Synthesis, Characterization and Optical Properties of CdSe Quantum Dots.

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Quantum dots (QDs) are semiconductor nanoparticles with very interesting optical properties, like high quantum yield or narrow and size-tunable fluorescence spectra. Current applications of QDs are wide-spread, their use as fluorescence labels in bioassays being one of the most promising applications. CdSe semiconductor nanoparticles (NPs) have been prepared by the organometallic pyrolysis method developed by Murray et al , and modified by Peng et al. Formations of the quantum dots nanoparticles were clearly seen in the TEM pictures. Powder X-ray diffraction (XRD) confirmed the structure of the products. In addition, the crystalline phase and size distribution of the nanocrystals are determined by XRD and TEM, respectively .The optical properties were assessed by UV-Vis measurements.

1. Introduction

The synthesis of semiconductor nanoparticles and Quantum Dots(QDs) has received extensive research interest in the recent years due to their special optical and electronic properties [1].Owing to promising functions and properties displayed by colloid semiconductor nanocrystals, especially II_VI quantum dots and their related nanostructures, they have been the subject of many scientific and technological applications. CdSe which is a medium band gap material with an energy band gap of 1.75 eV at 300 K, is one of the most important II_IV semiconductors [2].This material has been widely used for optoelectronic devices [3].In the past decade, a great deal of research has been done on controlling the size, shape and crystal structure of CdSe nanocrystals because these parameters strongly affect their electrical and optical properties [4-6]. CdSe nanoparticles exhibit strong photoluminescence(PL) in the visible region. The optical properties such as absorption and emission of the semiconductor nanomaterials can be tuned by the band gap engineering, which could be achieved by varying their shapes and sizes [7]. This is one of the important aspects in the synthesis /growth of the semiconductor nanomaterials.

Several stabilization agents have been reported in the literature for the synthesis of QDs, including various surfactants, organic or inorganic polymers, amines and polyphosphates [1,8-11]. In many of these processes, long chain organic molecules are used as capping agents and often the reaction is carried out at an elevated temperature and under inert atmosphere. The capping agents also assist to control the photoluminescence properties of as grown quantum dots [2,12-13]. However, the synthesis of semiconductor nanomaterials can also be conveniently carried out at ambient laboratory conditions without additional capping agents.

In this work we investigate the effect of preparation method on the optical properties of CdSe NPs. The structure and size of the NPs was examined by the absorption and emission measurements in addition to the high resolution transmission microscopy (HRTEM).

2. Experimental

2.1. Materials and Reagents

- Cadmium oxide {(CdO), Fluka, 99%}
- Oleyl amine {Aldrich 97%}.
- Oleic acid {(CH3 (CH2)7 CH=CH(CH2)7 COOH), Aldrich 98%} .
- Sulfur powder {(Se),Riedel, 99%}
- Selenium powder (Riedel-de Haën, 99%).
- Trioctylphosphine {(TOP), Aldrich 97%}
- Trioctylphosphine oxide {(TOPO), Fluka 97%}.

2.2 Experimental Methods: Synthesis of CdSe Quantum Dots.

Procedure: Luminescent CdSe QDs of multiple colors were synthesized based on a method introduced by Peng et al., with minor modifications [14]. Oleic acid (1.2 ml) and CdO (0.12 g) were put into a 100 ml three-necked flask, equipped with a thermometer and N_2 inlet under reflux and vigorous magnetic stirring with a Teflon-coated magnetic stir bar. The mixture in reaction vessel is heated up 125°C to fully dissolve the CdO and allow Cd complexation by the oleic acid to get a reactive Cd species; this can be optically observed by a color change from turbid violet-red to a pale yellow till a clear colorless homogeneous solution. It usually consumes ~15 min for the red color to disappear. At 130° C and upon red color disappearance, a mixture of 2ml Oleyl amine and 2.0 g TOPO were placed into the reaction vessel and the proper reaction temperature was selected (from 200 to 220 °C). When the temperature reaches 200 °C, the heat mantle is removed and 3.0 ml of Se in TOP (0.12 gm Se into 3.0 ml TOP to coordinate Se) are swiftly injected into the flask under vigorous stirring. Into a cold organic solvent (hydrophobic toluene or hexane) successive samples of

