Improved photoluminescence and monodisperse performance of colloidal CdTe quantum dots with Cannula method

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Abstract−Colloidal quantum dots are nano semiconductor materials that have been found in many applications, producing multiple exciton generation, unique optical and electronic properties, adjustable in size and bandwidth. Synthesized QDs are expected to exhibit high photoluminescence quantum yield and monodisperse properties according to their application area. Cannula method was adapted together with the organometallic synthesis method for the first time in the literature to increase the photoluminescence quantum yield of organometallic CdTe QD and minimize the full width at half maximum value of the photoluminescence band. Injection of precursors by the Cannula method is much faster than the injecting with the conventional method of using a glass syringe, which limits the size distribution in the solution during synthesis. In addition, the fastest injection method using Cannula method yields the shortest full width half maximum value of 27.20 nm for CdTe QDs in the literature. The photoluminescence quantum yield value of the CdTe QDs synthesized by the classical method was 8.12±2.1%, while the photoluminescence quantum yield of the CdTe QDs synthesized by the Cannula method was increased to 25.66±2.1%.

Keywords: Quantum Dots, CdTe, PLQY, FWHM, Cannula

INTRODUCTION

Quantum dots (QD) under the effect of quantum confinement, with a size smaller than the Bohr radius, have unique optical and electronic properties [1-4]. QD with distinctive properties such as adjustable size and band gap, multiple exciton generation (MEG) potentials, high photoluminescence (PL) features and cheap availability, enable QDs application and are used in various areas like medical, energy, biology, light emitted diodes (LED) [5-9].

Single-crystal QDs, which exhibit high PL and monodispersion properties, can be easily dispersed in the appropriate solvent, where high quality, dimensional and size distributions can be controlled, very important for QD applications [10]. It is desirable that the photoluminescence quantum yield (PLQY) indicating the extent to which the synthesized QD absorbs photons is as large as possible and that the full width at half maximum (FWHM) value of the PL band showing the size distribution of QDs in solution is as small as possible [11].

The synthesis of colloidal QDs is basically divided into two methods: (ex-situ) organometallic synthesis and (in-situ) water-based colloidal QD synthesis [12]. The method of organometallic synthesis is based on rapid injection, which is carried out in an inert environment at a temperature as high as 300 °C [13]. The QDs synthesized by this method containing chemicals such as trioctylphosphine and trioctylphosphine oxide (TOP-TOPO) have higher PLQY

values and shorter FWHM even though they exhibit toxic properties [13]. On the other hand, water-based QD synthesis method is a long-ligand chemical-free synthesis method, such as TOP-TOPO which does not require high temperature and the synthesized QD is soluble in water [1]. Synthesis processes of water-based QDs are cheaper; however, synthesis times are time consuming and require multiple passivation or treatments [14].

Bulk CdTe materials are the most preferred materials in dye-sensitized solar cells with a −1.45 eV band gap [15], −4.3 eV transmission band energy, and −5.7 eV valence band energies [16], Furthermore, the extinction coefficients at 370 nm are $4.4 \times 104 \, M^{-1} \, cm^{-1}$ [17]. In addition, the CdTe QDs are used in photovoltaic devices [18,19] and biological applications [20,21], and with adjustable band gap between 3.9 and 1.5 eV covering a large part of the solar spectrum [22] are one of the most preferred materials. CdTe QDs, which have great advantages especially in the solar spectrum and in terms of QDs [23] and nanocomposites [24,25], have not reached the expected PCE values in the literature despite these advantages. However, applications with CdTe QDs remain low compared to other different types of QDs [26-28]. The main reasons for this situation are the low PLQY, wide FWHM value and toxic structure of CdTe QDs synthesized [29].

Different chemical synthesis methods and studies have been carried out so that the synthesized CdTe QDs can have high PLQY and narrow FWHM values. Murray et al. [30] used the organometallic method to synthesize CdTe QD, but the FWHM value was not reported in their study for this QD. Talapin et al. [31] synthesized organometallic CdTe QD by modifying the organometallic synthesis method of Murray et al. The FWHM value describing the

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monodispersity feature was not reported again in this study too. Recently, water-based synthesis method has begun to receive more attention for the synthesis of CdTe QD. In 2002 Gaponik et al. [32] realized thiol-coated CdTe QD synthesis in water phase. They showed that the size of CdTe synthesized in the water phase may be much smaller than the size of CdTe QD synthesized organometallic, and the FWHM value of CdTe QDs was calculated within the range of 38-52 nm. In 2004, Li et al. [14] synthesized CdTe QDs with the help of temperature control by microwave radiation. The FWHM value of CdTe QDs synthesized throughout this study showed great variability in the range of 30-85 nm. Li et al. [33] reported that CdTe QD's PLQY changed according to the concentration value of used precursors. When the cadmium (Cd) concentration was 1.25 mM and pH was 8, FWHM was detected as 30-60 nm. Ge et al. [34] synthesized water-based CdTe QD using an electrical precursor, and mercaptoacetic acid (MAA) and N-acetylcysteine (ACYS) stabilization were applied to QDs. For MAA coated CdTe QD and ACYS coated CdTe QD, the lowest FWHM value remained at 40 nm. In 2008, in order to improve the performance of water-based synthesized CdTe QDs, Fang et al. [1] made ligand exchange with dihydrolipoic acid (DHLA) stabilization. FWHM values of the obtained CdTe QDs were found to be 50 nm. Tian et al. [35] coated glutathione and thioglycolic acid (TGA) on water-based synthesized CdTe QDs, whereas they did not test the monodisperse feature for synthesized QDs. Wang et al. [11] synthesized organometallic CdTe QD by modifying the synthesis that Murray had done and determined the FWHM value at a range of 33-50 nm. In 2012, Wang et al. [12] made TGA-coated the water-based CdTe QD synthesized. The one-pot method for synthesis was used as a telluride (Te) source, using Na_2TeO_3 instead of Te salt or Al_2Te. The FWHM value was reduced to 33 nm for water-based CdTe QDs.

