Malaysian Journal of Fundamental & Applied Sciences

available online at http://mjfas.ibnusina.utm.my

Hydrothermally Synthesized Cadmium Selenide Quantum Dot for Solar Cell Application

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ABSTRACT

Hydrothermal synthesis autoclave reactor offers simple, safer and environmentally friendlier process for the preparation of valuable nanoparticles. In this study, cadmium selenide (CdSe) quantum dot (QD) were successfully synthesized via one-step hydrothermal synthetic route at 195 ºC. The reactant mixtures used for the synthesis was added into Teflon and comprises 15 mg of selenium (Se) powder, 15 mg of cadmium oxide (CdO), 20 ml of octadecene (OTD), 10 ml of oleic acid (OA) and 1 ml of trioctylphosphine (TOP). The synthesis lasted for 3 hours 20 minutes. The synthesized CdSe QDs were characterized using optical absorption spectroscopy, fluorescence spectroscopy (PL), scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray analysis (EDAX). The broad absorption peak of the sample depicted the suitability of the sample for photovoltaic application while the fluorescence peaks was assigned to band edge emission to shallow and deep trap states. AFM and SEM microstructure images revealed the surface morphology and the crystal orientation of CdSe QD while the QD size and particles distribution were obtained using TEM and FESEM. The EDX were used to obtain the compositional ratio of the materials in the synthesized CdSe QD sample. The formation mechanisms were discussed on the basis of the experimental results and the quantum dots were found to be stable for about three months.

|Hydrothermal synthesis | Cadmium selenide| Surface morphology| Photoluminescence | Solar cell |

1. INTRODUCTION

Hydrothermal synthesis entails synthesis by chemical reactions of substances in a sealed-heated solution above ambient temperature and pressure. Research on hydrothermal synthesis was initiated in the middle of the 19th century and focuses on laboratory simulations of natural hydrothermal phenomena. In the 20th century, hydrothermal synthesis was clearly identified as an important technology for materials synthesis predominantly for single crystal growth [1]. Understanding of the underlying processes occurring in aqueous solution could be useful during hydrothermal synthetic processes. Control of thermodynamic variables such as reaction time, temperature and concentrations of the reactants and non-thermodynamic variable such as stirring speed during hydrothermal synthesis processes could be useful in commercial manufacturing of chemicals and these variables can be varied to obtain customized resultant samples.

2. HYDROTHERMAL SYNTHESIS

2.1 The technology and process

Hydrothermal synthesis utilizes single and heterogeneous phase reactions in aqueous media at elevated temperature (25 ºC to 1000 ºC) and pressure (100 kPa to 500kPa) to crystallize materials directly from solution and are usually conducted at autogeneous pressure corresponding to the saturated vapour pressure of the solution at specified temperature base on the composition of the solution [2] however; mild conditions (less than 350ºC and 50 MPa) are preferred for commercialized hydrothermal synthesis. Transition from mild to severe conditions could be as a result of corrosion and strength limits of materials as well as the hydrothermal reaction vessels. However, advances in hydrothermal chemistry has significantly reduced the reaction time, temperature, and pressure for hydrothermal crystallization of materials to T<200 ºC and P<1.5 MPa) [1-5]. Similarly hydrothermal synthesis reported in the present paper produced high quality CdSe QDs at comparable temperature (195 ºC) and reduces the risk associated with inhalation of toxic chemicals such as CdO and Se. The innovative breakthrough in reducing the synthetic temperature and pressure has promoted safer hydrothermal synthesis by

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eliminating the risk associated with blowout of autoclave vessel at high temperature [1]. Although, the hydrothermal synthesis reported in the present study utilizes low cost materials at reduced temperature (195°C), the operation was safer and produces high quality sample suitable for photovoltaic application.

2.2   Merit of the process

Hydrothermal synthesis is preferred to conventional and non-conventional nanocrstal synthetic methods because synthetic materials are safely enclosed as high temperature calcination, mixing, and milling phases are not necessary or minimized [4]. Although the ability to precipitate crystals directly from solution is not easily achieved through hydrothermal synthetic process h owever; uniform nucleation growth of hydrothermal process facilitates precise control of size and morphology of nanocrystals which is not possible with most synthetic methods [6]. Precise control over QDs particles aggregates combined with narrow particle size distributions facilitates reproducibility of the semiconductor CdSe QDs base on better microstructure control.

