Synthesis and characterization of Cdse Quantum Dot via pyrolysis of organometalic reagent

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ABSTRACT

We report colloidal synthesis of cadmium selenide (CdSe) quantum dot (QD) through pyrolysis of organometallic reagents injection into a hot non-coordinating solvent. Monodispersity of the size tunable CdSe QDs begins with the injection of organometallic reagents (TOPOSe) into the hot coordinating solvent anneal at 195^{o}C to produce a discrete homogeneous nucleation under slow growth to ensure uniform surface derivatives and regularity in the core structure. The difference in the injection temperature was responsible for the dissimilarity in the nanocrystal growth as well as the crystallinity, shape and size related properties. Oleic acid (OA) was used to protect the CdSe QD against oxidation and photon emission loss while an organic ligand layer trioctylphosphine (TOPO) were used to overcome predominant influences associated with agglomeration. The optical properties of CdSe QD in octadecene (ODE) with size ranges between 2.09 and 4.90 nm were characterized using transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy-dispersive X-ray spectroscopy (EDX) Optical Photoluminescence (PL) and Absorption Spectroscopy (UV-vis). The peak-to-peak values, irregularities in the surface texture and the root-mean-square values of the surface roughness of CdSe QDs were determined.

Keywords: *CdSe quantum dot, Nanocrystals, Photoluminescence, Solar cell.*

INTRODUCTION

Quantum dots are electromagnetic radiation emitters with tunable bandgap. This novel semiconductors nanoparticle exhibits size and compositionally tunable bandgaps which can be engineered to perfectly match the absorption of the solar

spectrum; surpassing the operating capacities of traditional semiconductors. The uniqueness of the nanoparticles is size dependent as they respond differently to solar spectrum however; their peak emission frequency's extreme sensitivity solely depends on the quantum dot sizes. 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 photon energy absorbed by quantum dot particles into the conduction band corresponds to the energy of the bandgap. The percentage of absorbed photons result in an emitted photon is referred to as quantum yield (QY) which could be controlled by nonradiative transition of electrons and holes between energy levels that produce no electromagnetic radiation.

Quantum dots are cost effectively produced in bulk via chemical manufacturing techniques that couple their potential to increase efficiencies leading to lower cost and higher output photovoltaic cells. Quantum dots can be incorporated into semiconductor polymers and deposited onto low cost substrates using high throughput roll-to-roll and printing techniques. The photoelectric potential of nanoparticles and their incorporation into photovoltaic cell fabrication has been intensively investigated [1-3]. Various approaches to CdSe QDs synthesis have also shown notable potential in light emitting devices, biotagging, 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 [4-6]. Another feature of QD is their electronic structure which facilitates the generation of electron–hole pairs during photoexcitation which forms the basis for their use as electrodes [7, 8].

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 PbSe and CdSe [9]. The structure of the 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 effect increases the effective barrier around the CdSe core causing remarkable blue shift [10].

CdSe QDs synthetic approach that relies on the injection of Se precursor into a mixture of solvent and ligands has been successful. This approach 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 [11]. 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 [12]. Murcia et al. [5] reported sono-chemical synthesis of CdSe quantum dots using TOPO, cadmium acetate and hexadecylamine. Mono-disperse zinc blende CdSe QD ranging from

2.5 to 4.3 nm have been synthesized in an open-air microfluidic reactor with PTFE (Polytetrafluoroethylene) capillaries as the reaction channels [13]. Similarly, our synthesis reported here produced comparable grain size range (2.09 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. We use ODE as a solvent for CdSe QDs owing to its excellent properties. ODE is stable in air and has a low melting point (below 20 $^{\circ}$C) and this makes it easier to be handled at room temperature. Besides, it has a high boiling point (about 360^{o}C) and coupled with its inert nature to the selenium 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 which can affect their optoelectrical properties. The synthetic approach to produce monodisperse CdSe QDs using octadecene as solvent is cheaper and environmentally friendlier. Oleic acid is used instead of the costlier HPA (heteropolyacid) or TDPA (thiodipropionic acid) [15] to dissolve CdO powder to form homogeneous cadmium oleate solution and also as capping ligand for the CdSe QDs.

EXPERIMENT

Chemicals

Organometallic selenium (Se, SCR, 99.5^{+}%, Sigma-Aldrich), with trioctylphosphine (TOPO, 90%, Sigma-Aldrich) and octadecene (ODE, Fisher, 90%) were used to prepare the precursor. The pyrolyfic 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^{o}C.