In this study, the hot injection method, which was proposed by Murray et al. [30] and modified by Wang et al. [11], was used to synthesize organometallic CdTe QDs. The hot injection method is a chemical synthesis method that is based on the rapid injection of precursors at high temperature. In the hot injection method, glass syringes are used for injection of precursors. However, in the hot injection method, where the temperature and chemical amounts are very sensitive, the glass syringe conflicts with this requirement for sensitivity. Furthermore, the glass syringe prevents the temperature from being maintained at the desired level, and the precursors remaining in the syringe during injection are problematic for this chemical process, which is very sensitive even at minimal level. Therefore, in this study, for the first time in the literature, Cannula method was modified to hot injection method to synthesize organometallic CdTe QDs to overcome this problem. With the Cannula method, the precursors are quickly injected with a steel tube without using a syringe, avoiding the temperature drop and chemical residue. In this way, CdTe QDs synthesized without any surface passivation process achieved a significant increase in PLQY yield, although the FWHM value for the CdTe QD in the literature reached the narrowest value. For comparison, UV-vis spectroscopy, photoluminescence spectroscopy, PLQY, FWHM calculations, XRD and HR-TEM analyses were performed for CdTe QDs synthesized by Cannula method and injection method using syringe. In addition, the duration of the durability in the oxygen environment was investigated by measuring the time-dependent PLQY.

EXPERIMENTAL

1. Materials

Harmane 98%, quinine sulphate, 0.1 M sulphuric acid solution (H_2SO_4), anthracene 99.8%, cadmium oxide powder, (trace metal based (CdO)) 99.5%, tetradecylphosphonic acid (TDPA) 99.0%, tetraethylphosphine 97% (TOP), octadecane 99.9% (ODE), tellurium powder (Te), 99.8%, dry toluene (99.8%) ordered from Sigma-Aldrich were used during experiment.

2. Synthesis of CdTe QD with Organometallic Method

Synthesis method of CdTe QDs in the study was based on the hot injection synthesis method reported by Wang et al. [11]; some modifications were made in the synthesis. First, the Cd-tetradecylphosphonate precursor was prepared. For this, cadmium oxide (CdO) (0.0326 g, 0.40 mmol), TDPA (0.139 g, 0.49 mmol) and octadecane (ODE) (10 ml) were mixed in a three-necked flask. TOP-Te precursors were prepared simultaneously in another three-necked flask. To prepare this precursor, TOP (2.5 ml), ODE (5 ml) and Te (0.066 g)(0.51 mmol) were mixed. Both precursors were heated to 315 °C and 200 °C under nitrogen, respectively. When both precursors were ready, the TOP-Te precursors were removed from the flask using a glass syringe and rapidly injected into the solution at 290 °C where Cd-tetradecylphosphonate precursors were present. With injection, the temperature was stabilized at about 260 °C and CdTe QD growth began. With a clean glass syringe, CdTe QDs were withdrawn from the solution at different reaction times to allow for analysis. Each CdTe QD solution was stored by adding dry toluene at 1 : 2 (v : v) ratio. Before optical and surface analysis of the synthesized CdTe QDs, the CdTe solution was washed four times by volume of methanol (1 : 4 (v : v)) and centrifuged to remove any unreacted excess chemicals from the solution. The liquid portions were discarded and the residue was dissolved in dry toluene and made ready for use.

When the Cd precursors were clear and ready at 290 °C in the hot injection method, a clear TOP-Te solution was prepared at 200 °C in the other three-necked flask. In conventional applications of the hot injection method, the injection of the precursors is carried out by means of a glass syringe. The use of a glass syringe in the injection of the first leads to partial cooling in the TOP-Te solutions at 200 °C. To determine the temperature drop occurring during injection by glass syringe, a decrease of about 17 °C was detected in 10 trials. To eliminate this temperature drop, experiments were carried out by increasing the glass syringe to 200 °C before being used to remove the TOP-Te solution. However, although the difficulty of use was removed, it had the risk of burning of the synthesizer.

One of the most sensitive points of the hot injection method can minimize the contact of the precursors with oxygen. However, the use of glass syringes is inevitable when the precursors come into contact with oxygen.

Another problem with the use of glass syringes during injection is the repeatability of the synthesis. The fact that the entire precursor cannot be withdrawn from the three-necked balloon or the partial chemical loss in the glass syringe causes problems in the repro-

ducibility of the synthesis process. The results of the study to determine this situation are given in "3.3. PLQY Analysis" section.

3. Synthesis of CdTe QD with Cannula Method

The use of glass syringes in the rapid injection of precursors has problems, such as sudden temperature decrease, chemical losses in the transfer of precursors, contact with oxygen. To remove these problems, the Cannula method was modified to the classical method of organometallic synthesis [36-38]. Uniquely to this work, the Cannula method was modified to the organometallic synthesis method to remove the problems that the use of the syringe had become apparent. In the Cannula method, Cd-tetradecylphosphonate and TOP-Te precursors were prepared as described in the previous section (see section 2.2). When the precursors were ready (clear, 290 °C-200 °C), a negative pressure was applied to the flask containing the Cd-tetradecylphosphonate precursor with a vacuum pump. Based on Pascal's law [39], the TOP-Te solution was injected through steel tube of 2 mm inner diameter very quickly into the Cd-tetradecylphosphonate precursors to stabilize the pressure in the second balloon of the TOP-Te precursor. A schematic diagram
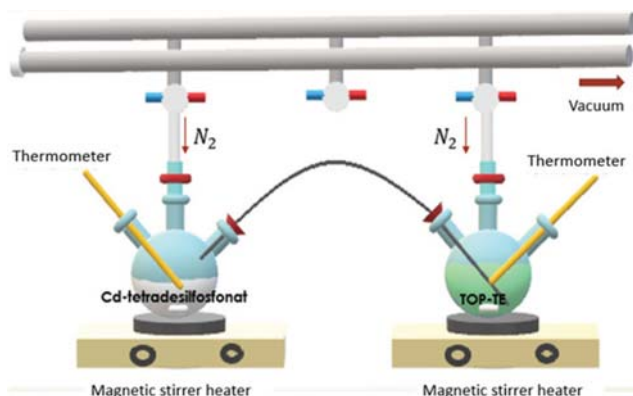

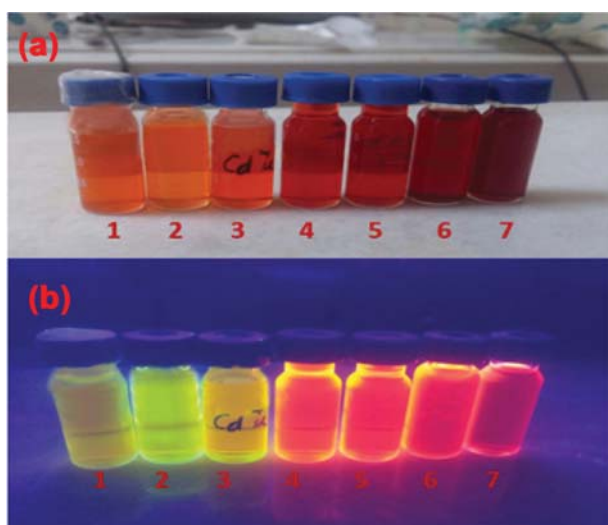**Fig. 1. Diagram of the setup for the Cannula method.**

Fig. 2. Images of CdTe QD/toluene blends having different reaction times (dimensions) synthesized by the classical method; (a) views under daylight, (b) views under fluorescence light (1-7 periods show reaction times of 30 s and 6 min).

of the setup for the Cannula method is shown in Fig. 1. CdTe QDs with different reaction times were withdrawn from the solution and stored for analysis by adding toluene at 1 : 2 (v : v) ratio. Similarly, the synthesized CdTe QDs were dissolved in methanol and re-dissolved in dry toluene for analysis.