reaction mixture are taken on intervals depending on the required nanocrystals size (deducted optically by the color of the liquid). The color of the mixture changed from clear colorless to yellow, green, orange or red depending on the exact temperature. Now, as prepared, CdSe NCs are stabilized against aggregation by the capping material. Addition of nonsolvent methanol (which is miscible with the initial dispersing solvent) destabilizes the NCs allowing them to precipitate. Precipitated NCs are then collected from non-reacting precursors via centrifugation and washed with chloroform 2-3 times before redispersion in toluene or hexane.

CdSe nanocrystals are prepared according to the organometallic pyrolysis method developed by Murray et al [14] and modified by Peng et al [15] In this synthetic method, the organometallic precursors injected into a hot coordinating solvent such as TOPO or long chain alkyl amine. This method has evolved over the last ten years to produce a variety of high quality materials in colloidal solutions ranging from II-VI semiconductor nanocrystals e.g. CdSe, and CdTe, as shown in the experimental section. In order to prepare CdSe nanocrystals, one should bring the precursor reagents of predetermined concentrations into contact under certain suitable conditions for continuous and homogeneous chemical reaction.

In a general synthesis, each of the atomic species that will form the NC is introduced into a reactor in the form of a precursor. A precursor is a molecule or a complex containing one or more atomic species representing the NC building blocks. Once the precursors are introduced into the reaction flask, they react or decompose, generating the reactive monomers that will cause the nucleation and growth of the NCs. The energy required to decompose the precursors and to crystallize the nanoparticles, is provided by the liquid of the reactor, either by thermal collisions or by a chemical reaction between the liquid medium and the precursors, or by a combination of these two mechanisms. CdO has been used as a precursor for Cd owing to the low cost and less toxicity with almost good quality. The key parameter in the size and shape controlled growth of colloidal NCs is the presence of one or more organic molecules in the reactor, here broadly termed as "surfactants". Surfactants are amphiphilic compounds, i.e. molecules composed by one hydrophilic part (a polar or a charged functional group) and one hydrophobic part (in the simplest case, one or several hydrocarbon chains). In particular the growth of NCs can be properly controlled in many cases by the use of special molecules that behave as "terminating" agents. Such molecules direct the growth of nanostructures by dynamically coordinating their surface under the reaction conditions. Some examples of suitable surfactants include molecules carrying functional groups with electron donor atoms, such as carboxylic, alkyl thiols, phosphines, phosphine oxides, phosphates, phosphonates, amides or amines, carboxylic acids, and nitrogen-containing aromatics. The choice of surfactants varies from case to case: a molecule that binds too strongly to the

surface of the quantum dot is not useful, as it would not allow the nanocrystal to grow. On the other hand, a weakly coordinating molecule would yield large particles, or aggregates as shown in Figure (1).

In past trials, performed by the author for his senior honors thesis, cadmium oxide was heated under an argon blanket in 90% purity trioctylphosphine oxide (TOPO) and Oleic acid (OA) at 340°C until the color changed from dark red-brown to nearly colorless. Simultaneously, selenium powder was stirred in trioctylphosphine (TOP) under argon until the selenium dissolved. The temperature of the Cd-TOPO solution was dropped to 270°C once the solution was nearly colorless. Once these step were finished, the selenium solution was injected into the cadmium solution and the reaction began immediately; aliquots were removed at various time intervals. The product of the reaction was washed with methanol and toluene and then stored in any of a variety of solvents such as hexane, dichloromethane, or toluene.
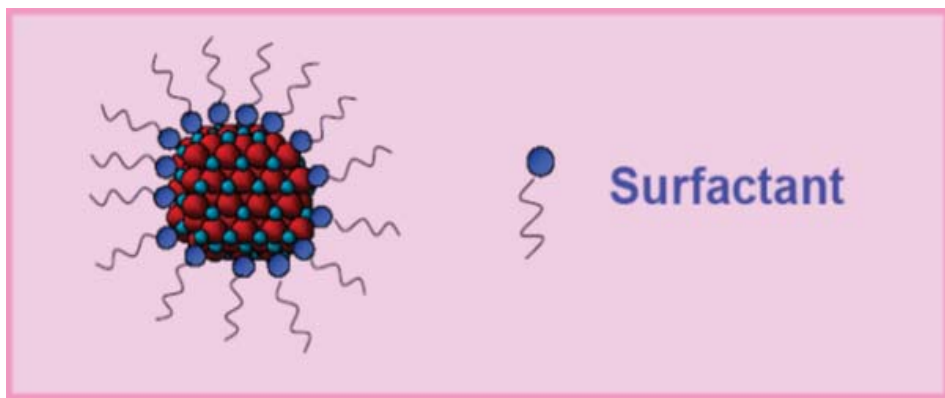