Methodology

The two different steps used for the synthesis are as follows; the first step is the preparation of the Se precursor. The second step is the preparation of CdSe quantum dots. Different reaction times were chosen to obtain different sizes of the CdSe quantum dots.

Selenium Solution

30mg of selenium powder (Se) and 5 ml octadecene were added to a 10 ml flat bottom flask over a stirrer hot plate in a fume hood. 0.4 ml trioctylphosphine was measured by syringe from its sure-seal bottle and add to the flask. A magnetic stir

bar was added to stir-heat the solution to completely dissolve the selenium 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.

Synthesis of CdSe Quantum Dot

13 mg of CdO was added to 25 ml round bottom flask clamped in 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 oleic acid and 10 ml octadecene after which a thermometer capable of measuring 195^{o}C was inserted into the mixture. The cadmium solution was heated until its temperature reaches 195^{o}C. A clean dry Pasteur pipette was used to quickly transfer 1 ml of the one week old room temperature selenium solution into the 195^{o}C heated cadmium solution. The introduction of selenium precursor into the heated solution evolved smoke which is believed to be as a result of temperature gradient and rapid formation of CdSe QDs. The samples were removed at 10 seconds intervals using a 9 inch glass pasteur pipette as the CdSe particles grow in size. The samples were synonymous with colour transition from light red to dark brown coloration which was as a result of different reaction time. We noted the visible properties transition before and after the formation CdSe QDs which are shown in table 1.

Table 1: Transition in physical properties of CdSe Qds

Properties		Before	After
Selenium solution			
	Color	Black	Transparent on cooling
	Appearance	colloidal heterogeneous	Homogenous
	Solution	Watery-heterogonous	Sticky transparent
CdO			
	Color	Dark brown	Orange at 195^{0}C
	Appearance	Viscous colloidal	Homogenous at 195 ^{0}C
	Solution	heterogonous	Oily at 195^{0}C
CdSe			
	Color	___	light red to dark brown
	Texture	___	Oily Jelly-like
	Solvent	___	Octadecene and Toluene

Sample Characterization

A one-cm path length quartz curette 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 PL spectra were recorded on Perkin Elmer Ls-

55 Luminescence Spectrometer with zenon lamp over 350 – 700 nm range. For SEM, AFM, FESEM and EDX sample preparation, transparent glass measuring 25.2 x 22.2mm (1"x3") having thickness of 1mm to 1.2mm was ultrasonically cleaned with distilled water for 10 minutes. The process was repeated with methanol. The ultrasonically cleaned glass was dried in nitrogen gas to keep moisture away from the glass. The sample was annealed at 300 ^{o}C for 90 minutes so as to get rid of solvent and other impurities which might have been contaminated the sample during the synthetic process. The TEM analysis was carried out in liquid form however; the presence of black dots could be attributed to the impurities which are not obvious in the annealed samples.

The atomic force microscopy (AFM) technique brings 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 the resolution similar to that obtained in the SEM. The AFM technique is carried out for CdSe nanoparticles samples at room temperature and atmospheric pressure. AFM analyzed surface parameters such as the peak-to-peak value, average surface roughness and surface root-mean-square values. The TEM and FESEM were used to evaluate the micro-structure of the CdSe QDs. The TEM analysis was carried out using CdSe QDs solution. For FESEM and EDX analysis, a drop of CdSe QDs was dried using carbon-copper grid in ODE dispersed solution and was left to dry at room temperature.

RESULT AND DISCUSSION

The UV-vis absorption and PL emission spectra of CdSe nanocrystals with diameter in the range of 2.09 to 4.90 nm are shown in Figure (1a), (1b) and (1c). The illustration in Figure (1a) shows that the absorption spectrum of CdSe QDs is a function of the growth time. The colour of the CdSe QDs changes from light red to dark-brown in 1 min with respect to there discharge time. The fast decolouration 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 542nm in 1 min. The numbering shown on the absorption peaks in Fig.(1a) illustrated the transition in size range (1 represent smallest and 6 the largest) as the temperature of the CdSe QDs increases however; the increase in sizes with respect to time as the peak shift to longer wavelength was as 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.

The corresponding PL spectra of the CdSe nanocrystals in Figure (1b) show the extension time of reaction which is obvious with emission wavelength shifts from 442nm to 533 nm. The intensity of the PL for the CdSe QDs increased with an increase in the growth time from 0 to 1 min. In addition, the PL 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.