Images of CdTe QDs with different growth reactions under daylight and under fluorescent light are shown in Fig. 2.

4. Characterization of CdTe QD

Absorbance measurements for the optical characterization of CdTe QDs synthesized by the organometallic synthesis method (classical method) and the Cannula method were performed with a Shimadzu UV-1800 UV-Vis Spectrophotometer. Emission measurements were made using Model TM-2/2005 Lifetime Spectrophotometer. FWHM values were calculated by emission spectroscopy results with the aid of ORIGIN PRO8. For the HR-TEM analysis of CdTe QDs, JEOL brand JEM 2100F model transient electron microscope with FEG electron gun and 80-200 kV accelerating voltage was used. XRD studies were performed on the Rigaku Ultima-IV X-Ray diffraction device to determine the crystal structure of the QDs.

5. PLQY Measurement

A comparative PLQY analysis method was used for the PLQY measurement [40]. Two different standards were used to achieve more accurate results in PLQY measurements (Harmane in 0.1 M H_2SO_4 (PLQY 83% [41]), Quinine bisulphate, in 0.1 M H_2SO_4 (PLQY 54% [41])). Comparison PLQY calculation was made with Eq. (1).

$$PLQY(X) = PLQY(ST)\frac{F_x f_{st}(\lambda_{ex})}{F_{st} f_x(\lambda_{ex})} \cdot \frac{n_x^2}{n_{st}^2} \qquad (1)$$

In this equation, the X symbol PLQY value refers to the desired CdTe QD, while ST refers to the standard material parameters. n_x is the solvent refractive index required to be calculated PLQY sample, and n_{st} is the solvent refractive index of the standard sample. F, shows the areas calculated by the integral of emission peaks, $f_x(\lambda_{ex})$ indicates the concentration values.

To reduce the error rate in the PLQY calculation, five replicate PLQY analyses were made with standard materials and the error rate was reduced to 2.1%.

6. Duration of CdTe QDs in Oxygen Environment

The organometallic Cd-based QDs have high oxidation properties due to long unbound ligands on their surface. This causes the PLQY to fall rapidly if the QDs come into contact with oxygen [29]. The duration of the CdTe QDs synthesized by classic organometallic and Cannula method was tested by emission spectroscopy and PLQY calculation. QDs were left in the oxygen environment and measurements were made at specific time periods and tested to see if the Cannula method could provide a positive improvement in the oxidation progress.

RESULTS AND DISCUSSION

1. Absorbance Analysis

The absorption spectrum provides direct access to the electronic levels of the materials and shows absorption transitions by absorbing a certain amount of energy at each level [42]. That is, the wave-
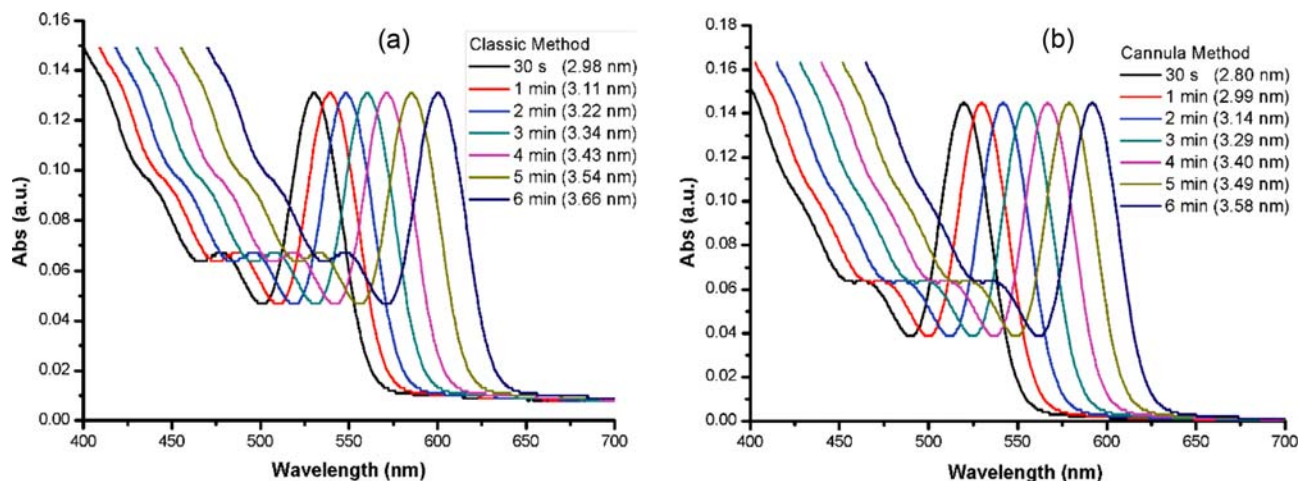
Fig. 3. Absorbance results of CdTe QDs with different reaction times synthesized by, (a) classical organometallic method, (b) Cannula method.

length corresponding to any transition represents the position of the energy state in the material. The steady-state absorption spectroscopy of QDs has the lowest absorption capacity, corresponding to a decreasing band gap as the size of the QDs increases [43]. As a consequence of limiting the QD structure of carriers in three dimensions, the absorption characteristic shows an excitonic absorption transition [44].

