

# Fabrication and study of structural and optical properties of Cadmium Telluride quantum dots

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Fluorescent semiconductor quantum dots (QDs) are nanocrystals with a diameter that usually ranges from 1 to 10 nm. QDs can be prepared by many techniques including plasma synthesis, mechanical fabrication, or colloidal synthesis. The current paper presents the synthesis of CdTe quantum dots (QDs) with wet chemical method at variable reaction time, variable temperature and variable trioctylphosphine (TOPO) concentration, to control the size of the produced QDs. Structural characterization was carried out with conventional transmission electron microscopy (TEM) and X-ray diffraction (XRD). Optical characterization was performed with optical spectrometer and Spectrofluorometre. TEM images revealed that the size of QDs increases with the increase in the three parameters' reaction time, temperature and TOPO concentration. This represents a new achievement in comparison to the previously produced similar QDs with random size ranges. Furthermore, the optical properties of the CdTe QDs showed that the characteristic emission and absorption of light could be controlled by changing these parameters as well. The observed results are very important and can be applied to increase the efficiency of solar cells.

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**Keywords:** Quantum dots, X-ray diffraction, Size control

## 1. Introduction

Quantum dots (QDs) are tiny nanocrystals scaled in nanometer boundaries of appropriate substance belonging to semiconductor or other matrices. There are many methods for synthesis of quantum dots of various sizes [1]. The electronic properties of quantum dots are intermediate between those of bulk semiconductors and of discrete molecules, closely related to their size and shape. Furthermore, their optoelectronic properties, for instance band gap, color emission and absorption can be altered as a function of shape and particle size for a given composition. In the past two decades quantum dots (QDs) have attracted great attention due to their unique characteristics intermediate between those of bulk semiconductors and discrete molecules, for instance, high quantum yields, photochemical stability, controllable spectroscopic properties and the ability to emit specific color fluorescence with a specific excitation frequency [2]. These spatial characteristics have enhanced QDs applications in industries and in various disciplines of scientific research. QDs have been used to increase the efficiency of solar cells [3-6], and enable broad bands of different frequencies of light sources [7]. Recently, QDs fluorescent protein pairs have been used as novel fluorescence resonance energy transfer probes [8, 9]. QDs are nanoparticles (NPs) having a diameter in the range of 2-10 nm. In this range the so-called 'quantum confinement effect' plays an important role. This effect arises when the size of the particles is less than the dimensions of the exciton [10-12]. Alexei Ekimov discovered nanocrystalline, semiconducting quantum dots in a glass matrix and conducted pioneering studies of their electronic

and optical properties [13]. There are many types of quantum dots like core-type QDs, core shell QDs and alloyed QDs etc. [14-16].

There are many methods for synthesis of QDs: microwave-assisted aqueous synthesis, chemical precipitation [17], hydrothermal synthesis [18], wet chemical [19] and organometallic synthesis [20]. In 2015, Verma M. et al. [1], demonstrated the production of the of quantum dots CdSe and ZnSe with cubic crystalline phase sized in 2–5 nm range using the solvothermal method. The size and morphology of the produced quantum dots were analyzed using high resolution transmission electron microscopy, and X-ray diffraction which confirm the narrow size of nanoparticles. Even though, they characterized the optical properties of the produced QDs very precisely using different techniques, failed to control the size of these nanoparticles. Moreover, similar QDs, were produced by Jiang Z. et al. [21] using organic synthesis to observe morphology variation during shell coating. Although they have successfully produced QDs with hexagonal and rod structures, they could not control the size of these nanoparticles. Moreover, the size of these QDs varied randomly which represents a disadvantage of the applied method.

In this paper, we have presented a wet chemical method to fabricate CdTe QDs and to control their size to be appropriate for the fabrication of solar cell. In addition, the size and morphology of the produced nanoparticles are characterized with TEM, and the optical investigations are carried out with spectrometer and fluorospectrometer.

## 2. Experimental

CdTe QDs were prepared by adding Cd and Te solutions at different reaction times, different temperatures and different Trioctylphosphine oxide (TOPO) (an organophosphorus compound with the formula OP ( $C_8H_{17}$ )<sub>3</sub>) concentrations. Cd solution was prepared by mixing an amount of 26 mg of Cadmium Oxide (CdO), and 20 ml of Octadecene (ODE) together with 1.2 ml of Oleic acid (OA) in a neck flask with reflux clamped and heated with a temperature controlled heating mantle instrument. In this procedure, the mixture was heated to 130°C under argon gas flow, which took 15 minutes. The mixture resulted in a colorless clear solution. At this temperature, 0.8 ml (16%) of Te solution was injected which was prepared by dissolving 42.2 mg of Te in 0.8 ml of TOPO and diluted with 4 ml of ODE. It was found that, when 0.8 ml of Te solution was quickly injected into the hot solution of Cd, the fabrication process of CdTe QDs started immediately. The reaction mixture changed its color instantly indicating the nucleation of CdTe nanocrystals. Small quantity of QD samples were taken from this mixed solution at 5 sec, 10 sec, 25 sec, 50 sec and 125 sec after mixing the Te and Cd solutions. These represent the nucleation of the CdTe QDs seeds at different reaction time to fabricate QDs which may affect the QDs size as discussed in the following section [23].