Fig. (1): Schematic representation of a colloidal quantum dot. A crystalline core is protected by a monolayer of organic molecules that are coordinated to surface atoms through their functional head group.

3. Characterization

Transmission electron microscopy images were recorded using Joel –JEM - 1230 electron microscope operated at 120 kV Equipped with a Gatan UltraScan 4000SP 4*4 kccd camera. The X-ray diffraction (XRD) patterns were obtained using an X'Pert Philips Materials Research Diffractometer at room temperature using $CuK_{\alpha}1$ radiation .Absorption spectra were recorded using a Hewlett-Packerd HP-8453 diode array spectrophotometer.

4. Results and dicussion

4.1) Optical spectroscopy of pure CdSe nanocrystals:
Absorption spectra and the particle size–optical band gap relationship

Absorption spectra of pure CdSe semiconductor nanocrystals (SNCs) in their solutions give valuable information such as: (a) the size of the nanocrystals that is calculated from maximum wavelength (λmax) of the first excitonic band; (b) the profile of the absorption spectra indicates the size distribution of nanocrystals (different absorption bands visible referring to the monodispersity of the nanocrystals); (c) an estimation of the concentration of the sample in the solution from the optical density of the first excitonic peak**.** Fig. (2) absorption & the emission spectra of the as prepared CdSe nanoparticles with different size at different time. Stokes shift is the difference (in wavelength or frequency units) between positions of the band maxima of the absorption and emission spectra (fluorescence and Raman being two examples) of the same electronic transition. It is named after Irish physicist George G. Stokes.
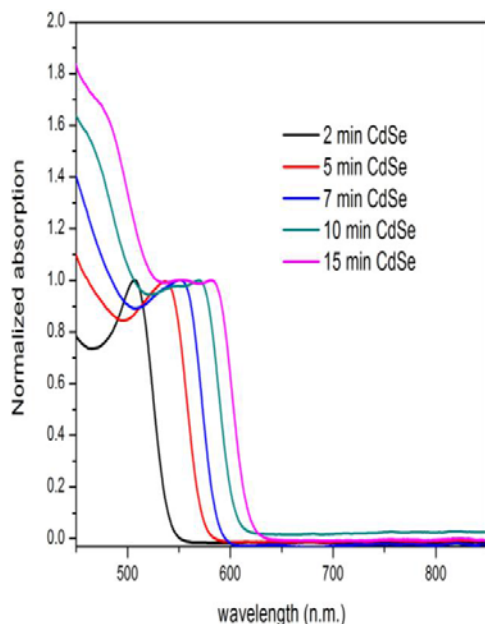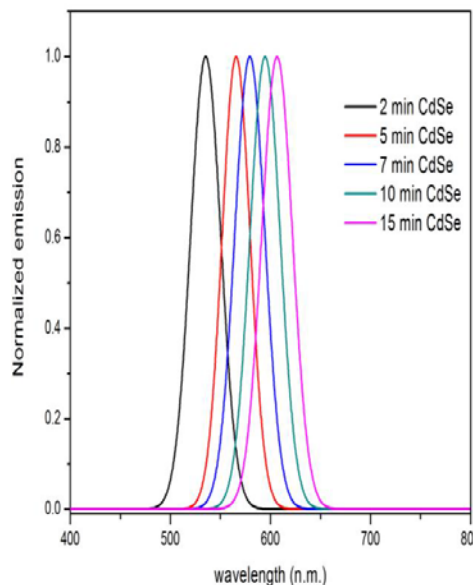

Figure (A)   Figure(B)

Fig. (2): (A) shows the absorption & (B) shows the emission spectra of the as prepared CdSe nanoparticles with different size at different time.