According to the results of UV-vis spectroscopy of the organometallic CdTe QD synthesized by the classical method, CdTe QDs with 30 s reaction time gave absorbance peak at 530 nm and CdTe QDs with 6 min reaction time gave a peak at 602 nm. Similarly, the results of UV-vis spectroscopy of CdTe QDs synthesized by the Cannula method with the same reaction time by the classical synthesis method showed that they were smaller. CdTe QDs synthesized by Cannula method and having a reaction time of 30 s gave a peak at 521 nm and CdTe QD with 6 min reaction time gave a peak at 591 nm. The results showed that the rapid injection by Cannula method prevents the accumulation of CdTe QDs in the growth process and enables the expression of smaller CdTe QDs. This result indicates that CdTe QDs were grown more stably by faster injection of the TOP-Te precursor. The rapid injection process, which was carried out with the Cannula method, provided simultaneous initiation of the growth reaction in the solution for all precursors and the size distribution became more consistent. The absorbance results of CdTe QDs with different reaction times with both methods are shown in Fig. 3.

Absorbance results showed that the increasing in synthesis time enhanced the size of CdTe QDs. This situation is similar to the studies in the literature [45-47]. Such an increase in the synthesis time leads to an increase in the size of the CdTe QD. The size of the CdTe QDs was calculated using the absorbance peak values obtained from the results of UV-vis spectroscopy and with Eq. (2) [45].

$$D=(9.8127\times10^{-7})\lambda^3-(1.7147\times10^{-3})\lambda^2+(1.0064)\lambda-194.84 \qquad (2)$$

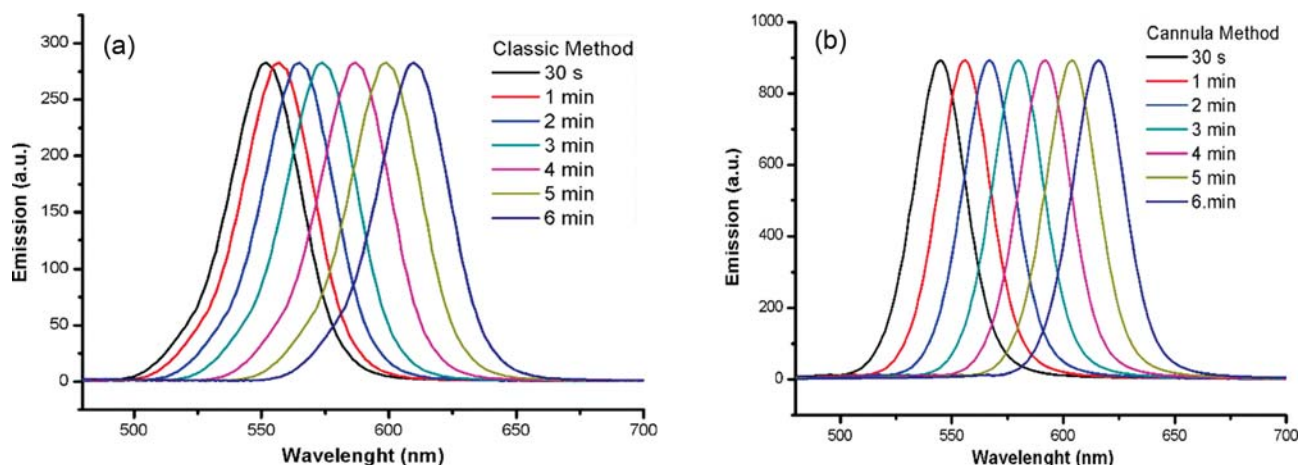In Eq. (2), D is the size of the CdTe QD (nm), λ (nm) is the absor-

Fig. 4. Emission results of CdTe QDs with different growth reactions by (a) classical organometallic method, (b) CdTe QD with different reactions times by Cannula method.

bance peak of the CdTe QD obtained from the UV-vis spectroscopy.

2. Emission Analysis

The photoluminescence in QD is produced by excitation recombination of randomly polarized excited electrons and hole pairs after excitation of the semiconductor by absorbed photons [48,49]. In contrast to absorption in PL spectroscopy, the intensity of light emitted from the sample as a function of the wavelength is measured. The PL line width allows measurement of the width of the radiation frequency band emitted or absorbed in an atomic or molecular pass to reach the width distribution of the materials; line width is an indication of the large size distribution.

Emission values of CdTe QD synthesized by Cannula method and classical method were analyzed by PL spectroscopy at different reaction times and are shown in Fig. 4(a) and Fig. 4(b). CdTe QDs synthesized by classical method with 30 s reaction time gave PL peak at 554 nm, whereas CdTe QDs with 30 s reaction time synthesized by Cannula method gave PL peaks at 547 nm. The CdTe QDs synthesized by the Cannula method had 7 nm blue shift. It is believed that the reason for this blue shift is due to the synthesis of CdTe QDs with smaller size and higher PL characteristics.

The difference between the absorbance and emission results of the CdTe QD is called the stoke shift [50], while the FWHM value of the emission peak is the monodisperse ability of the QDs [51]. FWHM values were calculated with ORIGIN PRO8. Figs. 5(a) and 5(b) show stoke shift and FWHM values for CdTe QDs synthesized by classical and Cannula method, respectively, with reaction time of 30 s. The stoke shift for the CdTe QDs synthesized by the classical method was 21 nm while the FWHM value was 33 nm. On the other hand, for CdTe QD synthesized by Cannula method, the stoke shift was 5 nm larger than the classical method and it was 26 nm. The FWHM value by Cannula method was narrowed to 27.2 nm. The 27.2 nm FWHM value of CdTe QDs synthesized by the Cannula method is narrower than the FWHM value of CdTe QDs synthesized by different methods and treated CdTe QDs, even the narrowest FWHM in the literature for CdTe QDs [32-34]. This result proves CdTe QDs synthesized by Cannula method are the highest monodispersity CdTe QDs in the literature. Moreover, the contact with oxygen was reduced to zero
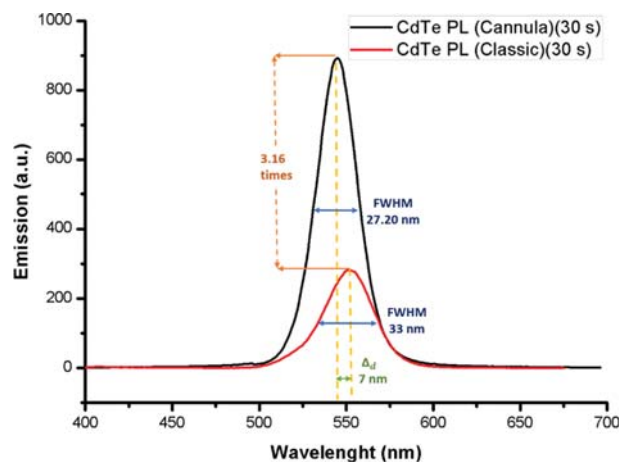

Fig. 6. Comparison of emission spectroscopy results of CdTe QDs with 30 s reaction time synthesized by Cannula and classical method.

and the injection was performed at a much faster rate. The monodisperse feature for QDs is especially important for QLED applications. It is important to obtain light at the desired wavelength to provide a color scale [52,53].

