



Original Research Article

Study of Optical and Structural Properties of CdTe Quantum Dots Capped with 3MPA Using Hydrothermal Method

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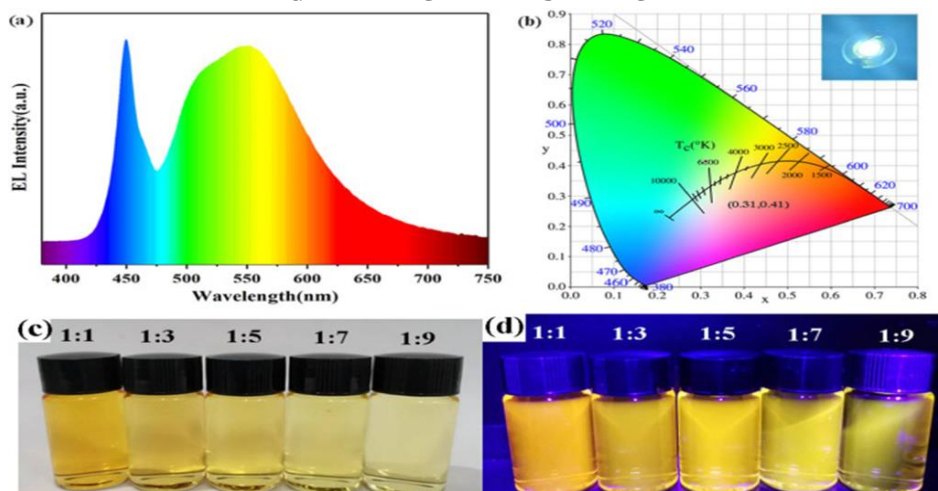
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ABSTRACT

Quantum dots (QDs) can be defined as nanoparticles (NPs) in which the movement of charge carriers is restricted in all directions. CdTe QDs are one of the most important semiconducting crystals among other various types where it has a direct energy gap of about 1.53 eV. The aim of this study is to examine the optical and structural properties of the 3MPA capped CdTe QDs. The preparation method was based on the work of Ncapayi *et al.* for preparing 3MPA CdTe QDs, and then, the same way was treated as by Ahmed *et al.* via hydrothermal method by using an autoclave at the same temperature but at a different reaction time. The direct optical energy gap of CdTe QDs is between 2.29 eV and 2.50 eV. The FTIR results confirmed the covalent bonding between the 3 MPA ligands and the QDs surface. The XRD results revealed that the synthesized QDs have two crystal structures, wurtzite and cubic zinc blend. FESEM results confirmed that the NPs have a spherical shape with an average diameter of nearly 33.85 nm. TEM analysis confirmed the particle's near sphericity, with an average diameter of around 49.33 nm. The sudden increase in temperature led to increase the particle size. It was found that ligand addition, maintaining the solution's acidity, and autoclaving the material enhanced quantum confinement.

GRAPHICAL ABSTRACT



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Introduction

Quantum dots (QDs) or zero-dimensional nanocrystalline semiconductors can be defined as nanoparticles (NPs) materials in which the movement of charge carriers is restricted in all directions [1]. These effects are known as quantum confinement. Therefore, nanocrystals under the quantum confinement effect are called QDs [2]. These effects are seen when the nanomaterials (NMs) dimensions become close to or less than the Bohr exciton radius (0.529 \AA). It is possible to manipulate the properties of the material through quantitative constraints to obtain the best optical and structural properties [3, 4]. Thus, applications based on these materials are highly efficient compared with applications based on the ordinary NMs and bulk materials [5-7]. Quantum dot sizes for semiconducting NMs play an important role in determining optical properties such as absorbance and transmittance, and thus determining the range of optical energy gap and help determine the appropriate application type [1, 2].

Cadmium telluride (CdTe) QDs is one of the most important semiconducting crystals among various other types where it has a direct energy gap of about 1.53 eV. Hence, CdTe has been widely used in light-emitting devices, photovoltaics, and biosensors in biomedical and other applications [8-10].