Table (1): Shows the absorption and the emission maximum, stock shift and the full width at half maximum (FWHM) of the as prepared CdSe quantum dots at different time intervals.

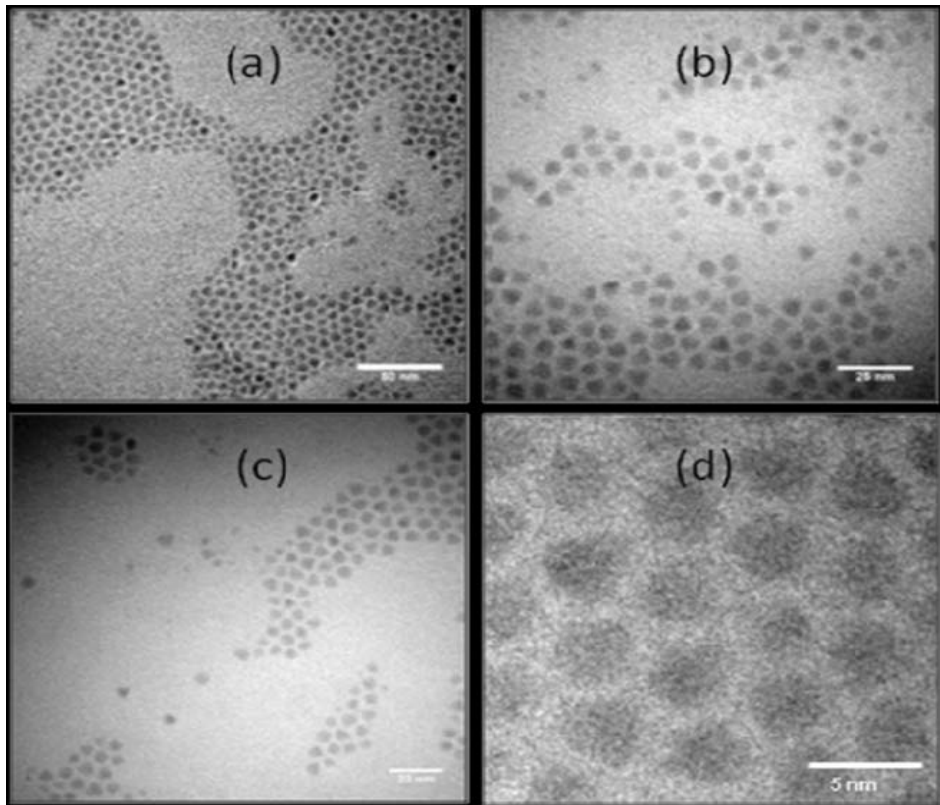| Growth time	? max Abs	? max Em	Stokes shift	FWHM
2 min	507 nm	537 nm	30 nm	26
5 min	537 nm	565 nm	28 nm	25
7 min	552 nm	579 nm	27nm	25
10 min	569 nm Broad	595 nm	26 nm	24
15 min	580 nm Broad	605 nm	25 nm	24

Fig. (3): TEM images of selected as prepared CdSe NCs sample at different magnifications.

