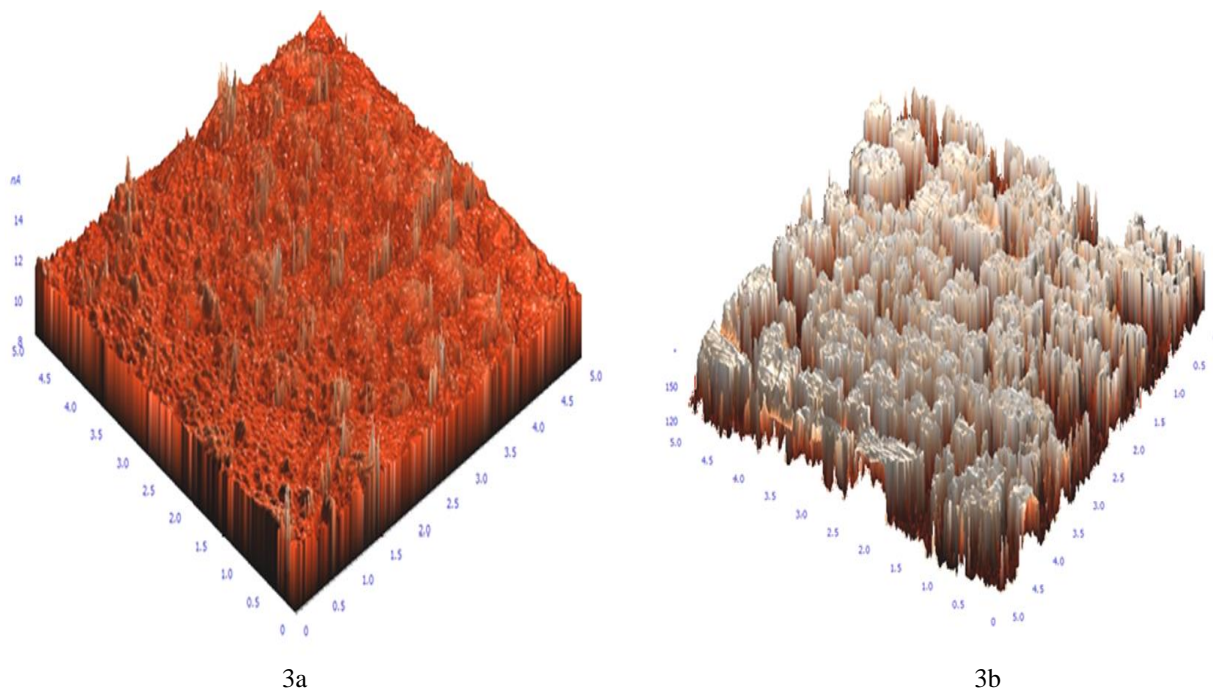


Fig. 2 SEM microstructure image of CdSe QDs

Figs. 3 shows AFM microstructure images of the synthesized CdSe QDs. 3(a) depicts 3D image of CdSe QDs annealed at 350 °C; 3(b) 3D image of CdSe QDs in octadecene solution and Fig. 3(c) shows the surface morphology; Fig. 3(d) shows the sensheight histogram based on which the surface profile information where obtained. For ten point count height of the atomic force microscopy images with scan size of 609.1 nm containing 65536 CdSe nanoparticles, the peak-to-peak value is 1218.7 nm, surface skewness is -0.04 and surface kurtosis is -1.23. The irregularities in the surface texture associated with surface roughness have an average value of 265.7 nm with the surface root-mean-square value of 303.94 nm.