Precise control of CdSe QDs morphology can also be significant. For instance, QDs with crystallites having well-developed shapes corresponding to particular crystallographic directions can be oriented to form materials with single crystal properties [3]. Another important advantage of the hydrothermal synthesis is that the purity of hydrothermally synthesized samples significantly exceeds the purity of the starting materials because hydrothermal crystallization is a self-purifying process during which crystals/crystallites tend to reject impurities present in the growth environment. The impurities are subsequently removed from the system together with the crystallizing solution, which does not take place during other synthesis routes, such as high temperature calcinations [5].

Hydrothermal processing can take place in a wide variety of combination of aqueous and solvent mixture-based systems. Generally, processing with liquids allows for automation of a wide range of unit operations such as charging, transportation, and mixing as well as product separation. Moreover, relative to solid state processes, liquids enables the acceleration of diffusion, adsorption, reaction rate and crystallization under hydrothermal conditions [4]. However, unlike many advanced methods that can be used to prepare large variety of forms and chemical compounds, such as chemical vapour-based methods, the respective costs for instrumentation, energy and precursors are far less for hydrothermal methods. Hydrothermal methods are more environmentally benign than many other synthesis methods, which can be attributed in part to energy-conserving low-processing temperatures, absence of milling, ability to recycle waste, as well as safe and convenient disposal of waste that cannot be recycled [4].

The low reaction temperatures also avoid other problems encountered with high temperature processes, for instance, poor stoichiometry control due to volatilization of components as found in lead (Pb) compound (Pb volatilization in Pb-based ceramics) [6]. Materials synthesized under hydrothermal conditions often exhibit homogenous properties when compared to materials prepared by high temperature synthesis methods. Moreover, lattice defects associated with oxygen interacted CdSe QDs sample can be overcome by either properly adjusting the synthesis conditions [7]. Another important technological advantage of the hydrothermal technique is its capability for continuous materials production which has been particularly useful in continuous fabrication of ceramic powders [8]. Moreover, hydrothermal crystallization can be monitored in-situ using a range of techniques [9-10], which allows for the determination of crystal growth mechanisms and better control of the hydrothermal synthesis process.

2.3   Design of hydrothermal synthesis

Most hydrothermal synthesis techniques are base on the Edisonian trial and error method. This approach is time-consuming and is difficult in discerning between processes that are thermodynamically controlled. Thermodynamic features such as temperature and reaction time enable the design of a hydrothermal synthesis to be thermodynamically favored using fundamental principles rather than Edisonian approach [11-12]. However, precursor concentration, temperature and pressure can be modeled to define the processing variable phase(s) of interest. With the thermodynamic variables, processing space can be well defined for the material of interest. Range of conditions can be explored for control of reaction time and crystallization kinetics for the purpose of developing suitable process to produce desired properties such as specific particular size, morphology and aggregation level [12] as applied to the present synthesis reported in this paper where particles sizes of CdSe QDs determines their properties and application. Other thermodynamic processing variables, such as temperature, pH, concentrations of reactants and additives, determine not only the processing space for a given material but also influences both reaction and crystallization kinetics. The phenomena that underlie the size and morphology control base on the thermodynamic variables include the nucleation and growth rates which control CdSe QDs crystal size as well as their morphology. Size of the CdSe QD crystals can be controlled by varying synthesis temperature and precursor concentration. Crystal morphology and size can be affected by surfactants adsorption of specific solvents and solubility. In the other hand, thermodynamic synthesis variables can be constrained by the phase boundaries in a specific phase diagram making it difficult to exploit all sizes and morphologies for a certain material through the modifying of the thermodynamic variables [13]. However, non-thermodynamic variables such as stirring speed is also important when operating in thermodynamically limited processing variable during nanocrystal synthesis and can also influence the particle size by orders of magnitude [14]. In addition, change in the

reactants concentration can be used to control crystallites size and shape [15-16].

