Determination of optimum cation to anion (Cd:S) ratio for the synthesis of mono sized CdS quantum dots through optical properties

Jai Kumar B, Sumanth Kumar D, Mahesh H. M*

Thin film solar cell lab., Department of Electronic Science, Bangalore University, Bangaluru, 560056, India

*Corresponding author, Tel: (+91) 9448233962; E-mail: hm_mahesh@rediffmail.com

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Abstract

The CdS quantum dots (QDs) were synthesized using double injection aqueous method and systematic studies were carried to determine optimum cation to anion (Cd:S) ratio to obtain mono sized CdS QDs. An efficient and convenient method is designed by utilizing the optical properties (absorbance and transmission spectra) as qualitative tool. CdS QDs was synthesized by varying cadmium and sulfur concentration from 0.01M to 0.1M and 0.01M to 0.05M respectively keeping MPA and other precursors constant. Through Concentration Optimization by Optical Spectra (COOS) method, it was found that for 0.02M sulfur and 0.04M MPA, 0.03 to 0.05M cadmium was the most favorable concentration and similarly for 0.04M cadmium and MPA the optimum concentration of sulfur was 0.02M. CdS QDs optical band gap varied from 3.09 eV to 3.69 eV with quantum dots size decreasing from 3.22 nm to 2.45 nm, respectively for Cadmium concentration from 0.02M to 0.07M. For Sulfur concentration variation, band gap varied from 3.55 eV to 3.03 eV, with size of QDs increasing from 2.58 nm to 3.33 nm, respectively for concentration 0.01M to 0.05M. All this results shows that synthesized quantum dots were well under quantum confinement effect. Further, the proposed COOS method can be extended to all QDs synthesis to obtain the optimum cation to anion ratio to synthesis QDs with narrow size distribution. Copyright © 2017 VBRI Press.

Keywords: CdS, quantum dots, MPA, concentration optimization by optical spectra (COOS) method, Cd:S ratio concentration study, optical properties.

Introduction

Semiconductor Quantum dots also called as semiconductor nanocrystals are the materials whose size is less than Bohr's exciton radius of the material. This unique size leads to Quantum confinement effect, which could be divided as strong and weak confinement. In Strong confinement, the size of Quantum dots (QDs) are below Bohr's radius of that material, whereas in weak confinement the size of QDs is above Bohr's radius. Therefore, size of QDs gives rise to interesting properties like quantum confinement effect and high surface to volume ratio. These special effects lead to many exceptional properties which the bulk materials do not exhibit, among them multiple exciton generation, size tunable optical, electrical and catalytic properties which are very important for many applications [**1–4**]. Especially CdS QDs have gained much interest due to their application in optoelectronic devices and biomedical applications [**1**–**4**]. Hence, the synthesis of mono sized QDs are currently gaining significant interest.

Among several synthesis methods developed by researchers worldwide, important synthesis routes are organometallic and aqueous synthesis. The former approach take place in elevated temperature in non-coordinating solvent like octadecene (ODE) or Trioctylphosphine oxide (TOPO), with natural surfactant like oleic acid as stabilizer or trioctylphosphine (TOP) which act as both stabilizer and solvent [**5–7**]. The QDs synthesized in organic solvents have narrow size distribution with good quantum yield. But, these QDs are water insoluble and usually require to be transferred to aqueous phase for biological applications. In addition, synthesis takes place at high temperature (200–400 ºC) under nitrogen atmosphere or in glove-box because reagents used are hazardous. The later one, aqueous synthesis is relatively simple, economical, and environmentally friendly compared with organic route. Here, capping agent and pH of reaction plays a major role in synthesis [**8–11**] and are biocompatible. Besides theses, there are other methods to synthesis CdS QDs like microwave hydrothermal method in which precursor are irradiated with microwave to initiate growth of QDs instead of direct heating [**12**]. Simillarly γ irradiation techniques are used to grow QDs [**13**]. QDs can also be synthesized using non-injection one pot synthesis which is similar to organometallic synthesis in elevated temperature with reduced synthesis step [**14**]. In addition,

CdS QDs are synthesized by passing H_2S gas in aqueous phase using chemical precipitation method which could be improved further to synthesis QDs [**15**].