In order to make CdTe QDs samples at different temperatures, we repeated the same procedure by heating the Cd solution at 130°, 150°, 180°, 200° and 230°C, then mixed it with the Te solution as described above. Then, we made CdTe QDs at different TOPO concentrations of 0.8 ml (16%), 1.6 ml (32%), 2.4 ml (48%), 3.2 ml (64%) and 4 ml (80%) using the same procedure by changing TOPO concentrations in Te solution correspondingly. After this process, the QDs were extracted from the mixtures using methanol in a centrifugal machine. The mixture was centrifuged many times using fresh methanol until the QDs couldn't be mixed further with methanol, then dispersed in Hexane.

In order to confirm QDs sizes, TEM images were recorded with a transmission electron microscope JEOL (JEM-2100F) with a point resolution of 0.23 nm operating at 100KV. For further structural investigations, x-ray-

diffraction (XRD) patterns were recorded with XRD instrument (model D8 DISCOVER, 6kW X-ray source producing Cu  $k\alpha$  radiation at a wavelength of 1.5406 Å, Bruker) with a step width of 0.02°. Optical characteristics were carried out with JASCO UV-Spectrometer model-V-760 and JASCO Spectrofluorometric model -FP-8200.

## 3. Results and discussion

The dispersed nanoparticles in hexane were examined by transmission electron microscopy (TEM). The TEM image of the nanoparticles is presented in Fig. 1.

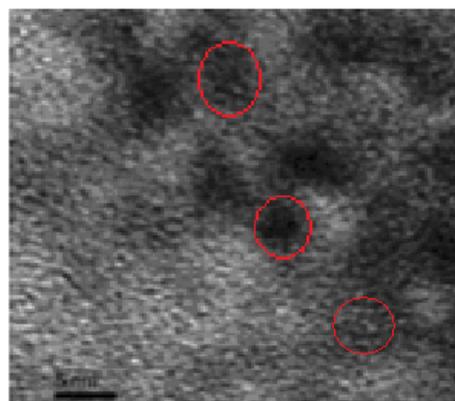


Fig. 1. The TEM image of quantum-dots CdTe

It is recognized from Fig. 1 that the shape of the observed CdTe QDs is spherical. During the preparation of the CdTe QDs, it is found that there are parameters affecting the size of these QDs. In the following, a detail study for each of these parameters is given.

Firstly, the effect of the reaction time between Te and Cd solutions on the produced QDs size was examined from TEM images and a small variation from 4.3 nm to 5nm at reaction time from 5 second to 125 second was observed. The TEM images at 5 sec and 125 sec reaction time are shown in Fig. 2. The TEM images reveal a small change in the size from 4.3 nm at 5 seconds to 5 nm at 125 seconds reaction time.

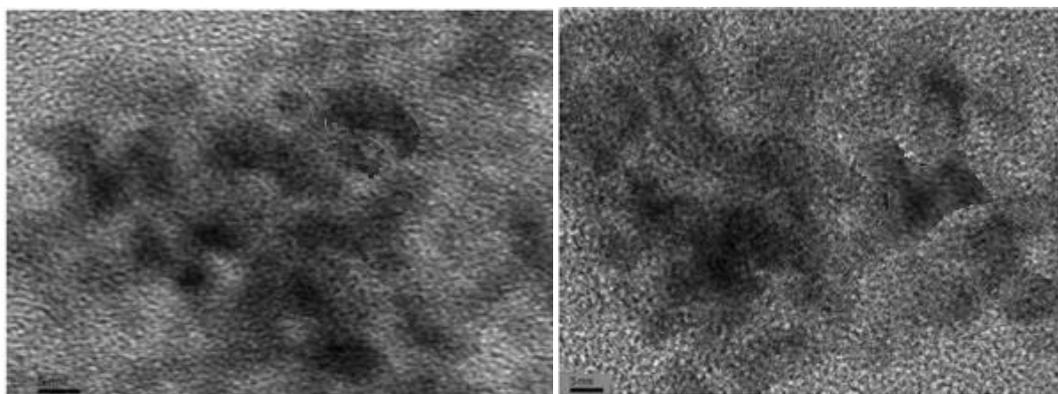


Fig. 2. TEM images for CdTe QDs prepared at different reaction time. The left TEM image is for 5 sec and the right TEM image for 125 sec reaction time

The second factor that affects the CdTe QDs size is the TOPO concentration. To examine this effect, the CdTe QDs were prepared at different TOPO concentrations

which were increased from 0.8 ml to 4 ml as shown in Fig. 3.