Colloidal NMs synthesis is one of the most widely used methods for preparing QDs [11]. There are two methods of colloid synthesis, the first being synthesis by using aqueous solvents (aqueous synthesis) and the second by using non-aqueous solvents (organometallic). Hydro-synthesis is used to prepare CdTe due to its low cost, environmental friendliness (compatible with biological environments, i.e. non-toxic), and ease of adjusting the energy gap values [10, 11]. In both preparation processes, surface ligands form complex bonds with Cd^+ ions by using groups of either polar hydrocarbon chains or charges. By the ligands presence on the NPs surfaces, they have stability against aggregations when adsorption or desorption occurs because they act as insulators between other NPs [12].

This research goal is to prepare CdTe simply and inexpensively in a single vessel at pH 12. Cadmium acetate dihydrate ($\text{Cd}(\text{Ac}_2)\cdot 2\text{H}_2\text{O}$) was used as a source of Cd. It was coated with 3-mercaptopropionic acid (3MPA) as a ligand to pave the atoms with a Te source from potassium tellurite (KeTeO_3), and also sodium brohydrate (NaBH_4) for rapid reduction of Te to Te^{-2} and preventing its diffusion.

This research initially aimed to study the optical properties of 3MPA capped CdTe QDs at pH 12 prepared by using an autoclave at $200 \text{ }^\circ\text{C}$ for 100 hours, and then the best optical properties are selected to study the NMs structural properties.

Materials and methods

The used materials were as follow: $\text{Cd}(\text{Ac}_2)\cdot 2\text{H}_2\text{O}$ (95%) (From Germany, Merck KGaA), KeTeO_3 (95%) (From India), sodium hydroxide (NaOH) (from India), NaBH_4 (95%) (From India, Alpha Chemika), 3-mercaptopropionic acid (3-MPA) (99%) (From Sigma Aldrich), and deionized water. All materials were used without purification.

Tools

Beaker 100 mL, three-neck flask 250 mL, macrodropper 1.5 mL, hot plat with a stirrer, magnetic bar, condenser, rubber stoppers, goedkope pH meter, tube centrifuge 5 mL, thermometer, and glass 7.5 cm as a substrate.

Equipment devices used for characterizations

The UV-Vis spectra of CdTe QDs capped with 3MPA were characterized by using Shimadzu model UV-160A in wavelength from (190-1200 nm) (the Netherlands). The PL spectra were characterized by using VARIAN/ECLIPSE CARY spectrometer (the Netherlands). The FT-IR was characterized by the device model AVATAR supplied by the Thermo company (the United States). The XRD pattern was identified by using device model PW 1730 supplied from Philips Company (the Netherlands). The FE-SEM spectroscopy and EDX were identified by using device model MIRA III supplied by TESCAN Company (the Czech Republic). Finally, the TEM analysis was identified by using the device model

EM 208S (100 Kv) supplied by Philips Company (the Netherlands).

Preparation method

Preparation of CdTe QDs

The preparation method was based on the work of Ncapayi *et al.* [13]. It had been adopted as the primary method for preparing 3MPA CdTe QDs solution but with different refluxed times and concentrations, and then, it was treated the same way as by Ahmed *et al.* [14] by hydrothermal method by using an autoclave at the same temperature but at a different reaction time. In a typical synthesis, 1 g of cadmium (4.1 mmol) was dissolved in 50 mL of deionized water in a 100 mL beaker containing a magnetic bar at 400 rpm. While stirred, two drops of liquid 3MPA were added to it by using a macro-dropper. At this point, the liquid's color changed from transparent to white. After 5 minutes, the acidity of the solution was adjusted from 3.67 to 12 by adding 1 M solution of NaOH by using a macro-dropper, and then the color of the solution turned colorless. A Ke_2TeO_3 solution was prepared in another beaker by dissolving 1.057 g (4.1 mmol) in 50 mL of deionized water. It was left with no disturbance for 5 minutes. After it was stirred and 0.08 g of NaBH_4 (2 mmol) was added. The solution color turned black. Finally, the two solutions were mixed in a 250 mL three-necked flask and left to stir for 5 minutes, followed by 3 hours of refluxing. After, the solution was placed in an autoclave for 100 hours at 200 °C. After the processing period,

the CdTe QDs powder was washed three times with a mixture of ethanol and deionized water (5:1). A centrifuge was used to ensure a complete separation process at 5000 rpm for 30 min to purify it of excess salts and bonds not connected to the core surface. Finally, the powder was dried at 500 °C in an oven for 24 hours.