Despite several synthesis methods available, it's very important to reproduce optically stable narrow sized QDs with good repeatability. This remained as a fascinating area for researchers to understand the effect of cation, anion, capping agent concentrations on optical properties of QDs. But there are hardly a few papers describing how Cd to S ratio can be optimized to synthesis high quality nano crystal with narrow size distribution. Hence, it was felt worth to develop a method by which the most favorable cation to anion ratio can be obtained. This paper focuses on the simplest experimental method to determine optimum Cd:S ratio for synthesis of mono sized CdS QDs using conventional optical spectra (i.e. Absorbance and transmittance) from now on called as Concentration Optimization by Optical Spectra (COOS) method. This can be extended to find optimum cation to anion ratio of any other QDs.

Experimental

Materials

The chemicals used for aqueous synthesis of CdS QDs were Cadmium nitrate tetra hydrate ($Cd(NO_3)_2 4H_2O$, 98%, Aldrich, India) as cadmium precursor, Sodium Sulphide (Na_2S, minimum assay 50%, Fisher scientific, India) as sulfur precursor, 3-Mercaptopropionic Acid ($C_3H_6O_2S$, 99%, Spectrochem, India) as capping agent, Sodium Hydroxide (NaOH pellets, 97%, Central Drug house, India) and Ammonia solution (NH_3, Minimum assay 25%, Merck, India) were used for balancing pH of the solution. Solvent used was distilled water and all chemicals were of analytical reagent grade and used without further purification.

Synthesis of CdS QDs

Synthesis of CdS QDs for different molarity concentration of Cd and S ratio was carried out using double injection aqueous method under ambient atmosphere. First stage consists of preparing Cadmium nitrate solution of 0.01M-0.1M, Sodium Sulfide solution of 0.01-0.05M, MPA solution of 0.04M, All solutions used in the synthesis were freshly prepared by dissolving appropriate quantity of $Cd(NO_3)_2)4H_2O$, Na_2S, MPA respectively in 4 ml of distilled water taken in 10 ml glass beakers each. In second stage, 4 ml of above prepared 0.04M MPA solution was added in to 100 ml glass beaker containing 40 ml of distilled water and stirred for 5 minutes. Followed by injection of 2 ml Cadmium solution to above solution and stirred for 10 minutes. Subsequently 1M Ammonium solution or sodium hydroxide solution was added to adjust pH to 9 with vigorous stirring for 10 minutes. The reaction taking place in this step is given in equation 1 and equation 2.

$$Cd(NO_3)_2 + 2NH_4OH \text{ (or } 2NaOH) \rightarrow Cd(OH)_2 + 2NH_4NO_3 \text{ (or } 2NaNO_3) \quad (1)$$

$$Cd(OH)_2 + 4NH_4OH \rightarrow Cd^{2+} + \text{(other byproduct)} \quad (2)$$

When NH_4OH or NaOH is added to MPA capped Cadmium solution first its result in formation of $Cd(OH)_2$ resulting in white precipitation. With additional few drop of NH_4OH, pH gets balanced to 9. Also $Cd(OH)_2$ dissociate to Cd^{2+} ion, which result in clear MPA capped Cd solution. To this 4 ml of Sulfur aqueous solution was injected (equation 3, when Na_2S is added to H_2O, Na_2S break up in to Na^+ and S^{2-} ions). The solution showed a pale green luminescence under UV light which decreases as stirring continues showing the starting of nucleation.

$$Na_2S \rightarrow 2Na^+ + S^{2-} \quad (3)$$

$$Cd^{2+}\text{-MPA} + S^{2-} \rightarrow \text{MPA-CdS} \quad (4)$$

The solution was stirred for 5min and finally another 2 ml of remaining Cadmium solution was added and stirred for 5 minutes; give rise to bright green luminescent solution under UV radiation confirms formation of CdS QDs. The final reaction is show in equation 4, Cd^{2+} ions and S^{2-} ions interact with each other forming CdS with ionic bonding between them, and capping agent MPA prevent it from forming bulk CdS material resulting in quantum dots. This QDs solution was quenched and stored in refrigerator for characterization. MPA capping on CdS QDs was confirmed from FTIR spectra with photoluminescence emission at 525 nm which are presented in our previous paper [**19**]. The obtained MPA-capped CdS QDs were well dispersed in solvent and their optical properties were characterized.