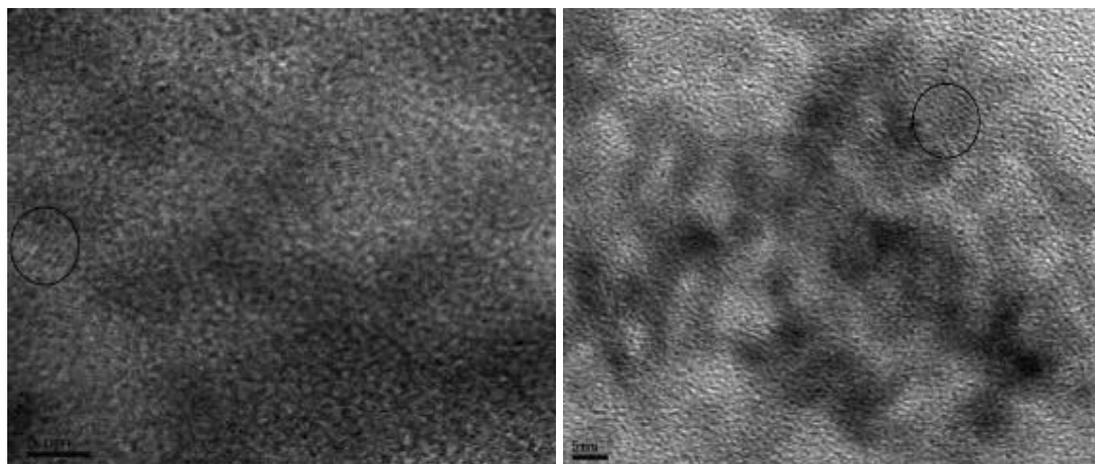


Fig. 3. TEM images for CdTe QDs prepared at different TOPO concentration increased from 0.8 ml (left TEM image) to 4 ml (right TEM image). The scale bar is 5 nm in both images

The obtained TEM images revealed a recognized change in the size from 5 nm at 0.8 ml to 5.7 nm at 4 ml TOPO concentration.

When CdO is dissolved in Oleic acid and Te is dissolved in TOPO, which are short chain length solvents, the nuclei concentration increases tremendously. Cd

precursor is consumed by nuclei, hence the increase of the nuclei concentration leads to an increase in the growth rate and the size of QDs.

The third factor is the effect of the varying Te and Cd solutions' temperatures on the produced QDs size as shown in Fig. 4.

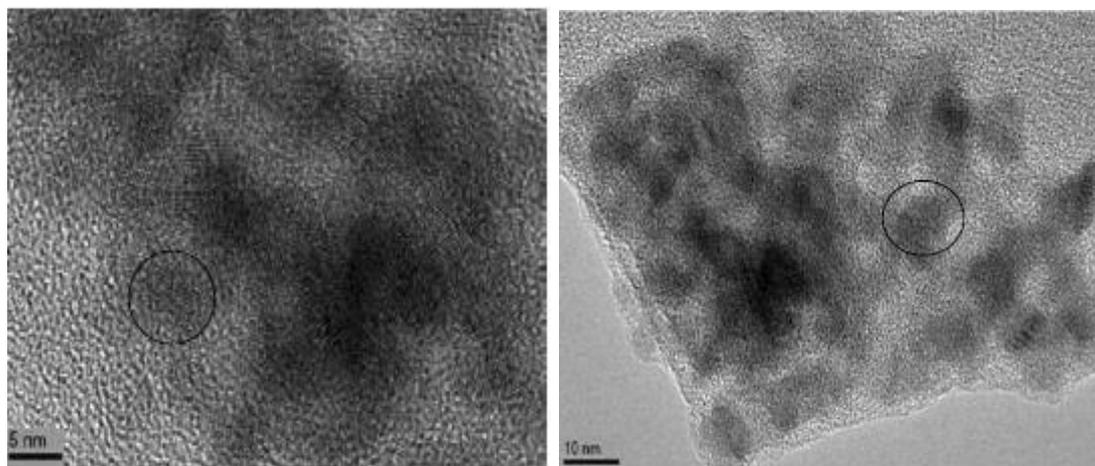


Fig. 4. TEM images for CdTe QDs prepared at different temperatures. The left TEM image for 130°C and the right TEM image for 230°C

The obtained TEM images revealed an abrupt change in the size from 4 nm at 130°C to 6 nm at 230°C. Increasing temperature during synthesis is a critical factor for QD crystal growth. By heating the solution, precursors decompose forming monomers which nucleate and form more QDs crystals. This is the reason that the size of QDs becomes larger at higher temperatures.

The formation of the crystalline phases of the crystals are revealed by the XRD patterns. XRD patterns of CdTe QDs prepared at different reaction time, different temperatures and different TOPO concentrations are depicted in Fig. 5 (a), (b) and (c) respectively.