Preparation of glass substrate

The glass substrate has been used to prepare CdTe QDs thin film. Glass substrates (type corning, Germany) were used for the structure measurements.

Procedure of cleaning glass

The glass was initially placed in a beaker filled with deionized water in an ultrasonic bath for 10 min to remove the impurities. The glass was washed with acetone and ethanol, respectively and the glass was re-placed in an ultrasonic device for 10 min. Finally, the glass was washed with deionized water and dried with a hair dryer.

Results and Discussion

Optical properties (UV Vis and PL spectrum)

Figure 1 displays the absorbance spectra (left) and photoluminescence (PL) spectrum (right) for different reaction times of 3MPA capped CdTe QDs. Table 1 contains the information on NPs calculated from Figure 1. The QDs size, such as CdTe QDs, can be calculated in terms of wavelength by using the following empirical relationship [15]:

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57) \quad (1)$$

Where, D (nm) is the average diameter of the QDs and λ is the first absorption peak of the QDs.

For the UV Vis spectrum, the expansion and shift can be attributed to the random nature of the material during the growth (nucleation) of NPs and the effect of quantum confinement, respectively. Or, as a result of the gradient increase in QDs diameter with increased interaction time, this change arises due to Ostwald rippling [16-18]. For the PL spectrum, the difference or increase in the peak intensity can be attributed to the uniformity of capped of QDs

surface by the ligands over interaction time [13]. As mentioned in previous research [19, 20], the increase of QDs size results in the emission of the PL spectrum with a larger wavelength due to the increase in the binding energy of exciton. The full width at half maximum (FWHM) and the peak's intensity depends on the nanoparticles' distribution. The FWHM values do not exceed 60 nm, giving a good impression that the material has good properties [21, 22]. Through the results, it was found that the best optical was at 180 min.

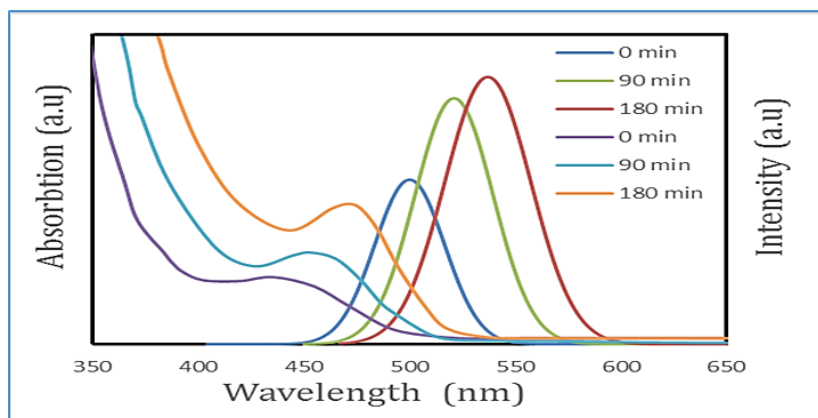


Figure 1: UV-Vis spectra (left) and PL spectrum (right) of 3MPA capped CdTe QDs at pH=12 at different reaction times

Table 1: The optical properties of 3MPA capped CdTe QDs at pH=12

pH=12						
Reaction Time (min)	Wavelength (nm)	Intensity of peak (a.u)	Emission intensity (a.u)	FWHM (nm)	Eg (eV) 1240/ λ (nm)	particle size (nm)
0	435	495	106	33	2.50	1.83
90	452	519	155	43	2.38	1.96
180	485	540	172	48	2.29	2.21

Fourier transform infrared radiation (FT-IR)

Figure 2 indicates the FT-IR spectra of CdTe QDs and 3MPA from 4000 cm^{-1} to 400 cm^{-1} . Table 2 represents the type and range of bonds. By comparing the bonds of CdTe and 3MPA in Table 2, it can be concluded that there is an overlap

between the core bonds and the 3MPA solution. The absence of the stretching S-H bond pattern between 2570 cm^{-1} and 2670 cm^{-1} in CdTe QDs is an evidence of the two substances being covalently bonded, i.e. between the core and 3MPA ligands [23, 24].