The above explained synthesis procedure was followed for synthesis of CdS QDs of various concentrations. For Cd concentration studies from 0.01M to 0.1M, MPA and Sulfur concentration was fixed to 0.04M and 0.02M respectively. For Sulfur concentration study from 0.01M to 0.05M, MPA and Cd concentration was fixed at 0.04M that is at 1:1 ratio, which is the minimum required concentration for capping. These concentrations were selected for test with a hypothesis that for synthesis of mono sized CdS QDs Cd to S ratio is to be 2:1, which in turn result in good chemical and quantum yield. CdS QDs of each concentration were synthesized multiple times keeping all parameter same, to test repeatability and it was found that result was repeatable. The synthesized QDs were characterized and analyzed based on COOS method.

Instruments used for characterizations

The as synthesized CdS QDs of varying concentration of Cadmium from 0.01M to 0.1M and sulfur from 0.01M to 0.05M, keeping other precursor concentration fixed, were characterized for optical properties. Optical absorbance and transmittance spectra were obtained using Ocean optics, Model No. USB4000-XR UV-Visible-NIR spectrometer in transmittance mode. In wavelength range from 200 nm to 1000 nm, with step size of 0.25 nm. All spectra were taken with comparison with reference sample i.e. cuvette filled with solvent with path length of

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1cm, deducting ambient light in room temperature conditions. FTIR spectrum was obtained using Bruker-Alpha Fourier Transform Infrared Spectroscopy (FTIR) liquid samples in transmittance mode, for the range 4000 cm^{-1} to 400 cm^{-1}.

Results and discussion

COOS method is a qualitative experimental method used to optimize concentration of cation to anion using optical properties. In QDs, due to quantum confinement effect conduction and valence band are not continues as in bulk but exhibits series of discrete electronic transition bands. Since energies of the transition are affected by amount of confinement and confinement depend on size of QDs. The optical spectra of QDs are strongly dependent on size of crystal. Among optical properties absorbance and transmittance properties are chosen. Among these, absorbance spectra are used predominantly which is plot of absorbance vs. wavelength. Absorbance is a measure of ability of material to absorb the incident light and the necessary condition for optical absorption to occur is that energy of the incident photon must exceed the band gap of semiconductor. If the synthesized QDs are highly monosized, its absorption spectrum appears as well defined distinct peaks and valleys as a result of discrete electronic band transition levels **(shown in Fig. 1)**.

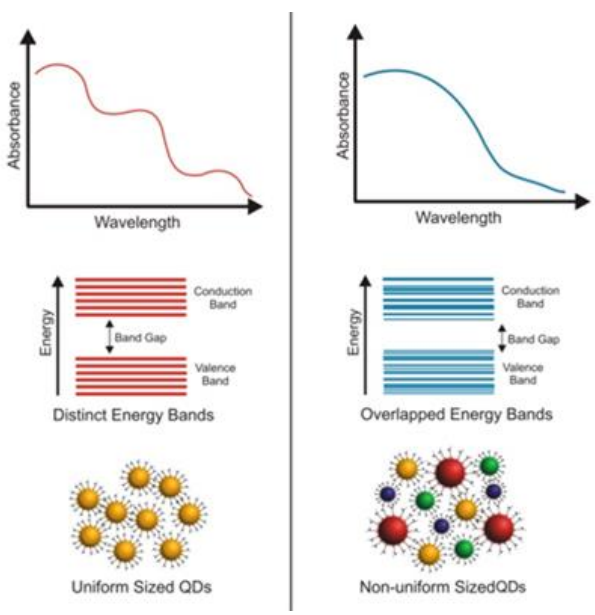

Fig. 1. Schematic diagram showing the effect of uniform and non uniform sized QDs on Absorbance and Energy bands.