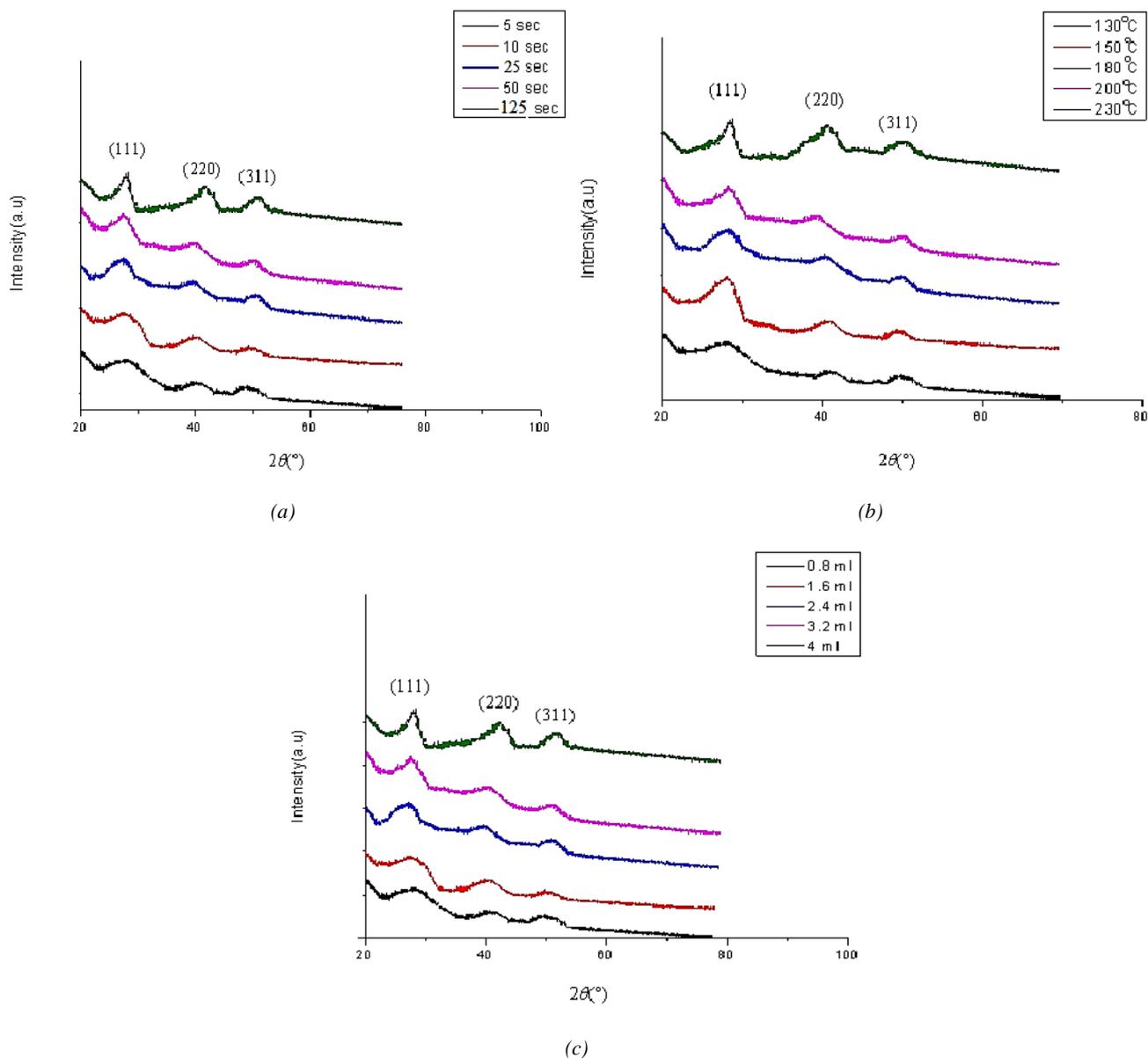


Fig 5. (a) XRD patterns of QDs fabricated at different reaction time; (b) XRD patterns of QDs fabricated at different temperatures; (c) XRD patterns of QDs fabricated at different TOPO concentration

The observed XRD patterns demonstrate the peaks located at  $2\theta = 25^\circ$ ,  $42^\circ$  and  $50^\circ$  which can be attributed to the (111), (220) and (311) planes of the crystalline phases of the CdTe QDs crystals. Figs 5 (a), (b) and (c) show that CdTe QDs exhibits cubic zincblende type structure with a preferential orientation along the (111) plane as indicated in JCPDS card No. 15-0770 [24]. The appearance of (220) and (311) indicates the high crystallinity of QDs. The XRD peaks are broadened due to their nature of being small QDs. The fundamental width at half maximum (FWHM) increases with a decrease of QDs crystallite size determined from reflection through plan (111) using following Scherrer formula [22].

$$D = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

where  $\lambda$  is the X-Ray wavelength,  $\beta_{1/2}$  is the line broadening at half the maximum intensity (FWHM),  $\theta$  is the Bragg angle. The calculations of crystallite sizes at different reaction time, different temperatures and different TOPO concentrations using the Scherrer formula are given in Table 1.

Table 1. FWHM and sizes calculated with Scherrer formula for CdTe QDs prepared at different parameters

Parameter		FWHM (rad)	Size (nm)
Tem(°C)	130	0.0350	4.5
	150	0.0330	4.7
	180	0.0325	4.9
	200	0.0310	5
	230	0.0305	5.2
TOPO (ml)	0.8 (16%)	0.0350	4.6
	1.6 (32%)	0.0330	4.8
	2.4 (48%)	0.0325	4.9
	3.2 (64%)	0.0318	5
	4 (80%)	0.0311	5.1
Time (sec)	5	0.0337	4.7
	10	0.0330	4.8
	25	0.0325	4.9
	50	0.0318	5
	125	0.0311	5.1

The optical band-gap of CdTe QDS can be calculated with following Brus equation [23]

$$E_{QD} = E_{bulk} + \frac{\hbar^2}{8 \times r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r} \quad (2)$$

where EQD is energy gap for QDs,  $E_{bulk}$  is the energy gap of the bulk material,  $r$  is the radius of the nanoparticle,  $m_e^*$  is the effective mass of the electron,  $m_h^*$  is the effective mass of hole.