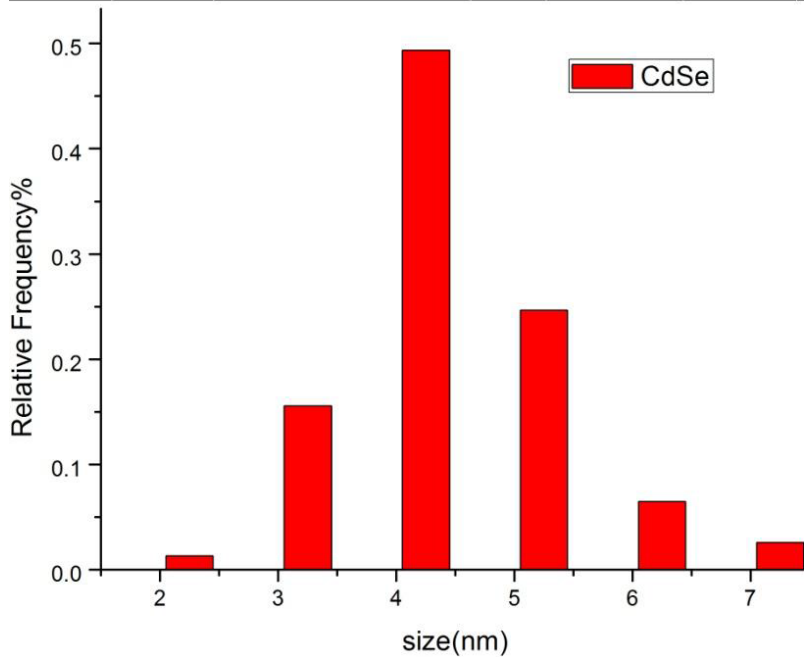| N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
77	4.2727	0.94083	329	2	4	7

Fig. (4): Histogram of the as prepared CdSe QDs

The TEM, HR-TEM and their corresponding Histogram from (Figure (4) respectively showed CdSe QDs monodispersed with uniformed shape and average size was approximately 4.2 nm with relatively good morphology and largest particle size 7.2 nm.

From (JCPDS-XRD Cards no: 04-014-0286) and the XRD pattern of the as prepared CdSe QDs shown in (Figure (5)) we could observe the presence of Zinc Blend (ZB) Cubic structure due to presence of distinct features: the first at $2\theta = 25°$ is owing to (111) reflection of planes and the two broad features appearing at $2\theta = 42°$ and $50°$ are due to (220) and (311) reflection of planes, respectively. The shoulder at $2\theta = 30°$ is due to the (200) planes. All of these features appear in the XRD pattern of the as prepared CdSe QDs sample. Moreover, from XRD pattern the presence of (102) reflection at $2\theta = 35°$ is a typical of the wurtzite (Hexagonal) lattice structure but from the XRD pattern we could understand that the ZB with the cubic structure is the predominant.
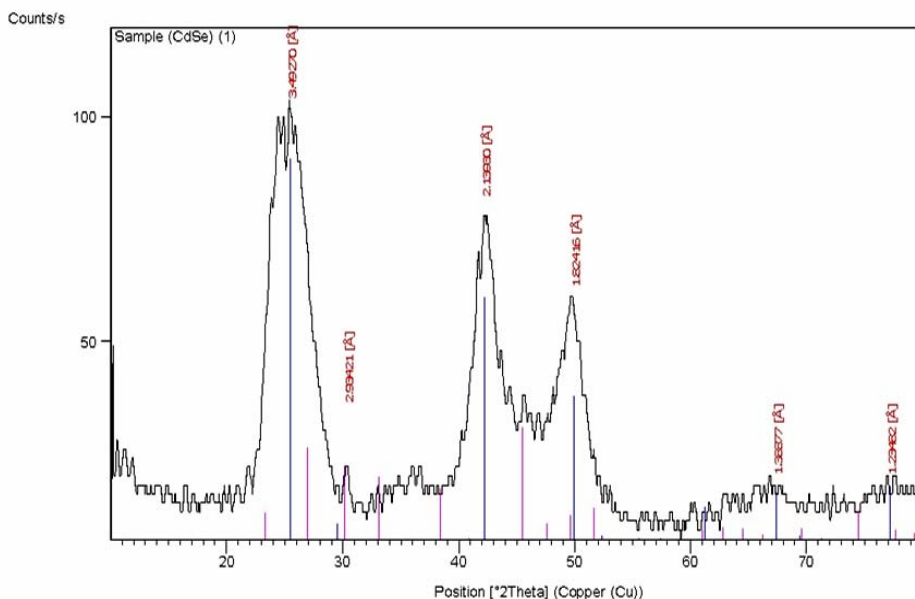
Fig. (5) : XRD pattern of as prepared CdSe QDs.

