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EFFECT OF OXYGEN ON SIZE-CONTROLLED SYNTHESIS OF CdSe QDs

Charles Ahamfeula Ubani^{1*}, MohamadYusof Sulaiman², Ibarahim Zahari¹, Kamarruzaman Sopian², Noor bayaa Ibrahim¹, Mohd Yusof Hj. Othman³.

¹School of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Eshan, Malaysia.

²Solar Energy Research Institute, University Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Eshan, Malaysia.

³Institute of Islam Hadhari, University Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Eshan, Malaysia.

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ABSTRACT

Unique properties of quantum dots (QDs) are controlled by their customizable particle sizes which can be engineered to suit local need. One-pot organometallic injection synthesis of cadmium selenide (CdSe) QDs is reported. The operation started with the injection of a week old selenium (Se) precursor into a boiling non-coordinating octadecene (ODE) at 195°C resulting in the formation of monodispersed size tunable CdSe QDs with discrete homogeneous nucleation. Differences in the injection and withdrawal time of the sample resulted to the dissimilarity in the shape, size and the optoelectronic properties of the QDs. The effect of oxygen on the synthesized CdSe QDs was studied by exposing freshly prepared sample to atmospheric oxygen for 206 days. The samples were characterized using optical absorption spectroscopy (UV-vis), optical photoluminescence (PL), X-ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM), electron dispersive X-ray (EDX) X-ray diffraction spectroscopy (XRD), and X-ray photoelectron spectroscopy (XPS). Noticeable deformation on the size, shape and the crystalline orientation of the CdSe QDs were observed on the oxygen-interacted sample. Although the synthesis method is safe and produced good quality CdSe QDs, the interaction of the sample with oxygen degrades their opto-electronic quality.

| Synthesis | CdSe QDs | Photoluminescence | Particle size | Agglomeration |

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1. INTRODUCTION

Particle size-dependent properties of quantum dots (QDs) form the bases for their suitability in different technological field. Manipulation of the surface properties of CdSe QDs such as particle sizes and shape can be achieved by varying the synthesis time and temperature as well as to control their hydrophobicity and photooxidation [1]. The synthetic approach used in this study offsets the repelling property (hydrophobicity) of CdSe by heating the reactant mixture above 140°C. The loss of electrons from a photoexcited electron during the reaction between CdSe QDs with oxygen in the presence of light energy were eliminated through heating. However, the present reported the deteriorating effects of oxygen on CdSe QDs on the resultant QDs particle shape and sizes.

Quantum dots (QDs) semiconductor nanoparticles exhibit size and compositional tunable bandgaps that can be engineered to match the absorption of the solar spectrum by varying their bandgap. Being size dependent on their optoelectronic properties, QDs respond differently to a specific solar spectrum wavelength which is clearly defined by the peak emission frequency's extreme sensitivity to both the dot's size and composition. A strong stimulus causes a valence band electron to take residence in the conduction band which results 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 bandgap. The percentage of absorbed photons that result in emitted photons commonly referred to as quantum yield (QY) is a measure of QDs efficiency and are influenced by the nonradioactive transition of electrons and holes between energy levels that produce no electromagnetic radiation which is a major effect of oxygen interaction with QDs.

Owing to the photoelectric potential of QDs, their incorporation into solar cell fabrication has been intensively investigated [2-4]. Numerous synthetic techniques used to produce QDs showed that the enhancement of the surface chemistry improves their optical properties, reactivity as well as stability [1, 5, 6]. Increasing interest in the use of QDs for various applications is partly due to the progress in their chemical synthesis and surface modification strategies [7, 8]. 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 with electrodes [9, 11] and allows for the ejection of conduction band electrons to the electrode or the injection of electrons from the electrode into the valence band of the QDs 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

*Corresponding author. E-mail: decharlington@yahoo.com
(Charles Ahamfeula Ubani) Tel: (60)-16-6974183.

significantly across different materials as have been shown in PbSe and CdSe [12]. 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 [13]. These opto-electronic properties and characteristic feature deteriorates on interacting with oxygen necessitating for surface passivation to enhance their surface chemistry during synthesis.