The emission peaks of CdTe QDs with 30 s reaction time synthesized by Cannula and the classical method prepared at same concentration are shown in Fig. 6. The CdTe QD synthesized by the Cannula method exhibited 7 nm blue shift, 27.2 nm FWHM, and its PL peak length was 3.16-times larger than the CdTe QD synthesized by the classical method. As a result, CdTe QDs synthesized by Cannula method had higher PL, higher monodisperse characteristics. On the other hand, as the size of the CdTe QDs synthesized by both methods increased, the FWHM values also increased. So, for CdTe QDs with 2 min, 4 min and 6 min reaction time synthesized by classical method, FWHM values were increased up to 36.12 nm, 40.01 nm and 41.17 nm, respectively. However, for CdTe QDs synthesized by Cannula method, FWHM value was determined as 28.16 nm, 29.58 nm and 31.97 nm, respectively, at 2 min, 4 min and 6 min reaction times.
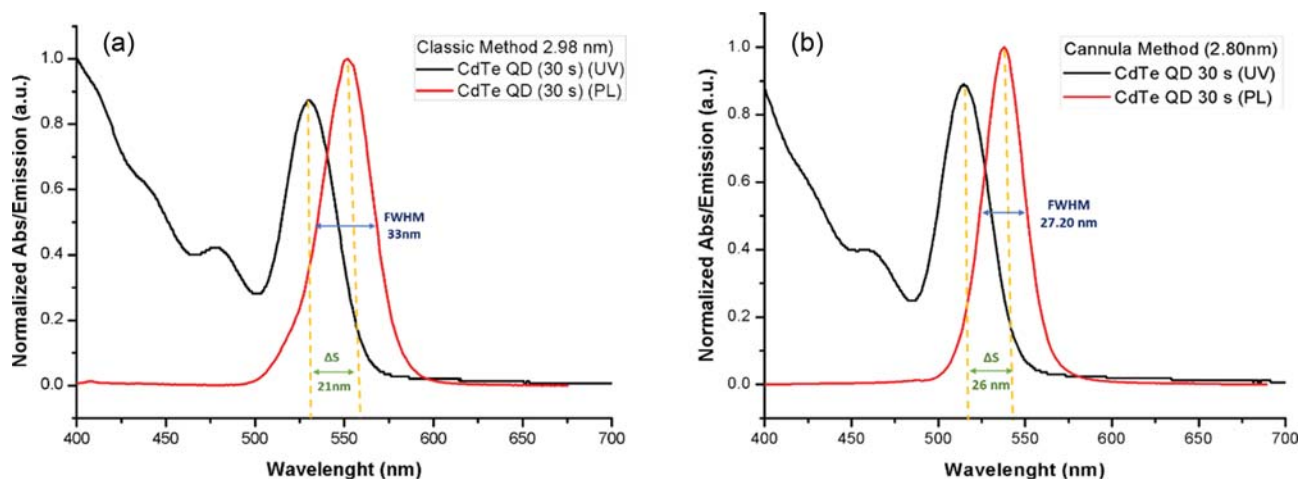

Fig. 5. Stoke shift and FWHM values for CdTe QDs with same reaction times by (a) classical organometallic method, (b) Cannula method.
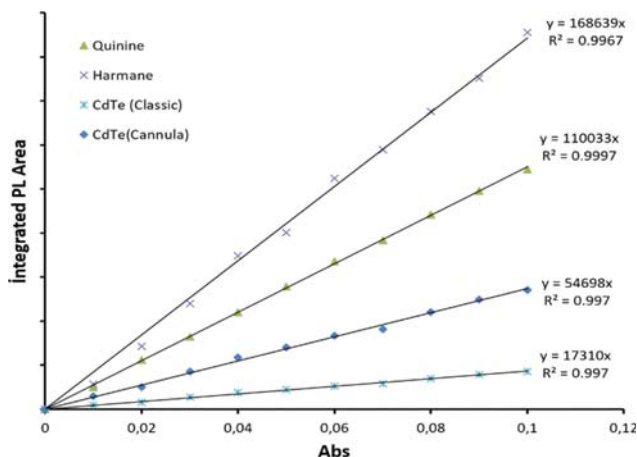
Fig. 7. Diagram of area under PL peaks versus different absorbance values of reference materials and synthesized QDs.

3. PLQY Analysis

The PLQY, which is an indicator of how much of the photons absorbed by the synthesized CdTe QDs can be emitted, was made by comparative method in this study [31]. Two different standards (Harmane in 0.1 M H_2SO_4, quinine bisulphate, in 0.1 M H_2SO_4) were used to obtain more accurate results in PLQY. For the PLQY account, first ten stock solutions of absorbance values ranging from 0.01 to 0.1 were prepared by UV-vis spectroscopy. The prepared stock solutions were tested in PL spectroscopy and the areas under PL peaks were integrated. Then, a graph of the calculated areas corresponding to the absorbance value was drawn and a linear line fitting was performed [31]. A sample plot of the PLQY account in this study is shown in Fig. 7. Then the curves of the lines were taken and the PLQY value of the QDs were calculated with the Eq. (1).

The PLQY value of CdTe QDs synthesized by the Cannula method was increased to 25.66±2.1% without any stabilization process on the CdTe QD surface, while 8.12±2.1% PLQY were obtained for the CdTe QD synthesized by the classical method.

PLQY analysis was performed with ten repetitions, CdTe QD synthesized by Cannula and classical method at different times to test the repeatability of the synthesis. The highest PLQY value obtained in the classical method was 8.12±2.1%. The PLQY values of the CdTe QD synthesized by the classical method over ten different times were calculated and shown in Fig. 8(a). Half of the ten repetition PLQY could be obtained at the level of 8±2.1%. In the Cannula method PLQY values of ten different syntheses showed 70% repeatability. As such, the PLQY value of seven out of ten syntheses was at 25±2.1%, while the lowest CdTe QD PLQY value remained at 18±2.1%. The PLQY distributions of CdTe QDs synthesized by the Cannula method are shown in Fig. 8(b). The results show that the highest PLQY obtained by the Cannula method is 25.66±2.1% and it is three-times of the classical method. It is thought that the rapid injection CdTe QD applied as a reason for PLQY increase was more crystallized and partly reduced in surface traps. Extra temperature drop from the syringe method was not experienced by Cannula method. This made the nucleation growth reaction faster and resulted in a more homogeneous QD size distribution in solution and increased PLQY.