3. SYNTHESIS AND CHARACTERIZATION

3.1 Materials

The materials used for the hydrothermal synthesis of the CdSe QDs comprises trioctylphosphine oxide (TOPO, Aldrich, 90%), selenium powder (Se, SCR, 99.5 +%, Sigma-Aldrich), octadecene (OTD, Fisher, 90 %) metal base cadmium oxide (CdO, SCR, 99.9 +%, Sigma-Aldrich) and oleic acid (OA, SCR, 90 %, Sigma-Aldrich). The materials were not subjected to further purification or treatment and were stored at 23 $^{\circ}$C.

3.2 Synthesis

The hydrothermal synthesis of the CdSe QD started by adding the reaction mixture which comprises 15 mg of selenium powder, 15 m g of cadmium oxide, 20 m l of octadecene, 10 ml of oleic acid and 1 ml of trioctylphosphine oxide into a Teflon housed with a stainless steel wall. The temperature of autoclave was set to 195 $^{\circ}$C. The operation lasted for 3 h rs 20 min and the resulting sample were characterized using optical absorption spectroscopy, fluorescence spectroscopy (PL), scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray analysis (EDAX).

3.3 Characterization

Perkin Elmer Lambda-20 UV-vis spectrometer was used for the optical measurement of the ultra-small CdSe QDs at 200 – 800 nm wavelengths using a one-cm path length quartz cuvette. The PL spectra were recorded with Perkin Elmer Ls-55 Luminescence Spectrometer incorporated with zenon lamp over 350–700 nm wavelength. To study the surface morphology of the CdSe QD, AFM and SEM were used. The AFM technique qualitatively analysed three-dimensional image of the hydrothermally synthesized CdSe QD including surface morphology and surface roughness profile of the sample. For AFM and SEM analysis, transparent glass measuring 25.2 x 22.2 mm having thickness range of 1 mm to 1.2 mm was ultrasonically cleaned with distilled water for 10 minutes and later with methanol. The cleaned glass was dried in nitrogen gas to keep moisture away from the glass. The SEM image of the hydrothermally synthesized CdSe QD was obtained at a magnification of 10.00 KX operated at 4.00 kV. The TEM and FESEM image were used to determine the CdSe QD particle size distribution and orientation. The TEM images were obtained from CdSe QDs in OTD solution. For FESEM analysis, a drop of CdSe

QDs was dried on carbon-copper grid in OTD dispersed solution and was left to dry at room temperature.

4. RESULTS & DISCUSSION

The absorption peak of the hydrothermally synthesized CdSe QDs is shown in Fig. 1. The broad peak spectral wavelength covering 470-550 nm wavelengths depicts the potential of the freshly prepared CdSe QD sample for photovoltaic application. The size of the CdSe QDs ranges between 1.88 nm – 2.93 nm. Alternatively, UV-vis absorption spectroscopy can be conveniently used to determine the CdSe particles sizes and energy bandgap. The size of the CdSe nanoparticles was calculated from the bandgap values, using the Brus equation as simplified below;

$$E_g = E_g(0) + \frac{h^2}{8d^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right]$$

(eq.1)

where, E_g is the bandgap of nanoparticle, $E_g(0)$ is the bulk bandgap, m_e^* is the effective mass of the electron and m_h^* is the effective mass of the hole, d is the size of the nanoparticle, and h is the Planck constant.

For CdSe nanoparticles, m_e^* and m_h^* are 0.13 m_0 and 0.45m_0, respectively, and $E_g(0)$ is 1.7 eV. Therefore, the size of CdSe nanoparticles is given by Equation 2.

$$E_g = 1.7 + \frac{3.7}{d^2}$$

(eq. 2)

where d is in nm.

The bandgap energy could be obtained from the absorption spectrum using eq. 2. The emission peak of the hydrothermally synthesized CdSe QD is as shown in Fig 2. The emission spectra peak is characterized with shape peak. The emission peak revealed the optical properties of the sample. The optical properties can be observed through the ability of the CdSe QD sample to emit absorbed photon energy which is as illustrated in Fig. 2.