The optical band-gaps of CdTe QDS at various reaction times are represented in Fig 6 and the values are listed in Table 2.

Table 2. Variation in optical properties and sizes for CdTe QDs prepared at different reaction time according to the formula (2)

Reaction time (sec)	absorption peak (nm)	Band gap energy (eV)	Size Measure By TEM (nm)
5	260.7	4.764	4.3
10	260.9	4.760	4.5
25	261	4.758	4.7
50	261.1	4.757	4.9
125	261.2	4.755	5

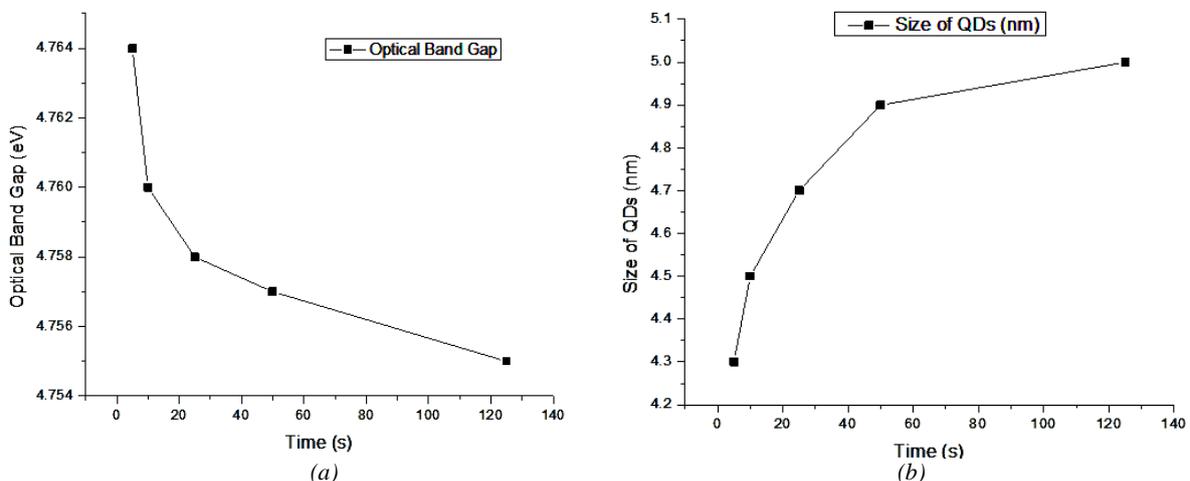


Fig. 6. (a) Band gap versus reaction times for CdTe QDs; (b) Particle size versus times for CdTe QDs

Fig. 6 (a) and (b) in addition to Table 2, demonstrate that band-gap decreases with increasing reaction time: this is due to the increase in QD size with increasing reaction time as depicted in Fig 6 (a). The variation in the value of the band gap is not linearly proportional to the reaction time. This is due to the injection of a 'cold' solution of precursor molecules into hot liquid ODE to fabricate CdTe QDs [24]. As time passes after mixing solutions,

instantaneous formation of nuclei and Te concentration is depleted due to growth, the critical size becoming larger than the average CdTe QDs size present in the solution.

The optical band-gaps of CdTe QDs at various temperatures, as calculated according to the Brus equation, are represented in Fig. 7 and the values are listed in Table 3.

Table 3. Variation in optical properties and sizes for CdTe QDs prepared at different temperatures

Temperature (°C)	Absorption peak (nm)	Band gap (eV)	Size Measure by TEM (nm)
130	260.5	4.77	4
150	260.8	4.76	4.5
180	261	4.758	4.7
200	261.2	4.755	5
230	262	4.74	6