CdSe QDs synthetic approach that relies on the injection of the Se precursor into a mixture of solvent and ligands has been successful and entail precise control of the synthesis temperature so as to separate the nucleation and growth stages of the QDs which solely depend on the temperature of the mixture, injection process utilized as well as the concentration gradient [14]. It has been reported that room temperature injection of cadmium acetate and sodium seleno-sulphite (Na_2SeSO_3) into oleic acid showed controlled fluorescence by CdSe QDs [15]. Sono-chemical synthesis of CdSe quantum dots using TOPO, cadmium acetate and hexadecylamine have been reported [8]. 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 [16]. Similarly, the synthesis reported in this study produced a comparable grain size range (2.09 to 4.90 nm).

In this study, size-controlled CdSe QDs synthesized via pyrolysis of organometallic reagents injected into a hot non-coordinating solvent. Octadecene (ODE) was used as the non-coordinating solvent while oleic acid (OA) was used to protect the CdSe QDs from oxidation and emission loss. Oleic acid is preferred to costlier HPA (heteropolyacid) or TDPA (thiodipropionic acid) [17] to dissolve CdO powder into homogeneous cadmium oleate solution and also as capping ligand for the CdSe QDs. To improve the optical properties of CdSe QDs, the resultant QDs were covered with TOPO to protect the sample from agglomeration. ODE was used as a solvent owing to its excellent dissolving properties. ODE is stable in air and has a low melting point (below 20 °C) which 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 selenium precursor, less toxicity, low cost and good dissolving power for the growth of high quality QDs [18].

2. EXPERIMENTAL

2.1 Materials

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 a 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.

2.2 Method

The two different steps used for the synthesis were as follows; the first step was the preparation of the Se precursor. The second step was the preparation of the CdSe QDs using different reaction times to obtain different sizes of the CdSe QDs particles.

2.2.1 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. 0.4 ml TOPO was measured by syringe from its sure-seal bottle and added to the flask. Using a magnetic stirrer bar, the mixture was stirred-heated to completely dissolve the selenium powder. The mixture was cooled to room temperature and was stored in a sealed container for one week to allow the precursor to form.

2.2.2 Synthesis of CdSe QDs

13 mg of CdO was added to 25 ml round bottom flask clamped onto a heating mantle. 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 195°C heated cadmium solution. Adding of the selenium precursor into the heated solution resulted to the temperature gradient in the rapidly formed CdSe QDs. The samples were withdrawn at 10 seconds intervals using a 9 inch glass Pasteur pipette as the CdSe particles grew in size. The samples were synonymous with light red to dark brown physical coloration corresponding to different reaction time. Observable before and after the formation of CdSe QDs as shown in table 1. All operations were done in a fume hood to avoid inhalation of cadmium compound.

2.2.3 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 PL spectra were recorded on Perkin Elmer Ls-55 Luminescence Spectrometer with xenon lamp over 350 – 700 nm range. For SEM and AFM sample preparation, transparent glass measuring 25.2 x 22.2mm ("1x 3") having a 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 atomic force microscopy (AFM) technique was used to obtain three-dimensional (3D) images, surface roughness, grain size, step height and the CdSe QDs sample surface topography and to view the QDs distributions with a resolution similar to SEM microstructure (Fig. 2). The AFM technique was carried out at room temperature and atmospheric pressure. Surface parameters such as the peak-to-peak value, average surface roughness and surface root-mean-square values of the CdSe QDs were obtained. The TEM and FESEM images revealed the micro-structure orientation and particle sizes of the CdSe QDs. The TEM analysis was carried out using the CdSe QDs solution. For FESEM analysis, a drop of CdSe QDs was dried on carbon-copper grid in ODE dispersed solution at room temperature. The effect of oxygen on the synthesized CdSe QDs particle sizes was investigated 5 ml part-mixture of the sample the was exposed to atmospheric oxygen for 206 days.