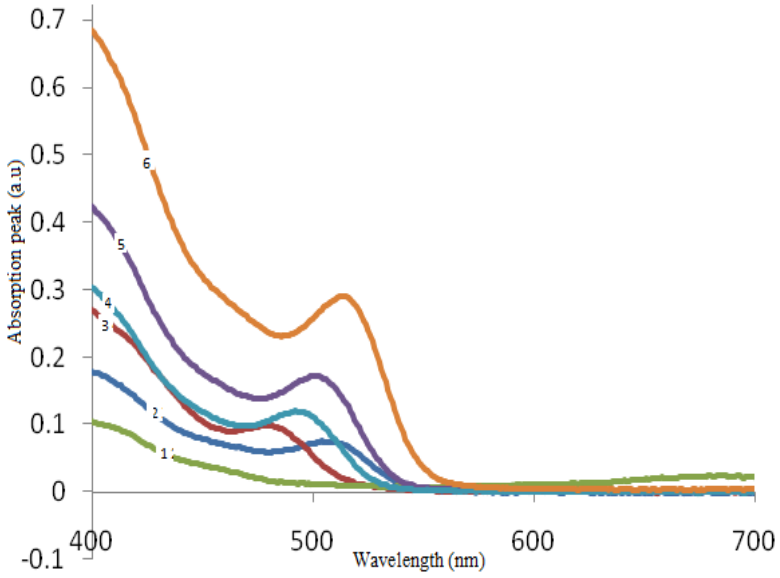


Figure 1a: UV–vis spectral peaks of the CdSe QDs.