4. Resistance of Oxygen

The CdTe QDs synthesized by both methods were selected to have a 2 min reaction time and left in the oxygen atmosphere. To determine the oxidation times of the QDs, emission spectroscopies were taken with specific periods and the results obtained are given in Fig. 9.

The emission peaks of the CdTe QDs synthesized by the classical method were reduced to the minimum level after 12 hours, while the QDs synthesized by the Cannula method decreased to the minimum level at 24 hours. These results show that CdTe QDs are suitable for oxidation and as expected [54] the rate of decline differs. After 4 hours in the presence of oxygen, the PL intensity of the CdTe QD synthesized by the classical method was reduced by 47.42%, while the decrease of CdTe QD synthesized by the Cannula method was 43.85%. The reduction in emission peak intensity of the QDs synthesized by the Cannula method gave 4% better results, but sufficient data on the increase in the duration of oxidation resistance was not obtained. The ligands suitable for long sagging and ligating were similar in both synthesis methods [29].
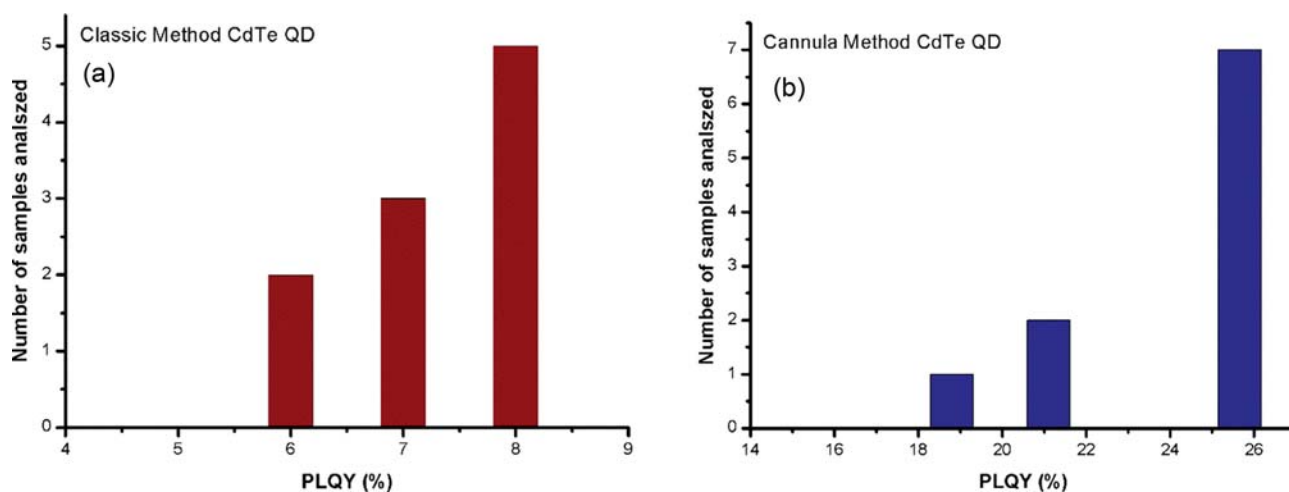

Fig. 8. PLQY distributions of CdTe QDs synthesized at different reaction times; (a) the classical method, (b) the Cannula method.
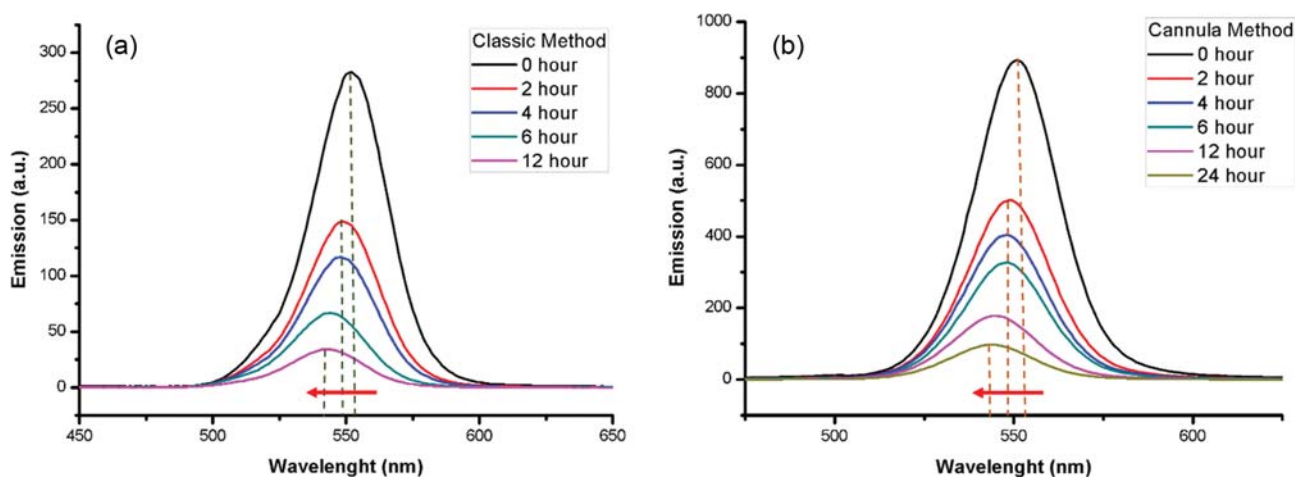
Fig. 9. Time-dependent emission spectroscopy results of CdTe QDs deposited in an oxygen environment; (a) the classical method, (b) the Cannula method.
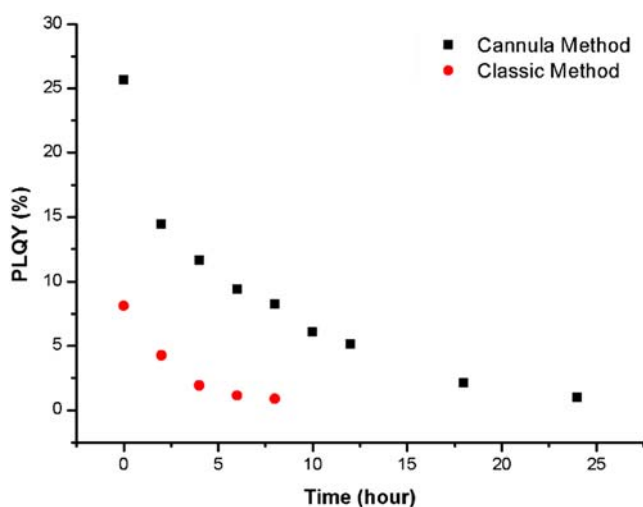

Fig. 10. Time-dependent change of PLQY in oxygen medium for CdTe QDs with 2 min reaction time synthesized by Cannula and classical method.