3. RESULTS & DISCUSSION

The UV-vis absorption and PL emission spectra of CdSenanocrystals with diameters in the range of 2.09 to 4.90 nm are shown in Fig. (1a), (1b) and (1c). The illustration in Fig. (1a) shows that the absorption spectrum of CdSe QDs is a function of the growth time. The CdSe QDs changes from light red to dark-brown in 1 min with respect to withdrawal time. The fast coloration 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 numbers shown on the absorption peaks in Fig. (1a) illustrated the transition in CdSe QDs particle 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 is as a result of transition in the interband of the CdSe QDs [19, 20]. It became obvious that the particle size of CdSe QDs can be tuned by varying the reaction time.

The corresponding PL spectra of the CdSenanocrystals (Fig. 1b) show the pronounced effect of extending the reaction time with increase in temperature. The dissimilarity in temperature and time were responsible for the changes in emission peaks and wavelength shifts from 442nm to 533 nm within a growth time ranging 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 has been reported [20] shows that under 1.5 min reaction time, the CdSenanocrystals particle size increases owing to the depletion of the monomer concentration in the reaction solution.

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

Properties	Before	After
Selenium solution		
Color	Black	Transparent after a week
Appearance	Colloidal	Homogenous
Solution	Heterogeneous	Sticky transparent liquid
CdO		
Color	Dark brown	Orange at 195 ⁰ C
Appearance	Viscous colloidal	Homogenous at 195 ⁰ C
In Solution	Heterogeneous	Oily at 195 ⁰ C
CdSe		
Color	_____	Light red to dark brown
Texture	_____	Oily jelly-like
Solubility	_____	Soluble in octadecene and toluene
206 daysOxygen-interactedCdSe QDs		
Color	_____	Brownish
Texture	_____	Sticky Jelly-like liquid
Solubility	_____	Not readily soluble in ODE/Toulene

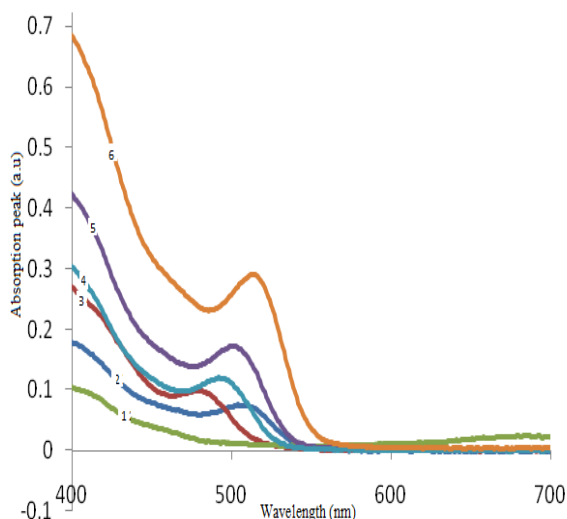


Fig. 1a. UV-vis spectral peaks of the CdSe QDs.