The compositional ratio of the hydrothermally synthesized CdSe QD was verified using EDEX (Fig. 3) as shown in table 1. Carbon (C), oxygen (O), where found to have interacted with the Cd and Se. These element gained access to the sample during the characterization. However, it is important that samples are kept away from deforming element during analytical study of the sample composition. To keep sample away from oxygen, synthesized sample should be stored in air-tight container such as desiccators and should not be handled with bare hand.
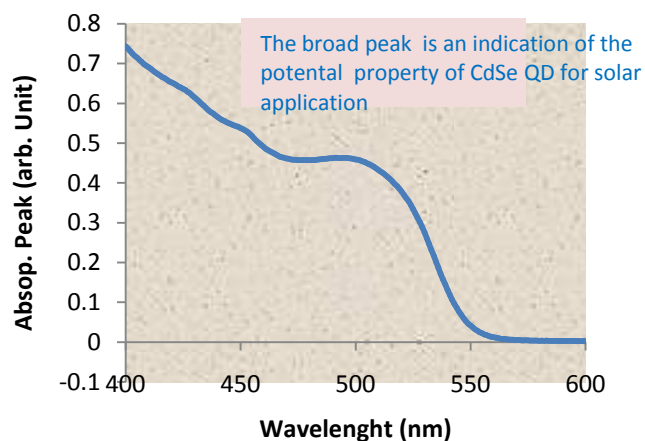
The broad peak is an indication of the potental property of CdSe QD for solar application

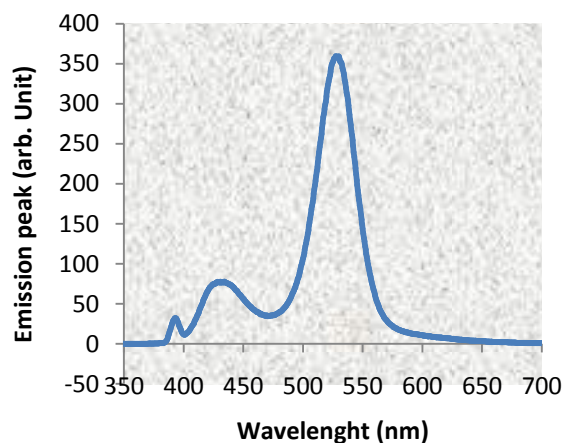**Fig. 1** Uv-vis spectra of the hydrothermally synthesized QDs

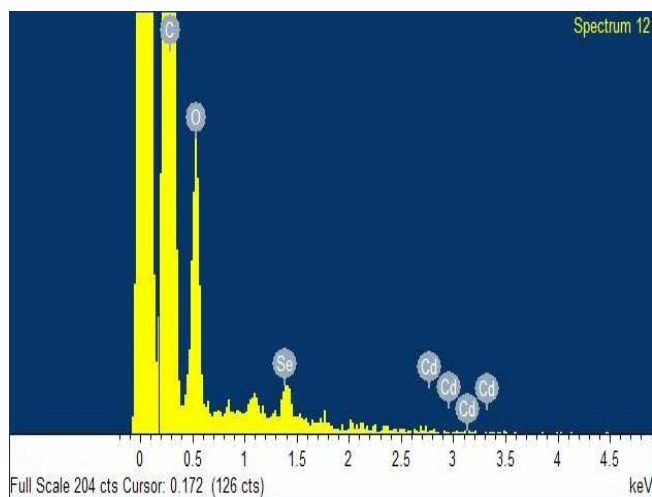**Fig. 2** Emission spectra of the hydrothermally synthesized CdSe QDs

Fig. 3 Electron disperse X-ray of the hydrothermally synthesized CdSe QDs
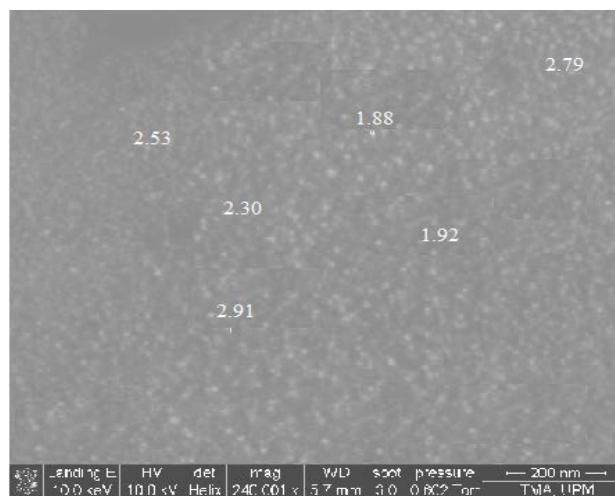