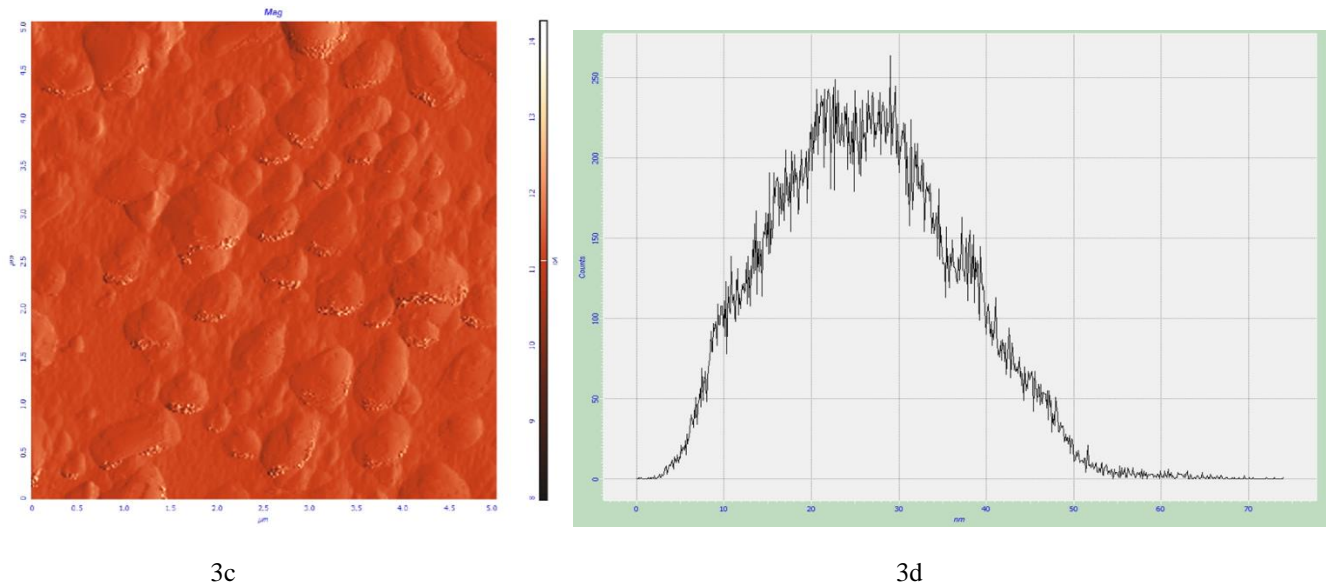


Fig. 3 AFM 3D microstructure image analysis

Figs. 4(a) and 4(b) show the transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) images of the CdSe QDs with respect to the successive lattice spacing. The transmission electron microscopy image reveals that the QD size distribution possesses almost spherical morphology. The spacing of the lattice plane obtained from TEM analysis depicting particle size spacing is as shown in Fig. 5.