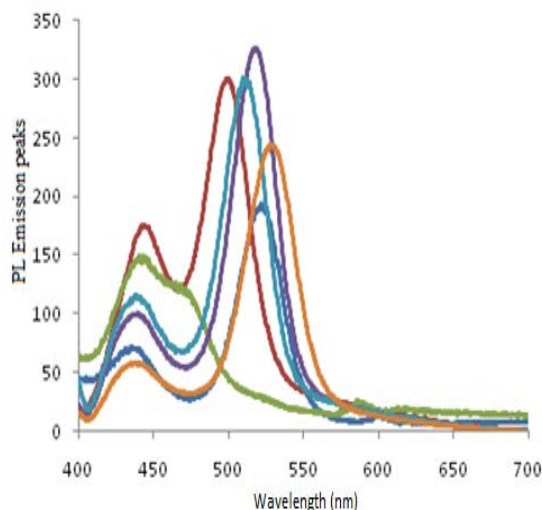


Fig. 1b. PL spectra emission of CdSe QDs

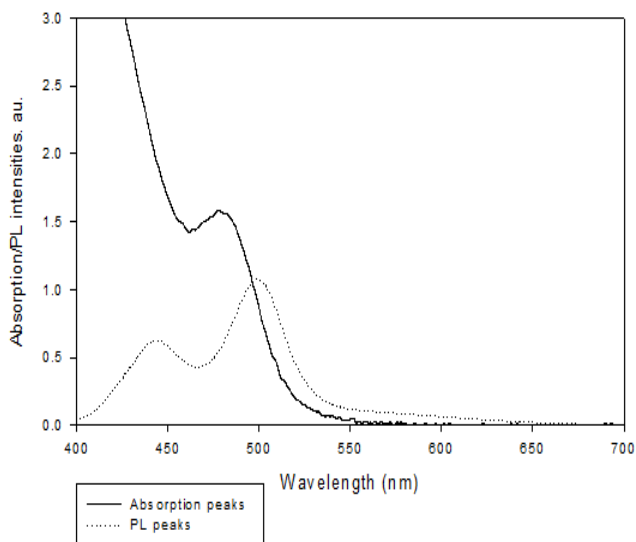


Fig. 1c. UV-Vis and PL spectra relationship

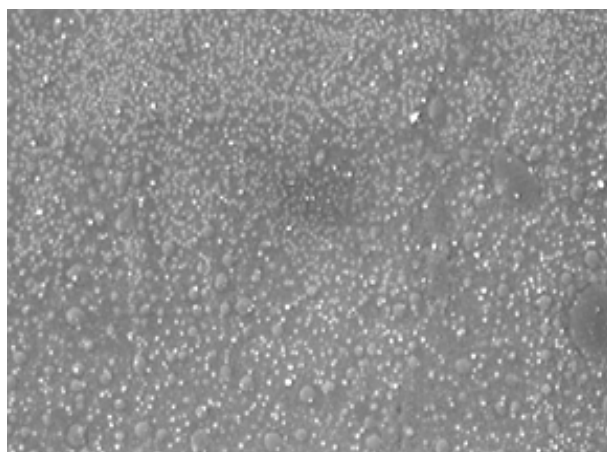


Fig. 2. SEM microstructure

The peak difference between the absorbed and emitted photons in Fig. (1c) 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 significantly influence CdSe QDs optoelectronics properties. 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 closest to the absorption peak called band-edge PL and the other is red-shifted peak referred to as trap-related PL.

SEM micro-structure image shown in Fig. 2 depicts CdSe QDs particle size orientation and distribution. Each bright spot corresponds to the crystal plane and the symmetry of the spot reflects the QDs crystal structure. The images of the surface topography and the 3D-representation for the CdSe QDs are as shown in Fig. 3a and b.

Fig. (3a) shows AFM-3D 1 micron surface orientation of CdSe QDs while Fig. (3b) illustrates the

surface morphology of CdSe QD. Fig. (3c) is the ten point height (609.089 nm) surface roughness histogram for the CdSe QDs.

Surface topography corresponding to 3D-representation measured by AFM is as shown in Fig. 3a and b. The hollow patches on the images (Fig. 3a) were attributed to dust or air interacting with the samples during the analytical process. Fig. 3b shows the CdSe QDs surface morphology and dot distribution while Fig. 3c depicts the surface roughness for ten point count height (609.089 nm) of AFM images containing 65536 QDs of CdSe. The qualitatively analyzed CdSe QDs has peak-to-peak value of 1218.65 nm, average surface roughness of 265.749 nm and surface root-mean-square values of 303.945 nm respectively. For the calculations, all the AFM images taken have a scan size of 100 x 100 μm .

Fig. 4a and b shows the TEM and FESEM images of the CdSe QDs with respect to their successive lattice spacing. The TEM image reveals that the CdSe QDs

particle sizes are spherical in shape. The lattice spacing plane of the samples is as shown in Fig. 5. The symmetry of nanocrystals lattices is helpful in determining their physical properties such as electronic band structure and optical transparency. In addition, the wavelength of CdSe QDs could be comparable to the lattices spacing in analyzing the crystals owing to the high dependence of particle orientation to emission surfaces.