Fig. 4 FESEM Image of the hydrothermally synthesized CdSe QDs

Table 1 Composition of the hydrothermally synthesized CdSe QDs

Element	App. conc.	Intensity . conc	Weight %	Weight % (sigma)	Atomicity%
C	189.73	1.6459	115.28	3.49	81.34
O	18.92	0.5415	34.95	2.94	18.51
Se	0.89	0.6721	1.33	0.42	0.14
Cd	0.11	0.7200	0.15	0.24	0.01
Total			151.71		

FESEM image of the hydrothermally synthesized CdSe QD is shown in Fig. 4. The analytical technique revealed the QDs particle distribution as well as the particle sizes similar to that obtain from TEM. The TEM image of the CdSe sample is as shown in Fig. 5. TEM technique was used to obtain information about the CdSe QD particle sizes and individual dot spacing. TEM analysis reveals CdSe QD sizes and their morphological alignment to neighbouring QD. The diameter of the particle sizes obtained using FEEM ranges between 1.88 to 2.91 nm while that of TEM

ranges between 1.88 to 2.93 nm. This shows that reliable estimation of particles sizes can be obtained using either analytical measurement. Fig. 6 de picts QDs particle size distribution obtained from TEM while Fig. 7 is a plot showing the orientation of the particle sizes and their respective spacing between neighbouring QD particle.

The atomic force microscopy (AFM) images of the CdSe QD is as shown in Fig. 8a and b. The AFM images revealed surface morphological and surface roughness profile of the sample. Microstructure image obtain from scanning electron microscopy (SEM) is as shown in Fig. 9 and depicts the surface morphology of the hydrothermally synthesized CdSe QD sample. The AFM and SEM microstructure reveal surface morphology and surface features of the CdSe QDs. The average surface roughness profile of the sample and average surface roughness of the CdSe sample can be evaluated base on microstructure images obtained from AFM.
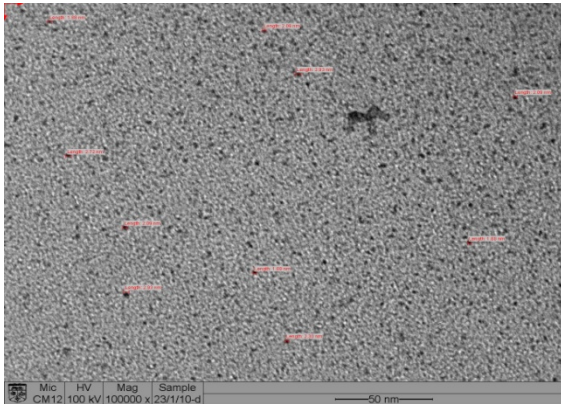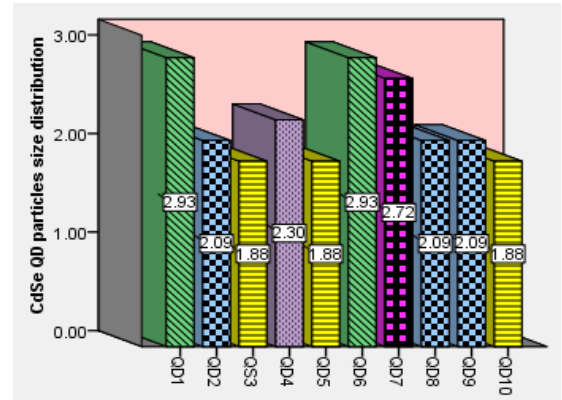

Fig.5 TEM microstructure of the CdSe QD

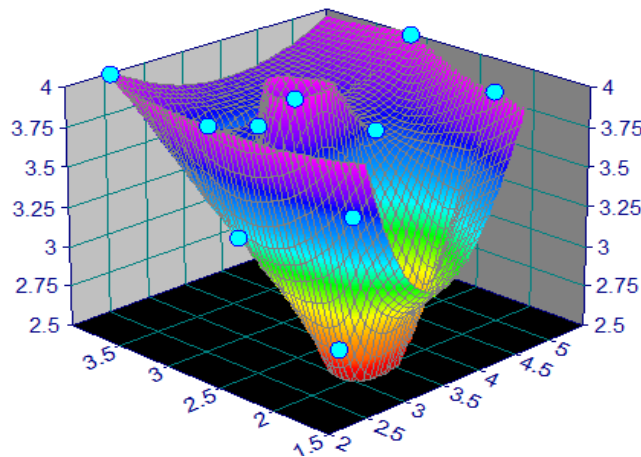**Fig. 6** Particle size distribution of the CdSe QD