The FT-IR spectroscopy has been used to identify the capping agent on the surface of the as prepared CdSe QDs. The wave numbers corresponding to the vibrational modes of the functional groups of both references O.Am, TOP and CdSe QDs were identified where; (ν indicates stretching modes and δ deformation modes, subscripts "s" and "a" stand for symmetric and asymmetric vibration modes correspondingly) FT-IR spectra of the pure Oleyl amine "reference"; see (Figure(6)) revealed two intense peaks at 2922 cm^{-1} and 2855 cm^{-1} correspond to vas asymmetric and vs symmetric C–H stretching vibration of the CH2 group, the band at 3010 cm^{-1} is assigned to the C–H stretching vibration in C=C–H cis-double bond. The absorption peaks related to the CH2 deformation scissoring and rocking of multiple (–(CH2)n–, n≥4) methylene groups are specified at 1458 cm^{-1} and 721 cm^{-1}, respectively. The weak peak at 1630 Cm^{-1} indicates the presence of the C=C stretching vibrations of the Oleyl group. The absorption peaks in the IR spectrum of pure Oleyl amine, having characteristics of an amine group, are assigned as follows. The absorption band at 3375 cm^{-1} corresponds to N–H stretching mode; the band position at 1616 Cm-1 and 789 Cm^{-1} corresponds to deformation modes (scissoring and out of plane) of NH2 amine group, respectively. In addition, the weak peak observed at 1071 cm^{-1} corresponds to C–N stretching mode.

The FT-IR spectrum of the pure trioctylphosphene "reference"; see (Figure (6)) revealed two intense peaks at 2924 cm^{-1} and 2855 cm^{-1} correspond to vas asymmetric and vs symmetric C–H stretching vibration of the CH2 group. The

absorption peaks related to the CH2 deformation scissoring and rocking of multiple (–(CH2) n–, n≥4) methylene groups are specified at 1461 cm^{-1} and 720 cm^{-1}, respectively. The absorption peaks in the IR spectrum of pure trioctylphosphene, having characteristics of the C–P bond, are assigned as follows. The C–P stretching modes of TOP appeared at 1195 cm^{-1}, 1113 cm^{-1}, and 1022 cm^{-1}, respectively.

FT-IR spectra of as prepared CdSe QDs passivated with oleyl amine (O.Am) and trioctylphosphene (TOP); see (Figure (6)) revealed the CH2 stretching mode of O.Am and TOP at about 2924 Cm^{-1}, and 2856 Cm^{-1}, the absorption peaks related to CH2 deformation scissoring and rocking of multiple (–(CH2) n–, n≥4) methylene groups of O.Am and TOP at 1458 cm^{-1} and 720 cm^{-1}, respectively. In addition, the C–H stretching vibration in C=C–H cis-double bond of the O.Am observed at 3010 Cm^{-1}. These band positions approximately match with that of the pure O.Am and TOP; these observations indicates the O.Am and TOP remains in their original form after being capped the CdSe QDs. At the same time, there are some considerable changes due to the interaction between the nanoparticles and capping layer with respect to the pure O.Am and TOP.

The principal difference between the IR spectra of pure TOP and coated QDs is disappearance of two peaks at 1113 cm^{-1} and 1022 cm^{-1} corresponding to the two C–P stretching modes, and shift of the third C–P stretching mode from its position situated at 1195 cm^{-1} to lower wave number of about 1150 cm^{-1} with decreasing its intensity. These observations permit us to assume that; the CdSe QDs are capped by the TOP. Also, the principal difference between the IR spectra of pure O.Am and coated QDs is the broadening and shifting of the N–H stretching mode from its position situated at 3375 cm^{-1} to higher wave number of about 3417 cm^{-1}, shift of the scissoring and out of plane NH2 deformation modes from its position situated at 1616 Cm-1 and 789 Cm^{-1} to the wave numbers of about 1576 Cm^{-1} and 876 Cm^{-1} respectively with decreasing the intensity of the scissors mode, also shift the weak peak of C–N stretching mode from its position situated at 1071 Cm^{-1} to lower wave number of about 1033 Cm^{-1}.