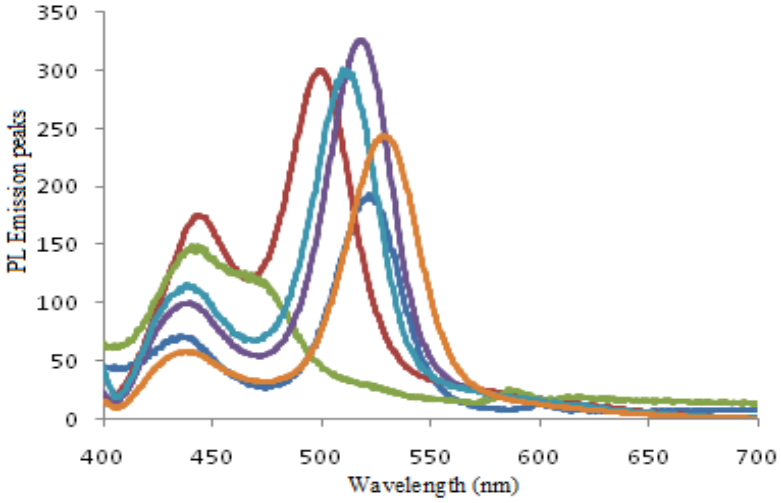


Figure1b: PL spectra emission of CdSe QDs

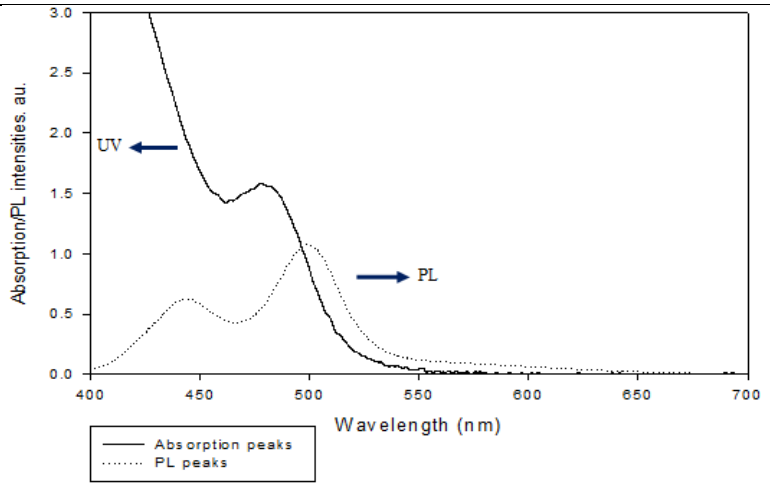


Figure 1c: UV-vis and PL spectra relationship

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

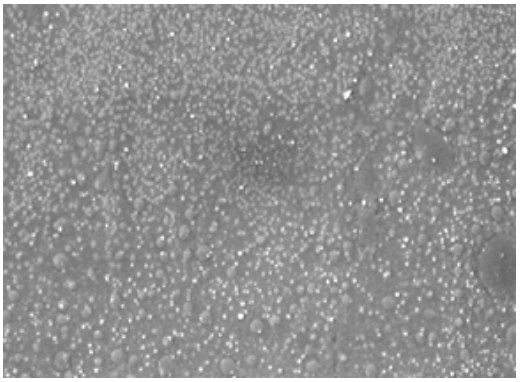
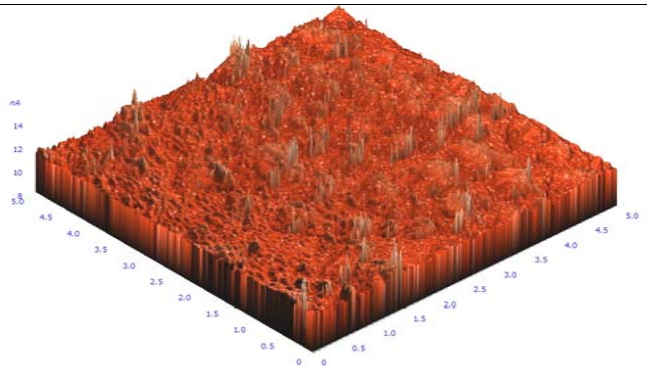
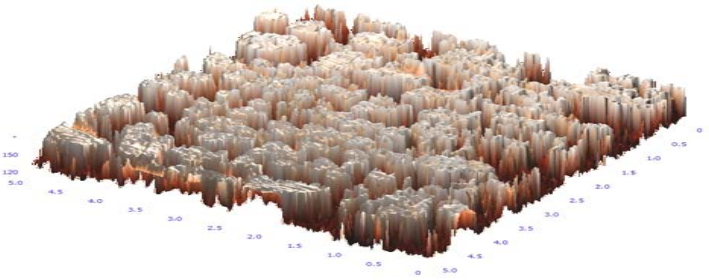


Figure 2; SEM representation

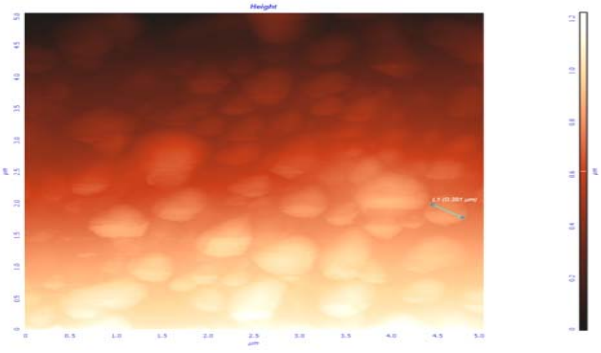
SEM diffraction pattern of the CdSe QDs shows regular arrangement of CdSe QDs images. Each bright spot correspond to the crystal plane and the symmetry of the spot reflects the crystal structure.



3a



3b



3c

Figure 3d: Surface roughness histogram of CdSe QDs

Figure 3a and b shows AFM 3D 1micron surface orientation of CdSe QDs while Figure 3c illustrated the surface morphology of CdSe QD. Figure 3d is a typical surface roughness histogram of CdSe QDs.

Figure (3a) and 3(b) show AFM 3D images. Fig. 3(c) shows the surface morphology while fig. 3(d) shows the surface roughness. For ten point count height of AFM images with scan size of 609.089 nm containing 65536 CdSe nanoparticles have peak-to-peak value of 1218.65 nm, surface skewness of -0.0396428 and surface kurtosis of -1.23324. The irregularities in the surface texture associated with surface roughness have average value of 265.749 nm with the surface root-mean-square values of 303.945 nm.

Figure (4a) and (4b) show the TEM and FESEM images of the CdSe QDs with respect to successive lattice spacing. The TEM reveals the QDs size distribution posses almost spherical morphology. The spacing of the lattice plane is as shown in Figure 5. Energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 6a and b) investigates CdSe QDs interactions with electromagnetic radiation and matter as they response to charged particles. This analytical approach allows energy of the X-rays to be characterized through energy differences existing between the dissimilar shells and of the atomic structure of the element from which they were emitted allowing the compositional elements of the specimen to be measured by EDX. Its fundamental principle of characterization relies on the uniqueness of the atomic structure which allows X-rays of an element's atomic structure to be uniquely identified individually. Carbon tap used for the analysis were believed to be the dominant source of carbon (C) as illustrated in Fig. 6(a) and (b). The presence of oxygen (O) could be due to the exposure to the atmosphere during when the sample was characterized. Selenium (Se) and cadmium (Cd) was the major compound form during the sample synthesis. Other unidentified peaks could be dust or rare gases resulting from air interaction with the sample.