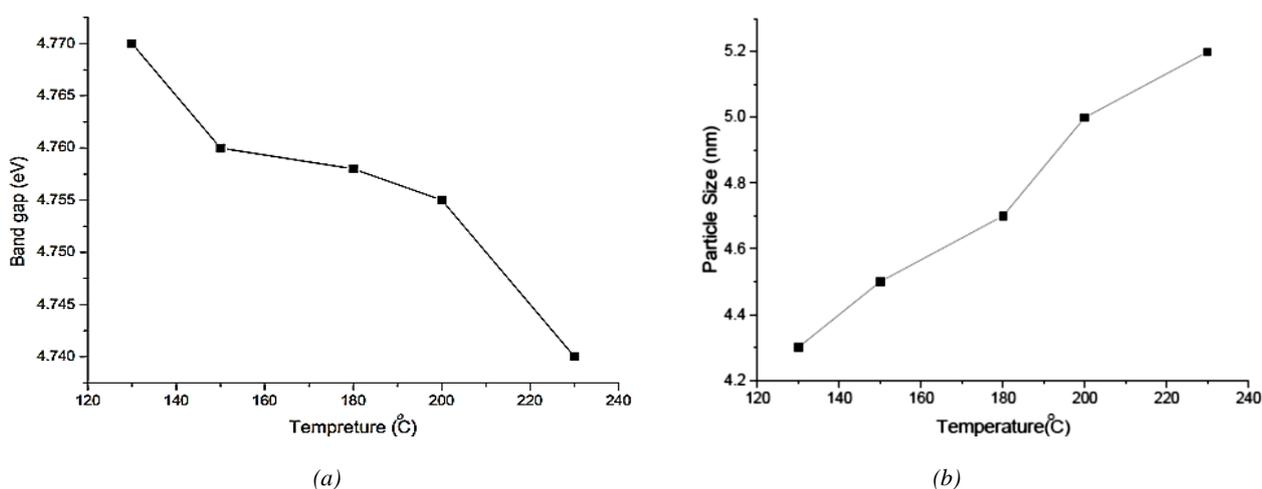


Fig. 7. (a) Band gap versus temperature for CdTe QDs synthesis; (b) Particle size versus temperature for CdTe QDs synthesis

Fig. 7 (a) and (b) in addition to Table 3, reveal the variation of band gap calculated with Brus equation at different temperatures. The band gap variation is not linear with increasing temperature. This is because increasing the

interaction temperature affect the size of QDs (see Fig. 7(b)).

The optical band-gap of CdTe QDs at various TOPO concentrations are represented in Fig 8 and the values are listed in Table 4.

Table 4. Variation in absorption peak, band gap and size for CdTe QDs prepared at different TOPO concentration

TOPO concentration (ml)	Abs (nm)	Band gap (eV)	Size Measure By TEM (nm)
0.8	260.4	4.77	5
1.6	260.7	4.764	4.6
2.4	261	4.758	4.7
3.2	261.2	4.755	4.9
4	261.4	4.75	5.7

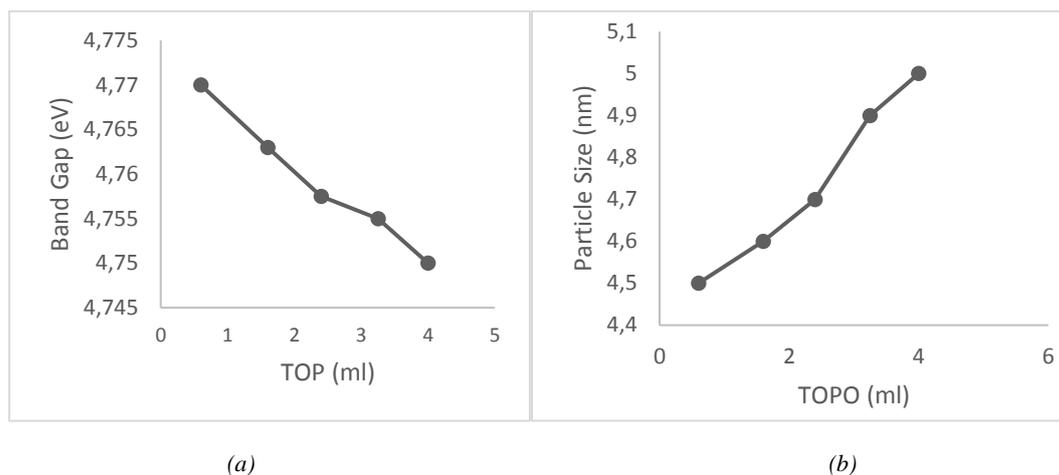


Fig. 8. (a) Band gap versus TOPO concentration for CdTe QDs; (b) Particle size versus TOPO concentration for CdTe QDs

Fig. 8 (a) and (b) in addition to Table 4, reveal the variation of band gap calculated with Brus equation at different TOPO concentrations. The band gap variation is almost linear with increasing TOPO concentrations in this small range which is demonstrated in Fig. 8 (a). This is due to linear increase in the size of QDs with increasing TOPO concentrations (see Fig. 8 (b)).

Absorption spectra of the fabricated CdTe QDs at different reaction time, different temperature and different

TOPO concentrations are depicted in Fig. 9 (a), (b) and (c), respectively. Fig. 9 demonstrates an absorption peak around 261 nm. A shift in the peak and variation in intensities are observed in absorption spectra with changing parameters. Summary of the shift in experimental absorption spectra with changing parameters is given in Table 5.