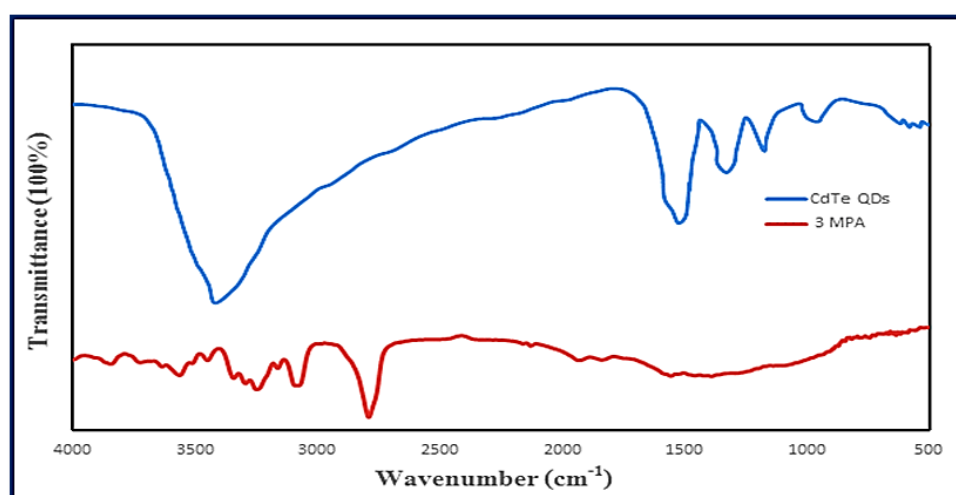


Figure 2: FTIR spectra 3MPA and 3MPA capped CdTe QDs at pH=12 at 180 min

Table 2: A range of bonds and types of the bond of 3MPA capped CdTe QDs

Substance	Range of bonds (cm ⁻¹)	Bonds	Mode of vibration bonds
CdTe QDs	3417	N-H	Stretching
	1526	C=C	Stretching (Aromatic ring)
	1330	C-O-H	Symmetric Stretching
	1178	C-O C=O	Stretching Bending
	988	=C-H	Out of plane bending
3MPA	3142	O-H	Stretching (Carboxylic acid)
	2938	C-H	Stretching (Carboxylic acid)
	2656	O-H	Stretching (Carboxylic acid)
	2570	S-H	Stretching (Carboxylic acid)
	1700	C=O	Stretching
	1418	C-O-H	Bending
	1249	C-O	Stretching

X-Ray diffraction (XRD)

Figure 3 exhibits the XRD diffraction pattern of a powder of CdTe QDs nanocrystals. Table 3 illustrates the calculated information from the XRD analysis. Based on Figure 3, it is observed that five peaks are $2\theta = 24.020, 31.720, 39.730, 41.580,$ and 46.970 attributed to Miller's coefficients (111), (102), (220), (103), and (311), and this is an agreement with JCPDS No.15-770 [14]. The first three peaks indicate that the CdTe QDs

composition is a cubic zinc blend [25, 26]. At the same time, the appearance of the second two peaks indicates that the CdTe QDs structure contains a hexagonal wurtzite structure. The appearance of the last two peaks may be due to high temperatures suddenly throughout the preparation, as these two peaks are absent when temperatures are lower than $240\text{ }^{\circ}\text{C}$ for an aqueous synthesis and lower than $300\text{ }^{\circ}\text{C}$ for organic synthesis [27]. The crystalline size of CdTe QDs was calculated by using the Scherer formula.