Fig. 6 shows the morphological structure of 206 day oxygen-influenced CdSe QDs. Oxygen interaction with the sample were evaluated based on the variation in size of the resultant QDs. This was considered from the fact that the particle sizes of CdSe QDs determine their relative properties and their range of appropriate application. Therefore FESEM image provided a comparison of the

variation of the sample sizes. From the FESEM image, it becomes obvious that oxygen interaction with CdSe QDs results to agglomeration of the dots and increases the particle sizes (26.1 to 219.9nm). Defect in CdSe QDs particle sizes and shaped could wear the efficiency and stability of devices that depends on them for functionality. Base on the pronounced deteriorating effect on CdSe QDs morphology, we recommend that CdSe QDs synthesis, characterization process and should be kept away from moisture. Although CdSe QDs is not soluble in water, result shows that its particle sizes are prone to deformation under prolonged interaction therefore; their suitability for outdoor application necessitates for adequate preservative measures to ensure long lasting stable.

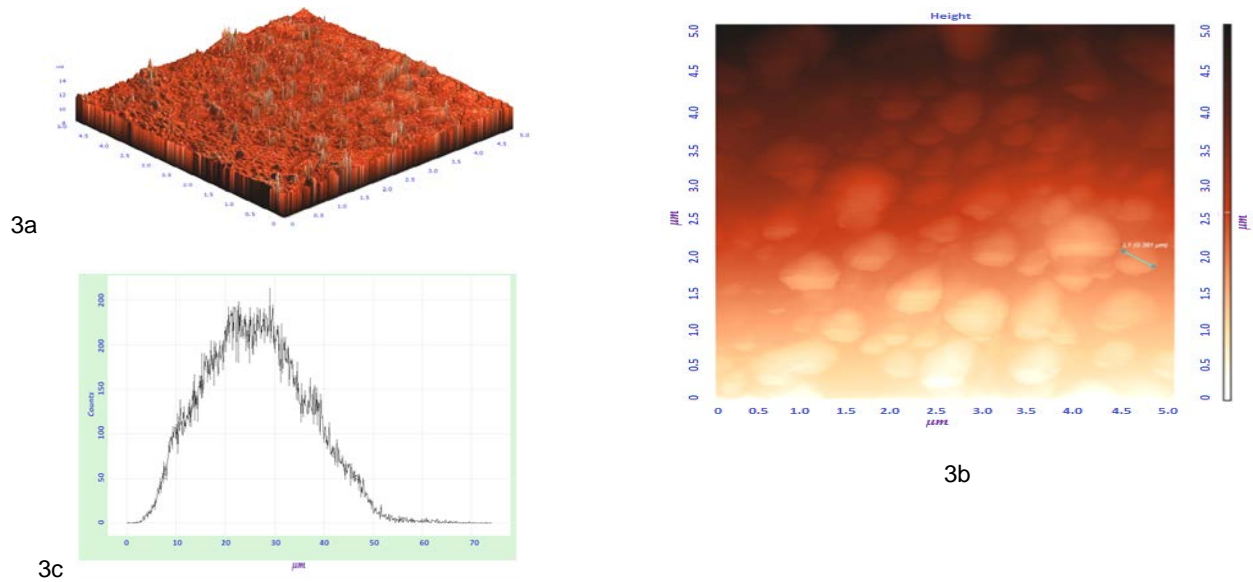


Fig.3. Surface roughness histogram of CdSe QDs sample

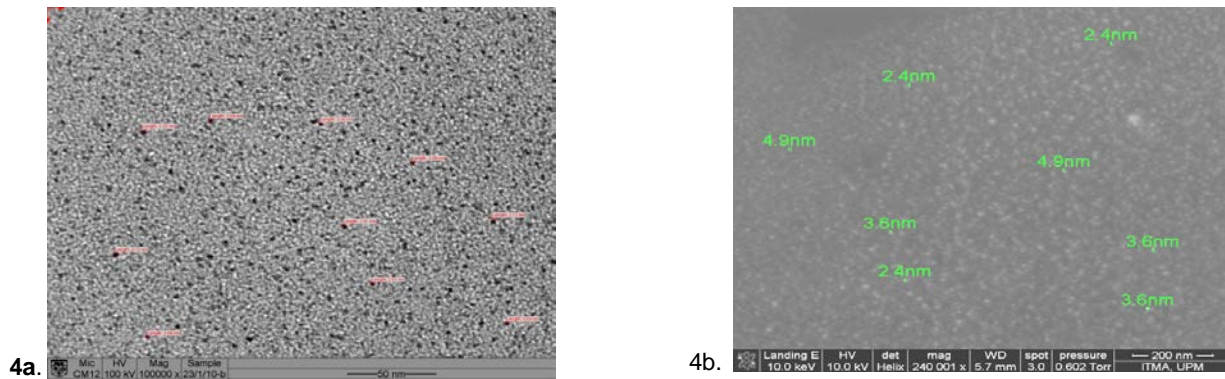


Fig. 4a.is the TEM image of freshly synthesized CdSe QDs showing lattice plane spacing and particle size range of CdSe QD while Fig. 4b is the FESEM image of the CdSe QD showing the particle size and their crystal lattice (bright spots).