CdTe QDs were released with oxygen and PLQY measurements were made at different time intervals. The results obtained in the study are given in Fig. 10. The PLQY value of the CdTe QDs synthesized by the classical method decreased to 8.12±2.1% at 0.8 hours and decreased to 0.88% at 8 hours and the analysis was terminated. The PLQY value of 25.66% of CdTe QDs synthesized by Cannula method decreased to 5.13% at 12 hours and 0.69% at 24 hours. These results are similar to the time-dependent results in emission peak intensity but cannot be mentioned without a clear improvement. The QDs synthesized via the Cannula method had a higher PLQY, with the PLQY extending the duration of minimization, but showed no improvement over time-dependent reduction rates.

5. HR-TEM and XRD

HR-TEM analysis was performed for CdTe QDs synthesized by both methods and having a reaction time of 2 min (Fig. 11). It is seen that the results of the synthesized CdTe QDs were consistent when the theoretically calculated sizes with Eq. (2) were compared with the HR-TEM. The CdTe QDs were synthesized by the
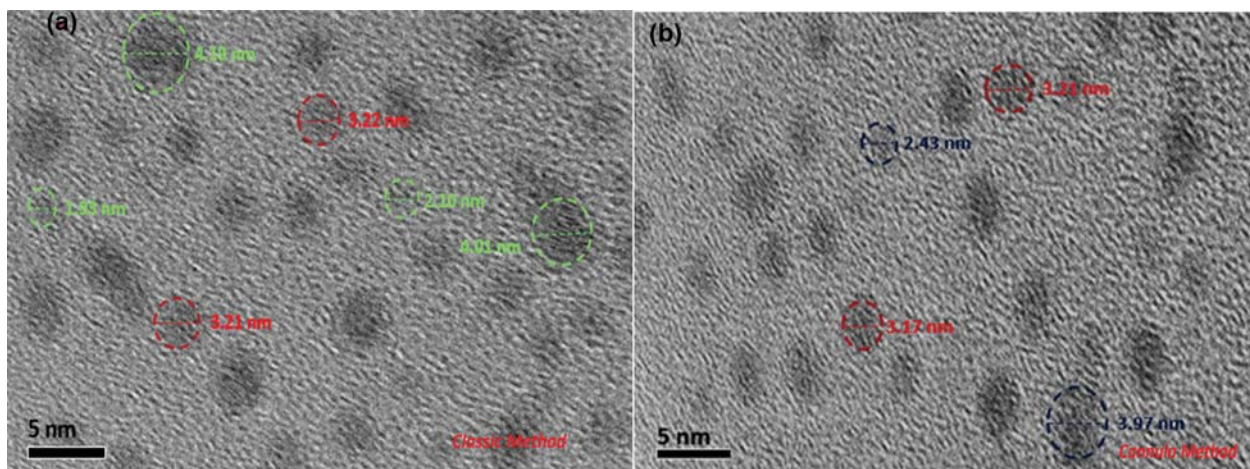

Fig. 11. HR-TEM images CdTe QD with (a) classical synthesis method, (b) Cannula synthesis method.
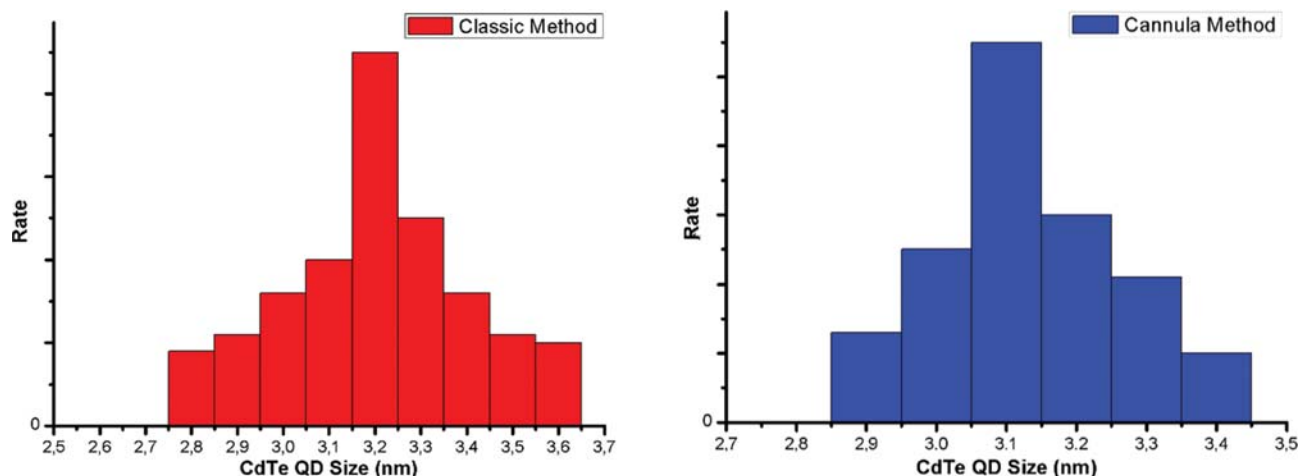
Fig. 12. Size distribution for CdTe QDs synthesized by both methods.

Cannula method, which have the same reaction time and are smaller by 0.1-0.2 nm than the CdTe QDs synthesized by the classical method.

The size distributions described above are shown more clearly in Fig. 12. Here, it is seen that the size distribution in the CdTe QD solution synthesized by Cannula method is in a narrower range than the CdTe QD solution synthesized by the classical method. In the Cannula method, the faster the injection process, the better it is in reducing the size distribution. Size distribution

Fig. 13. XRD results of CdTe QD synthesized by (a) classical and (b) Cannula method.

graphs are plotted and normalized, and the proportions below a certain range are subtracted from the graph to make it clearer.