Owing to this effect, appropriate care should be taken during the preparation and storage to reduce contamination with the constituent's impurity as well as atmospheric gases. Such care includes and not limited to storing the freshly

prepared sample in toluene, and the annealed sample in desiccators to prevent moisture from entering into the sample. Since the CdSe is inorganic compound, prolonged contact with air could result to agglomeration of the CdSe QDs. Table 2 shows details of the composed elements, their respective concentration and intensity of the ejected electron, weight of the compositional matters and the atomic percentage of the CdSe QD sample. The concentration ranges from Carbon (189.73), Oxygen (18.92), Selenium (0.89) and Cadmium (0.11). Their respective intensity to X-ray was 1.6459, 0.5415, 0.6721, and 0.7200 for Carbon (C), Oxygen (O), Selenium (Se) and Cadmium (Cd). Weight in percentage for the composed matters were 115.28 (C), 34.95 (O), 1.33 (Se) and 0.15 (Cd). The atomic percentage were 8134 (C), 18.51 (O), 0.14 (Se) and 0.01 (Cd) respectively. Though Cadmium was the least in weight and contration, its optoelectric property is better than that of oxygen and selenium and with equal proportion of carbon.

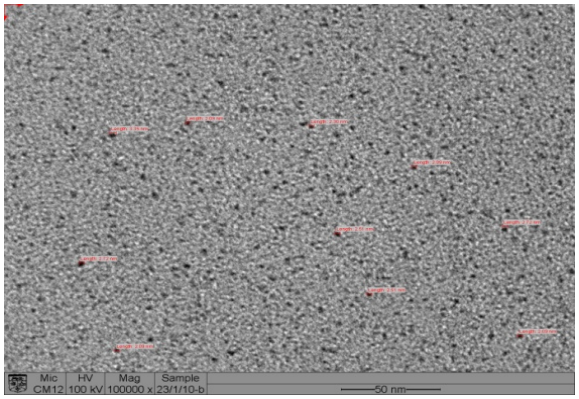


Figure 4a

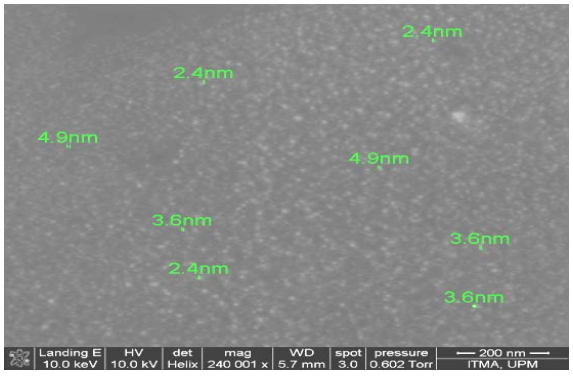


Figure 4b.

Figure 4a (TEM) and 4b (FESEM) images showing CdSe QD lattice plane spacing and particles sizes ranging from 2.09 to 4.9 nm respectively.

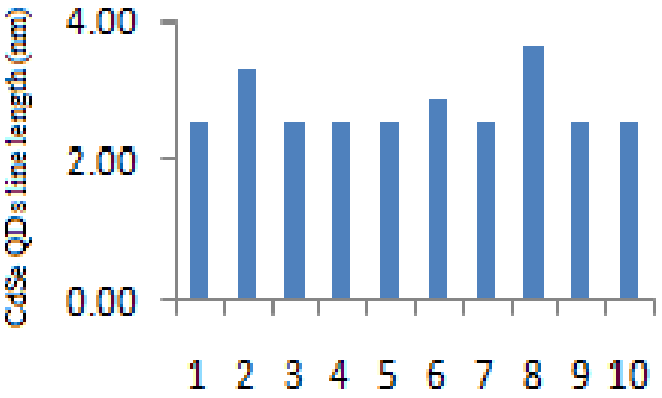


Figure 5: Line length distribution between successive CdSe QDs.