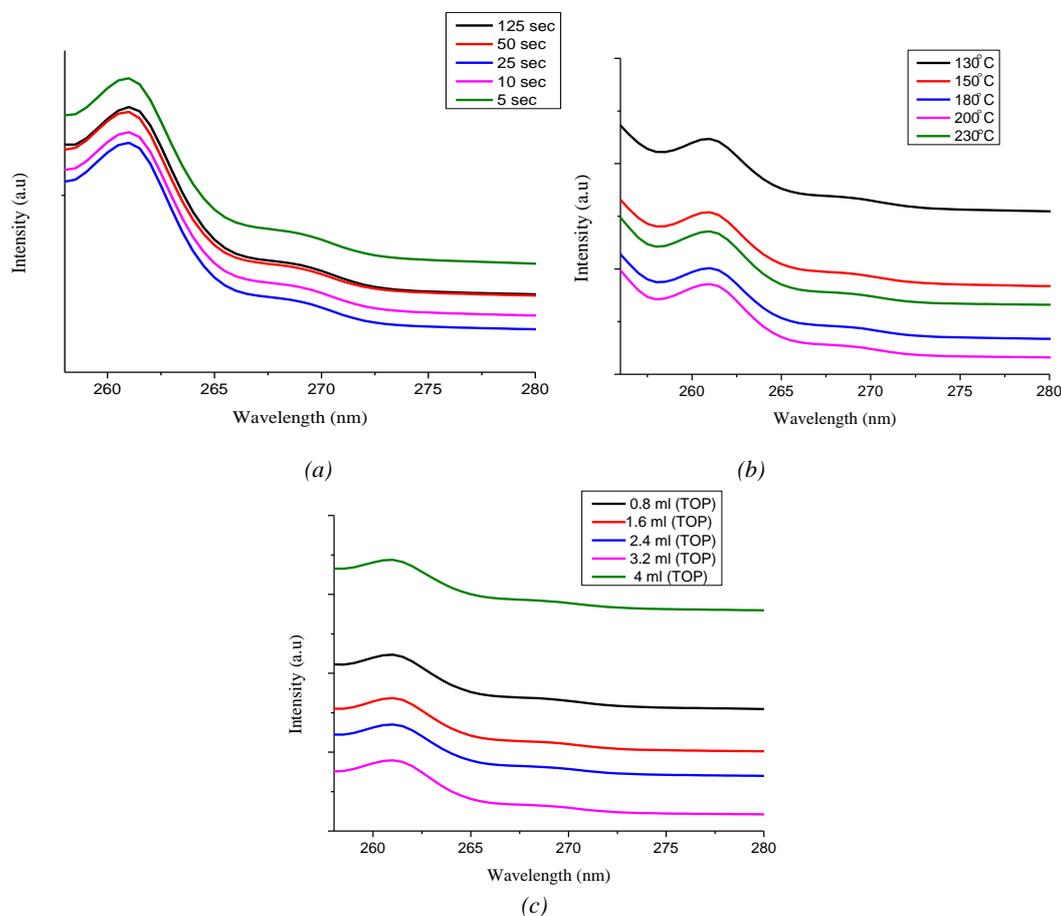


Fig. 9. (a) Absorption of CdTe QDs Prepared at Different Reaction Time; (b) Absorption VS wavelength for CdTe QDs prepared at different temperatures; (c) Absorption VS wavelength for CdTe QDs at different TOPO concentrations

Photoluminescence (PL) spectra of CdTe QDs from 410 to 435 nm excited at 425 nm at different reaction time, different temperature and different TOPO concentrations are depicted in Fig. 10 (a), (b) and (c), respectively. Figures 10 demonstrate PL peak around 422 nm. A shift in

the peak and variation in intensities are observed in PL spectra with changing parameters. The shift is due to change in sizes of QDs. Summary of the shift in peak of PL spectra with changing parameters is given in Table 5.