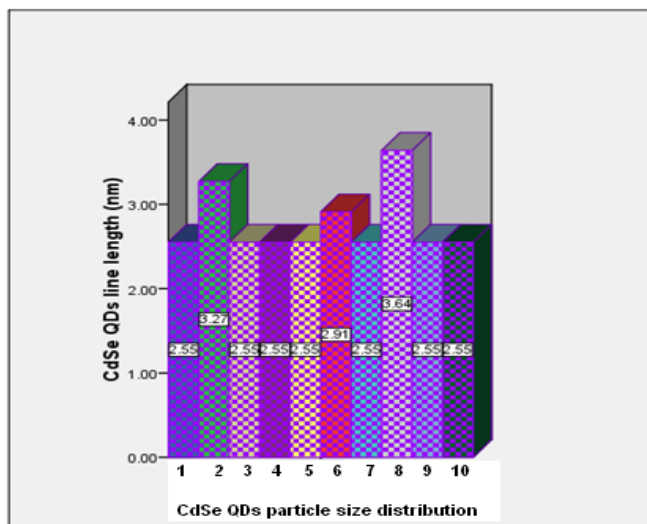


Fig. 5.

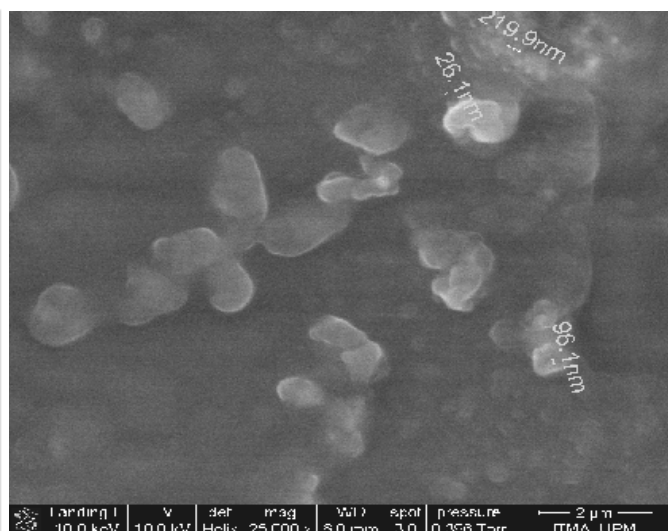


Fig. 6

Fig. 5. Depicts the average particle size distribution of the synthesized CdSe QDs shown in Fig 4a. Fig. 6: FESEM image showing 206 day's oxygen-influenced CdSe QDs. The result showed that the interaction between oxygen and the synthesized CdSe QDs sample resulted to agglomeration of the particle sizes from an average particle size of 2.09 nm to 114 nm.

4. CONCLUSION

This study has successfully synthesized and characterized CdSe QDs prepared using cheap materials and has evaluated the effect of atmospheric oxygen on the particle sizes of the resultant sample. The effect of oxygen on size-controlled synthesized CdSe QDs with particle size in the range of 2.09 to 4.9 nm affects their opto-electronic properties which are particle-size dependent. Quantitatively analyzed CdSe QDs surface parameters showed that the surface texture is 265.749 nm with a surface root-mean-square value of 303.945 nm. The effect of oxygen of the synthesized CdSe QDs sample resulted in an increase of the particle sizes from 2.09 nm to 114 nm after 206 days exposure to atmospheric oxygen. Although cheap and efficient method was used for the CdSe QDs synthesis, the quality of the resultant sample degrades on exposure to oxygen.

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