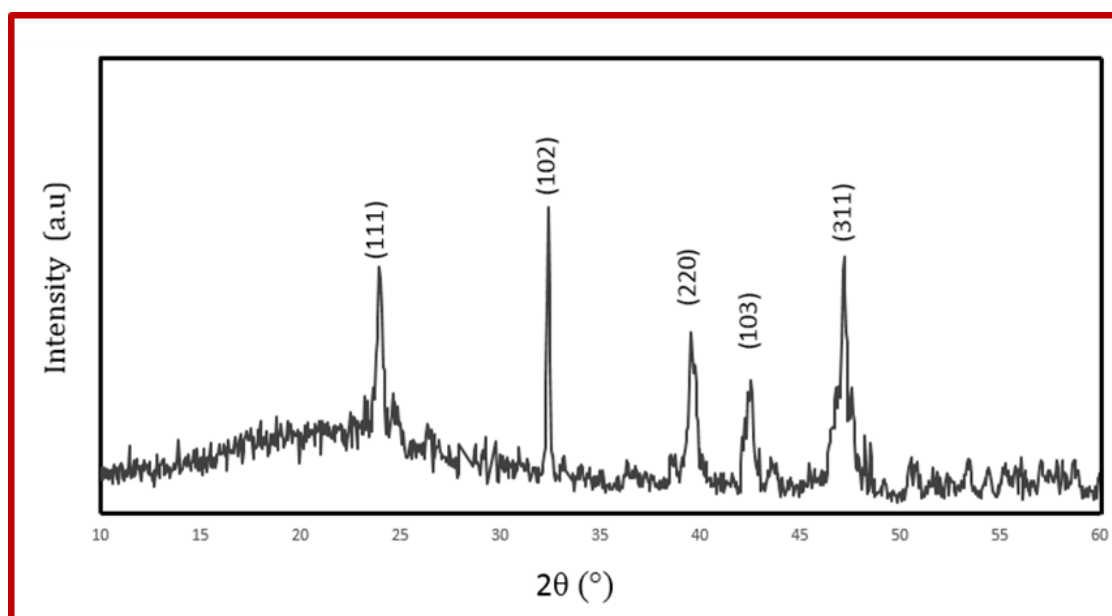
**Figure 3:** The XRD pattern of 3MPA capped CdTe QDs at pH=12 at 180 min

Table 3: The structure parameters of 3MPA capped CdTe QDs

2θ (Degree)	hkl	dhkl (nm)	FWHM (Deg.)	Crystallite size (nm)	Grain size (nm)
24.02	111	3.66	0.301	277	27.7
31.72	102	2.81	0.201	428	42.8
39.73	220	2.32	0.401	214	21.4
41.58	103	2.17	0.502	172	17.2
46.97	311	1.95	0.245	365	36.5

Field emission scanning electron microscopy (FE-SEM)

Figure 4a demonstrates the surface morphology of 3MPA capped CdTe QDs at pH=12 by using FESEM. Figure 4b displays the distribution of NPs size in a range from 10 nm to 85 nm. Figure 4a

shows the NPs assemblies of the CdTe QDs sample, which appear as spherical particles with an average diameter of about 33.85 nm, and this is in agreement with [14]. The large size of NPs may be attributed to an increase in nucleation or aggregation of NPs due to an increase in temperature.

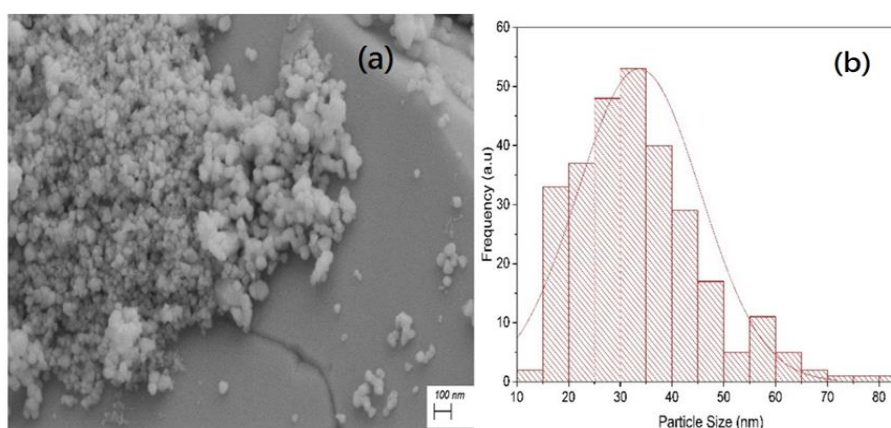


Figure 4: (a) morphology structure, and (b) size distribution of 3MPA capped CdTe QDs at pH=12 at 180 min

Energy dispersive X-ray (EDX)

Figure 5 depicts each element's percentage weight in CdTe QDs at pH=12 at 180 min. Based on Figure 5, it can be observed that the Cd peak is higher

than the Te element. The higher peak of Cd compared with the Te element confirms corrections of the added concentrations. Furthermore, it confirms the formation of the core successfully which is in agreement with [14].