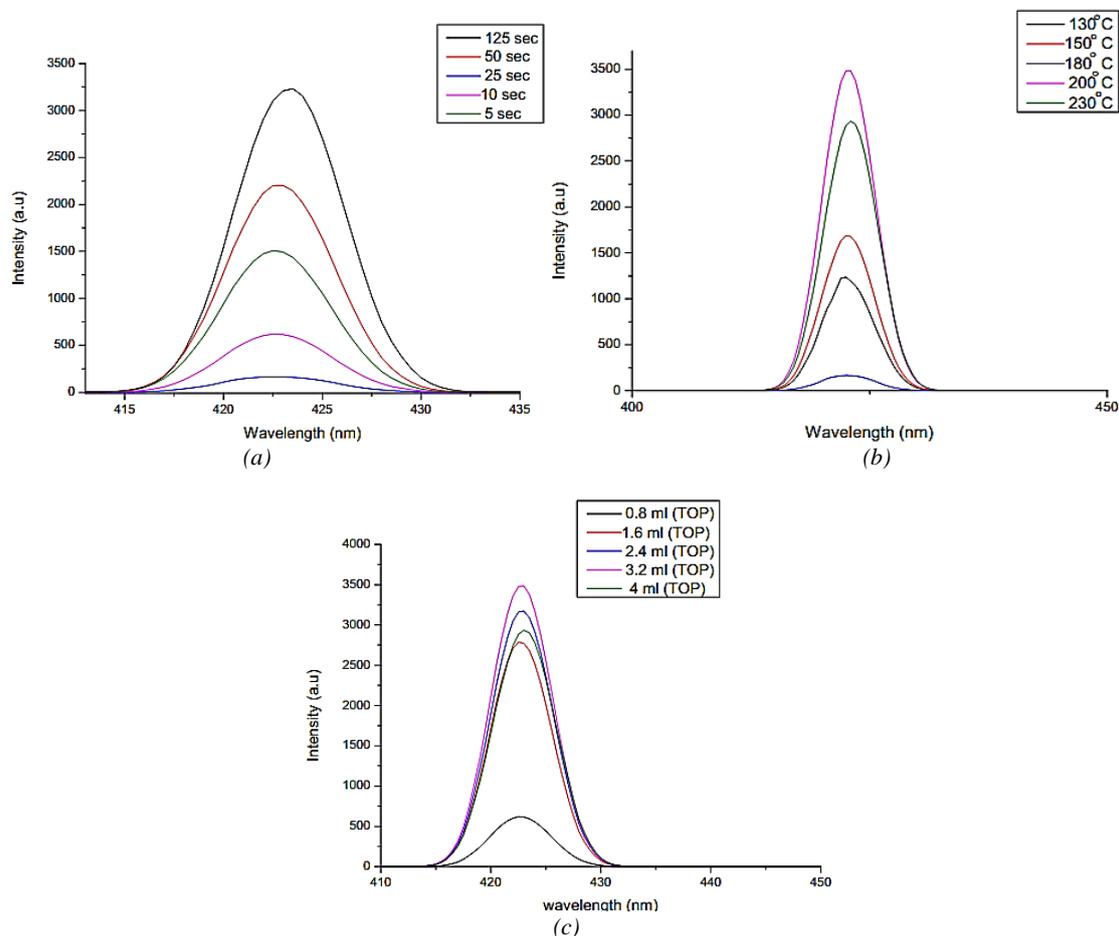


Fig. 10. (a) Photoluminescence of CdTe QDs at different reaction time; (b) Photoluminescence of CdTe QDs at different temperatures; (c) Photoluminescence of CdTe QDs at different TOPO concentrations

Table 5. Summary of shift in absorption and PL peaks with changing parameters

Parameter	Abs	PL	Size (nm)	
Temp (°C)	130	260.5	422.3	4
	150	260.8	422.5	4.5
	180	261	422.7	4.7
	200	261.2	423	5
	230	262	423.3	6
TOP (ml)	0.8 (16%)	260.4	422.2	5
	1.6 (32%)	260.7	422.5	4.6
	2.4 (48%)	261	422.7	4.7
	3.2 (64%)	261.2	422.9	4.9
	4 (80%)	261.4	423.2	5.7
Time (sec)	5	260.7	422.4	4.3
	10	260.9	422.6	4.5
	25	261	422.7	4.7
	50	261.1	422.9	4.9
	125	261.2	423.4	5

Quantum Yield (QY) of a luminescence material is a basic property and its measurement represents an important step in the characterization of the species. The details of QY measurement of luminescence materials in solution can be found elsewhere [25-27]. Different strategies have been investigated to measure QY, depending on whether the fluorophore is in solution or in solid phase. Chemically synthesized nanocrystals can be found in colloidal suspensions, usually with small solution concentrations. To calculate the QY of CdTe QDs in colloidal suspension, the following equation has been used [28], considering Hexane as a reference material;

$$QY = Q_R \frac{I E_R n^2}{I_R E n_R^2} \quad (3)$$

where  $Q_R$  is the quantum yield of the reference (Hexane,  $Q_R=0.83$ ),  $I$  is the integrated fluorescence intensity,  $I_R$  is the integrated fluorescence intensity of

the reference,  $E$  is the extinction coefficient,  $E_R$  is the extinction coefficient of the reference,  $n$  is the refractive index, and  $n_R$  is the refractive index of the reference.

Due to small variation of size of QDs prepared at different reaction time, different temperature and different TOPO concentrations, mean size was calculated in each case to calculate QY. Following formula was used to find standard deviation

$$\sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}} \quad (4)$$

where  $\sigma$  sigma is the symbol for standard deviation,  $X$  represents each individual value of QD size in Table 5,  $\bar{X}$  is the arithmetic mean, and  $n$  symbolizes the number of data points in each case.

Table 6. Statistical data of QD

	Time(s)	Temp( $^{\circ}$ C)	TOPO(ml)
Mean	4.68nm	4.84nm	4.98nm
Standard dev	0.286356	0.74364	0.432435

Using eq. (3), the QY of CdTe QDs prepared at different reaction time, different temperature and different

TOPO concentrations are calculated with mean values from Table 6 and listed in Table 7.

Table 7. Summary of Quantum Yield of CdTe QDs prepared with different parameters

QY at different Reaction times (sec)	QY at different Temperatures ( $^{\circ}$ C)	QY at different TOPO concentration (ml)
0.82786	0.8283	0.828

From the above observed results, it can be inferred that the applied method could be performed to control the size of the produced CdTe QDs to range from 4 – 5 nm approximately, using different parameters. This capability represents a new achievement in comparison with previous results of other groups [1, 29] that produced similar QDs but failed to control their sizes.

#### 4. Conclusions

Quantum dots of CdTe have been synthesized using wet chemical method at different reaction times, different temperatures and different stabilizer (TOPO) concentration to control their size. It has been observed that size of the prepared QDs increases with the increase in these parameters. With this method it is possible to synthesize CdTe QDs with the size suitable for particular optical properties. Due to increase in the size of QDs, variations in absorption peaks, fluorescence peaks and band gaps are observed. Absorption and fluorescence spectra demonstrate that there is a shift in peaks due to

variation in QDs sizes with variations in the above parameters as a result of changes in quantum confinement. QY is calculated using mean values of QDs at different reactions. The obtained results may be applied to control the absorption band width to enhance the efficiency of solar cells.

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