The XRD results for CdTe QDs synthesized by the classical and Cannula method are given below by Fig. 13. These results are consistent with the CdTe QD XRD results in the literature [14,29,55]. When the XRD patterns of CdTe QDs synthesized by the Cannula method and classical method were examined, it was determined that three different peaks occurred in CdTe QDs synthesized by both methods. The diffraction peaks observed for the CdTe QDs synthesized by the Cannula method were determined at 24.1, 39.1, 47.5, respectively, based on the 2 theta. However, in the diffraction peaks of CdTe QDs synthesized by the classical method, shifts in the 0.1-0.2 range occurred according to the diffraction peaks of CdTe QDs synthesized by Cannula method. As a matter of fact, diffraction peaks depending on 2 theta were observed at 24.2, 39.5 and 47.8, respectively. It was determined that CdTe QDs synthesized in both methods matched the crystal structure of cubic zinc blend in bulk CdTe structure (<111>, <220>, <311>) [56]. When XRD diffraction models were compared, the diffraction peaks for the CdTe QDs synthesized by Cannula method were larger than the FWHM value. This is in agreement with the Scherrer equation [57], which indicates that the synthesized CdTe QDs have a smaller mean size.

Table 1 compares the PLQY and FWHM values obtained in this study with some studies in the literature. Although the number of studies in which both parameters were investigated is rather limited, research with the majority is usually based on water-based CdTe synthesis. Page et al. used the organometallic method for the synthesis of CdTe QDs and obtained 33 nm FWHM. The PLQY of the synthesized CdTe QDs varied between 5-12%. In contrast, the PLQY value was increased to 97% by the $CdCl_2$ ligand exchange. However, the FWHM value was up to 44 nm [29]. Most of the studies carried out stabilization and ligand exchange procedures and an increase in PLQY [58-63]. In these studies, passivation and different types of treatments were applied to increase the PLQY of CdTe QDs synthesized. However, FWHM values of the synthesized CdTe QDs remained in a wide range. In this study using Cannula method, PLQY was increased from 8.12±2.1% to 25.66±
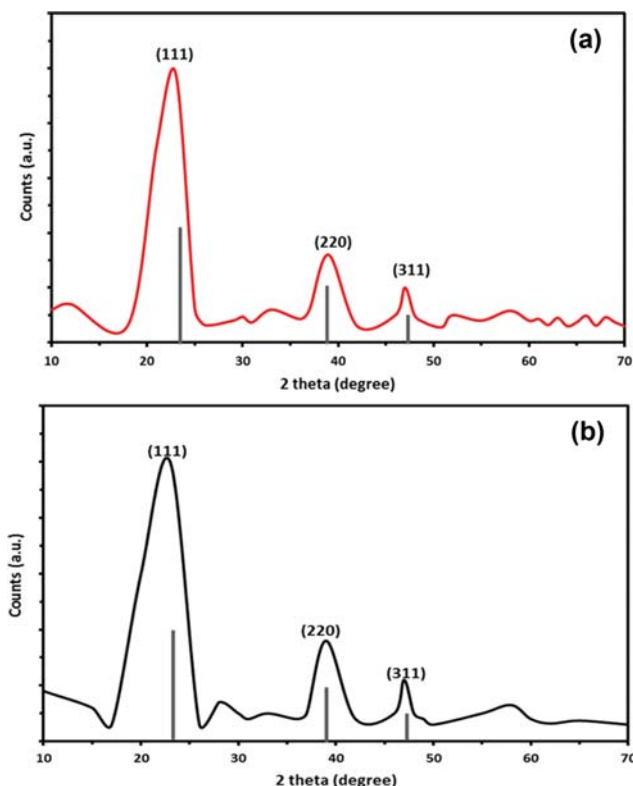
Table 1. The list of PLQY and FWHM of Synthesised CdTe in literature

Type	Synthesis method	Stabilization	PLQY (%)	FWHM	Ref.
In-situ	Electrochemical synthesis	-	36	-	[13]
In-situ	Aqueous synthesis	-	-	35 nm	[63]
In-situ	Hydrothermal synthesis	-	27.4	40-80 nm	[14]
In-situ	Electrogenerated precursors	MMA, ACYS Capping	68	44 nm	[34]
In-situ	Aqueous-PH controlled	MPA capping	40-67	30-60 nm	[33]
In-situ	One pot synthesis	TGA capping	63	-	[35]
In-situ	Aqueous Synthesis	DHLA capping	42	50 nm	[1]
In-situ	Aqueous Synthesis	Thiol capping	40	38-52 nm	[32]
In-situ	Aqueous Synthesis	TGA capping	28	33-45 nm	[12]
Ex-situ	Organometallic	-	5-12	33 nm	[29]
Ex-situ	Organometallic	CdCl₂	97	45 nm	[29]
In-situ	Hydrothermal synthesis	TGA capping	22	35.8	[22]
In-situ	Microwave heating	Thiol capping	60	39-76 nm	[58]
In-situ	One pot synthesis	Cystine		40-70 nm	[59]
In-situ	Aqueous Synthesis	5-HSCH₂Tz	60		[60]
In-situ	Aqueous Synthesis	Thiol capping	40-60	39 nm	[61]
In-situ	Aqueous Synthesis	L-cysteine capped	-	33-59 nm	[62]
Ex-situ	**Organometallic**	**-**	**8.12**	**35 nm**	**This study**
Ex-situ	**Organometallic, Cannula**	**-**	**25.66**	**27.2 nm**	**This study**

2.1% by changing only the injection method without any stabilization, treatment or ligand exchange process. Also, as clearly seen in Table 1, CdTe QDs synthesized by the Cannula method have the narrowest PL emission peak with 27.2 nm FWHM. It is believed that this is caused by the fast injection process. In the Cannula method, reduction of contact with oxygen, the injection of the precursor in the planned amount, the rapid injection process, exhibited high monodispersity and high PLQY oat synthesized CdTe QDs.

CONCLUSION

This study focused on the synthesis of the colloidal organometallic CdTe QD and the improvement of the synthesis phase. For the first time in the literature, organometallic CdTe QD was synthesized by Cannula method. One of the most important criteria of the hot injection method is to inject the precursors as quickly as possible. The Cannula method used in this study enables the injection process to be performed faster than the classical method, and it also reduces the interaction with oxygen in synthesis. The use of the Cannula method affects the size distribution in the QD solution positively. CdTe QDs with a FWHM value of 27.2 nm, showing the highest monodisperse feature in the literature, have been synthesized. The injection process is very rapid, allowing the CdTe QD to be better crystallized, and the PLQY ratio increased by 3.16 times to 25.66±2.1% without any need for surface stabilization. Although the method employed achieved a 4% improvement in the time-dependent reduction of emissions and PLQY ratios due to oxidation in the oxygen environment of the CdTe QD, insufficient data were obtained to demonstrate that more durable QDs are synthesized. These results are promising for future studies about quantum dot-sensitized solar cells (QDSSCs) and QLED.

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