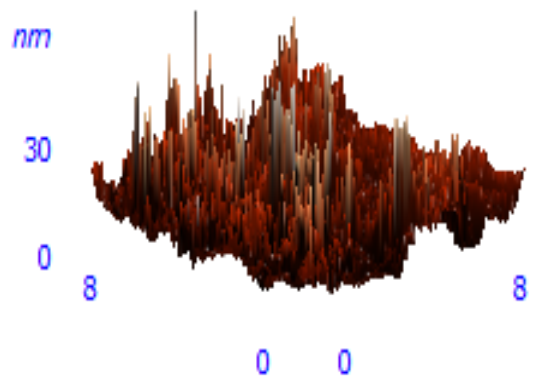**Fig. 7** Line length distribution of CdSe QDs particles

Fig. 8a AFM 3D surface microstructure image of the hydrothermally synthesized CdSe QDs
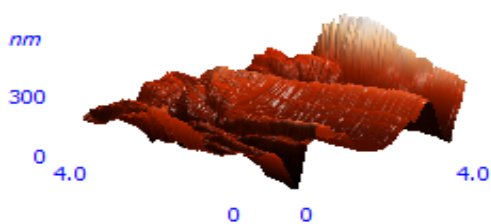
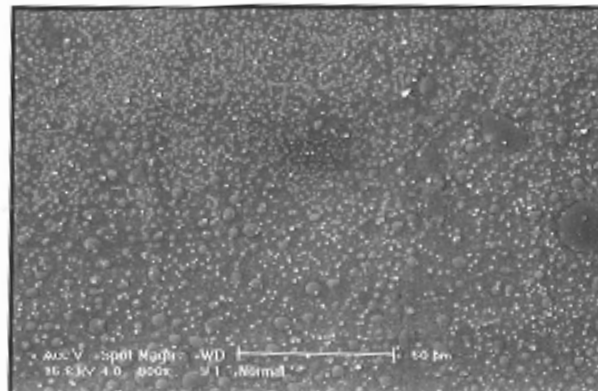**Fig. 8b** AFM 3D microstructure image of the CdSe QDs

Fig. 9 SEM micrograph of the hydrothermally synthesized CdSe QDs

5.   CONCLUSION

Hydrothermally synthesized CdSe QDs were successfully prepared at 195°C in autoclave. Although various controllable qualities of the CdSe QDs sample such as particle size were not directly controlled, the synthesis produced varied particle sizes of CdSe which implies that different solar spectrum can be absorbed by specific particle size. Despite safer and convenient approaches offered by hydrothermal synthetic method, the use of low-cost material makes the entire synthetic operation economically viable. In addition, the use of non-coordinating solvent (OTD) as matrix for the synthesis of high the quality CdSe QDs and oleic acid (OA) as ligand protected the CdSe QD surface from surface passivation of the luminescent QDs and agglomeration resulting from interaction from oxidizing elements. Analytical techniques utilized for the characterization of the hydrothermally synthesized CdSe QD revealed variation in the morphology and particle sizes of the CdSe QDs which depicts that the optical properties of the CdSe QDs which are size dependent and can be tuned by varying the reaction time of the synthesis. The customizable participle sizes determine the optical properties of CdSe QDs which were obtained via safer and lower cost materials. The particle sizes of the hydrothermally synthesized CdSe QDs distinctively have particle diameters ranging between 1.88 nm to 2.91nm. The broad absorption peaks and narrow emission peaks depicts the unique optical properties of the hydrothermally synthesized CdSe QDs while the resulting surface morphology were revealed in AFM and SEM images. Result from the microstructure images of TEM and FESEM shows that the CdSe QDs are spherical in shape with physical dimensions smaller than that of the exciton Bohr radius.

ACKNOWLEDGEMENT

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