These observations permit us to assume that, the CdSe QDs are capped by the O.Am, the presence of the C=C stretching mode at its original position situated at about 1630 Cm^{-1} without effect; prove that the Oleyl amine attach to the surface of the CdSe QDs through the amine group only. From these data, it could be confirmed that the O.Am and TOP were successfully capped on the
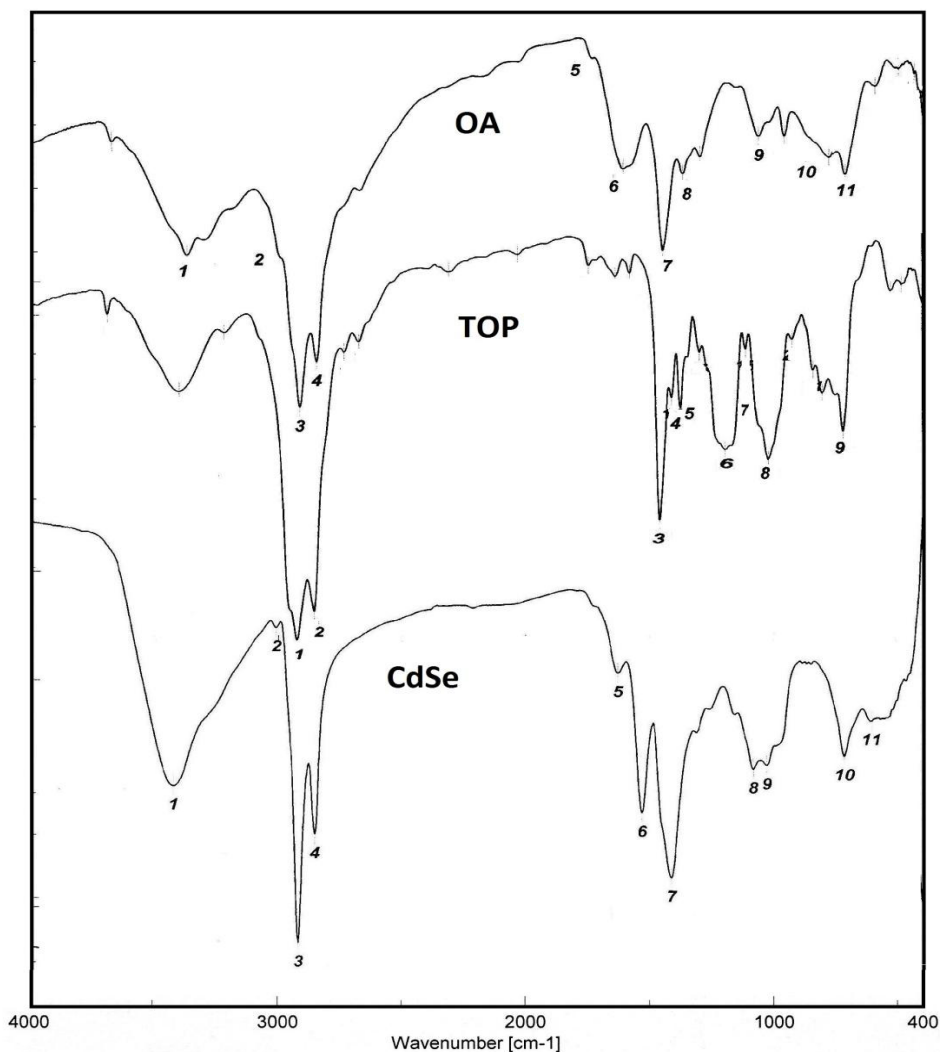
CdSeQDs.

Fig. (6): FT-IR transmission spectra of the as prepared CdSe QDs and the reference spectra of the O.Am and TOP.

5. Conclusions

From all previous data (absorptaion – Emission) spectra, TEM with histogram, XRD pattern and finally FT-IR data we conclude that we have CdSe QDs sample that satisfy our demands with broad absorption spectrum, narrow emission spectrum, good shape, size distribution and well capped with TOP and O.Am with ZB cubic structure.

Acknowledgment

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