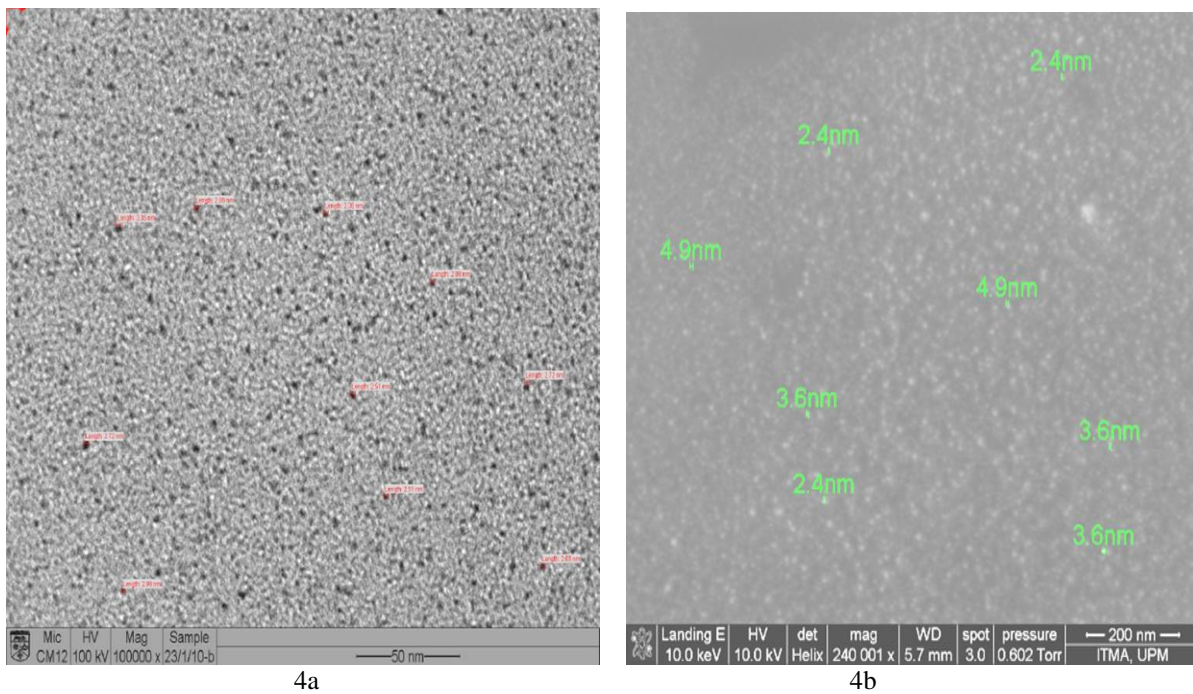


Fig. 4a Depicts TEM cross-sectional analysis and Fig. 4b Depicts FESEM surface image of the CdSe QDs

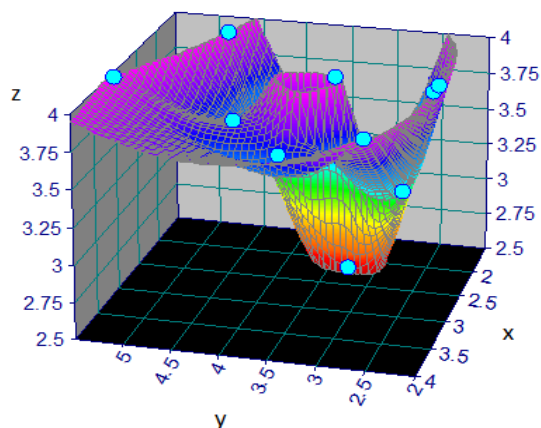


Fig. 5

Fig. 5 CdSe QDs particle spacing

IV. CONCLUSION

We demonstrate cheap and efficient method for CdSe QDs synthesis via pyrolysis of organometallic reagents. Despite the low cost, the synthesis produced high quality CdSe QDs. The synthesized CdSe nanocrystals showed a relatively narrow size distribution with particles size ranging from 2.09 nm to 4.9 nm. OA was used to protect the CdSe QDs from oxidation and emission loss. Their vulnerability to this effect degrades the photoluminescence quantum yield of nanocrystals semiconductors. The organic ligand layer TOPO was added to improve the optical properties of the CdSe QDs. Spectral relationship of UV-vis and photoluminescence shows that the photoluminescence spectra are typical of CdSe QDs consisting of two peaks; one with the position near the absorption peak called band-edge photoluminescence and the other red-shifted referred to as trap-related photoluminescence.

The quantitatively analyzed CdSe QDs surface parameters for ten point count height of atomic force microscopy images with scan size of 609.1 nm containing 65536 CdSe nanoparticles have peak-to-peak value of 1218.7 nm, surface skewness of -0.04 and surface kurtosis of -1.23. The irregularities in the surface texture have an average value of 265.7 nm and a surface root-mean-square value of 303.9 nm. We estimated the surface roughness, grain size, step height and pitch of the CdSe QDs sample. The surface topography reveals the particle distributions with the resolution similar to that obtained with scanning electron microscopy. The scanning electron microscopy reveals surface alignment of the QDs. Transmission electron microscopy and field emission scanning electron microscopy images show the lattice spacing. The transmission electron spectroscopy illustrated size distribution pattern of the CdSe QDs, its spherical morphology and the lattice plane spacing.

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