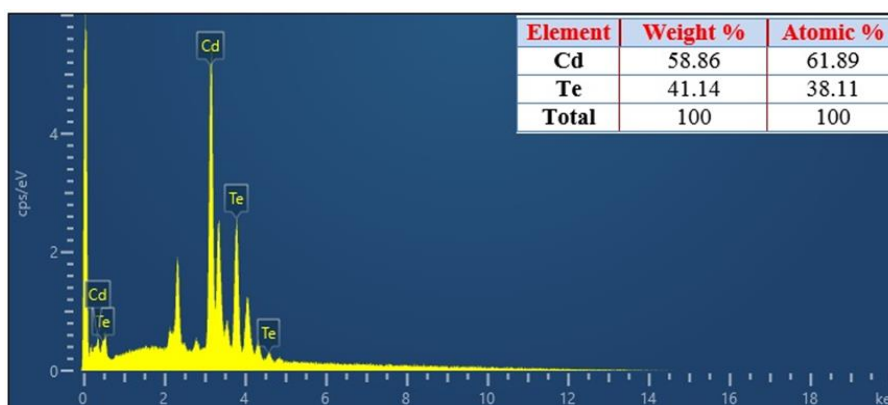


Figure 5: The percentage weight of each element in 3MPA capped CdTe QDs at pH=12 at 180 min

Transmission electron microscopy (TEM)

Figure 6a shows the internal structure of 3MPA capped CdTe QDs at pH=12 at a scale of 50 nm by

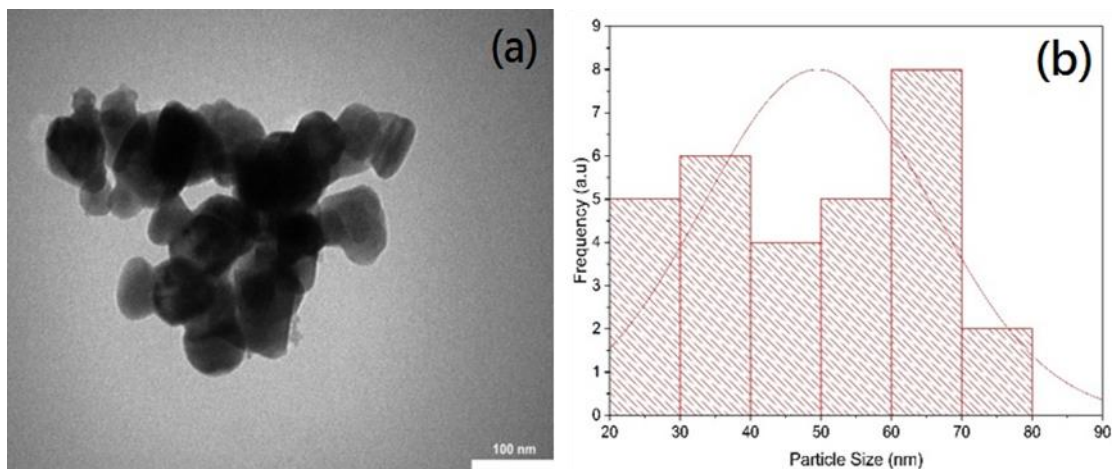


Figure 6: (a) internal structure, and (b) size distribution of 3MPA capped CdTe QDs at pH=12 at 180 min

Conclusion

3MPA CdTe QDs were prepared by using a simple, inexpensive, and environmentally friendly method. The hydrothermal technique is considered as a clean and inexpensive method. The spectroscopic results confirmed that the best properties were at 180 min reaction time. The XRD and EDx results confirmed the success of the quantum dot preparation process. The FESEM and TSEM results confirmed spherical particles with average diameters of 33 nm and 49.33 nm, respectively.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

using TEM. Figure 6b indicates the distribution of NPs size in a range from 20 nm to 90 nm. For TEM analysis, Figure 6a demonstrates a sample of CdTe QDs as spherical particles with an average diameter of around 49.33 nm.

Conflict of Interest

There are no conflicts of interest in this study.

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