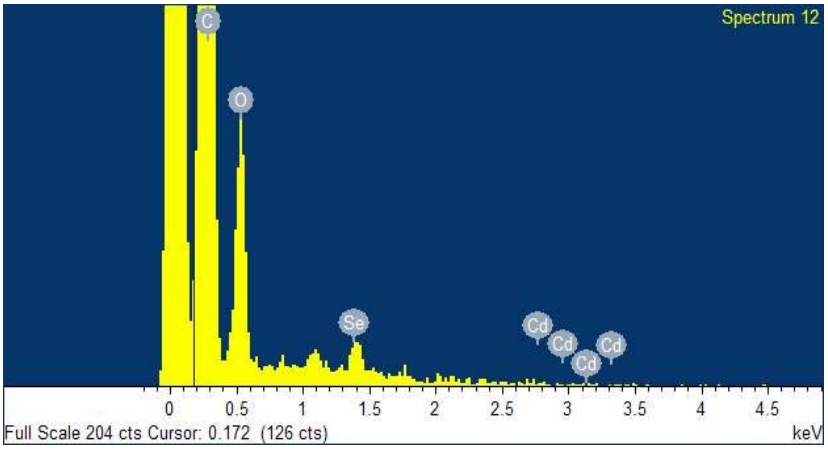


Figure 6a: EDX spectrum of CdSe QDs.

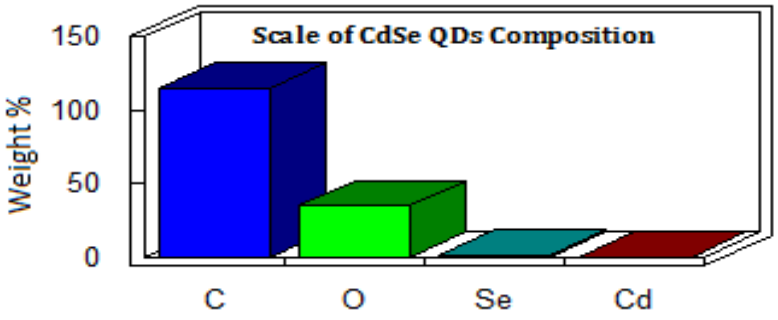


Figure 6b: Compositional scale result of the CdSe QDs annealed sample.

Table 2: composition of a typical CdSe QDs sample.

Element	Concentration	Intensity	Weight%	Atomic%
C	189.73	1.6459	115.28	81.34
O	18.92	0.5415	34.95	18.51
Se	0.89	0.6721	1.33	0.14
Cd	0.11	0.7200	0.15	0.01
Total			151.71	

CONCLUSION

We demonstrated cheap and efficient method for CdSe QDs synthesis via pyrolysis of organometallic reagents. The synthesized CdSe nanocrystals showed a relatively narrow size distribution with particles sizes ranging from 2.09 to 4.9nm. The role of oleic acid is to protect against oxidation and emission loss because of the vulnerability of CdSe QDs to oxidation which degrades the photoluminescence quantum yield of nanocrystals semiconductors. The organic ligand layer TOPO was added to improve optical properties of the CdSe QDs. 1cm path length quartz curette was used for the spectral study. Perkin Elmer lambda 20 UV-vis spectrometer were used to carry out the optical measurement in the range of 200 – 800nm wavelength at room temperature. The absorption peak (Fig.1a) are signatory to CdSe QDs. The PL spectra were recorded on Perkin Elmer Ls 55 luminescence spectrometer with zenon lamp over 350 – 700 nm range. Spectral relationship of UV-vis and PL in (Fig. 1c) shows that the PL spectra are typical CdSe QDs consisting of two peaks: one with the position near to the absorption peak called band-edge PL and red-shifted peak refer to as trap-related PL. Samples for PL UV-vis were prepared by dissolving a drop of CdSe QD solution in 3ml octadecene.

Quantitatively analyzed CdSe QDs surface parameters for ten (10) point count height of AFM images (Fig. 3a, b and c) with scan size of 609.089 nm containing 65536 CdSe nanoparticles have peak-to-peak value of 1218.65 nm, surface skewness of -0.0396428 and surface kurtosis of -1.23324. The irregularities in the surface texture have average value of 265.749 nm and the surface root-mean-square values of 303.945 nm. We estimated the surface roughness, grain size, step height and pitch of CdSe QDs sample. The surface topography reveals the particle distributions with the resolution similar to that obtained with SEM. The SEM (Fig. 2) reveals surface alignment of the QDs. TEM and FESEM (Fig. 4a and b) image show the lattice spacing. The TEM illustrated size distribution of the CdSe QDs and spherical morphology with spacing of the lattice plane as shown in Figure 5. EDX result shows that CdSe QDs is an ideal candidate for the processing of cheaper and efficient optoelectric devices owing to the high degree responsiveness of Cd and Se to light intensity.

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