The intensity and full width half maximum (FWHM) of peaks also depends on size of QDs and as QDs size distribution becomes uniform it results in increased peak intensity and narrow FWHM. As all QDs of uniform size absorb same energy to get exited leading to well defined absorption peaks. For optimization of cation to anion ratio, the lowest electronic band transition is considered than other higher peaks. The optimum ratio is selected experimentally by comparing its first absorbance peak intensity and FWHM, the good intensity with narrow FWHM implies QDs are of mono sized. Further, by comparing transmittance of QDs, desired values can be chosen and optimum cation - anion ratio can be obtained.

FTIR spectra of synthesized CdS QDs

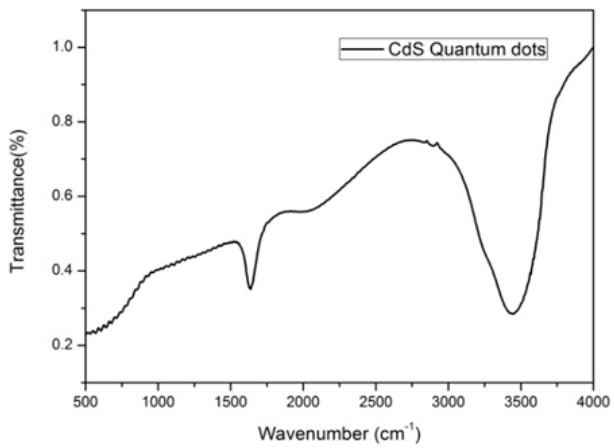

Fig. 2. FTIR spectra of CdS QDs.

Fig. 2 show FTIR spectrum of CdS QDs in aqueous solution of Cd: MPA: S concentration ratio taken as 0.4: 0.4: 0.2 respectively. The spectrum was taken in range of 400cm^{-1} to 4000cm^{-1} wavenumber. The MPA capping on CdS QDs was confirmed from the disappearing of S-H bond vibration peak of MPA at 2574 cm^{-1}, due to bonding between thiol groups of MPA with CdS. While other peaks belong to MPA, the broad peak above 3000 to 3700cm^{-1} is due to –OH stretching of –COOH group and also this broad peak coincides with intermolecular H bond of water. The peak at 1637 cm^{-1} and a small peak at 2064 cm^{-1} are attributed to carboxylic group of MPA. MPA capping increases QDs water solubility and stabilities resulting in good photoluminescence.

Optical properties of synthesized CdS QDs

Absorbance and transmittance spectra of CdS QDs of varying concentration are shown in fig. 3 to 5. It can be seen that for all samples, the excitonic absorption onset has blue shifted with respect to bulk CdS absorption onset of 515 nm, due to Qauntum confinement effect, confirms CdS QDs formation.

To determine optimum Cd to S ratio each spectrum is analysed in detail. When Cadmium concentration is increased from 0.01M to 0.1M, absorbance and transmittance curve exhibits distinct variation which is clearly depicted in **Fig. 3A, 3B, 4A and 4B**. For concentration 0.02M to 0.07M (fig. 3B) absorption peak wavelength as shifted to lower wavelength region as Cd concentration is increased. This blue shift is mainly due to decrease in QDs size, as higher Cd to S ratio facilitates growth of small sized crystals. For 0.01M and above 0.07M Cd concentration **(Fig. 3A)**, absorption peaks and absorption edge has shifted irregularly. This random shifting without absorption peak for 0.01M Cd

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concentration is directly due to high MPA to Cd concentration 4:1. Furthermore, less Cd concentration than sulfur (1:2; Cd:S) leads to Cd being tightly capped by MPA apparently reduces speed of formation of QDs. The haphazard behavior again appears above 0.07M which is due to higher Cd concentration and less availability of sulfur and MPA. As S to Cd ratio varies from 4:1 (0.08M: 0.02M, Cd:S) to 5:1 (0.1M:0.02M, Cd:S) will leave solution with mostly unreacted Cd and as MPA ratio decreases below Cd concentration, it couldn't cap Cd completely leading to white turbid solution. It was also found that transmittance **(Fig. 4A)** of solution has reduced drastically around 95% to 60% for concentrations between 0.07M to 0.1M.

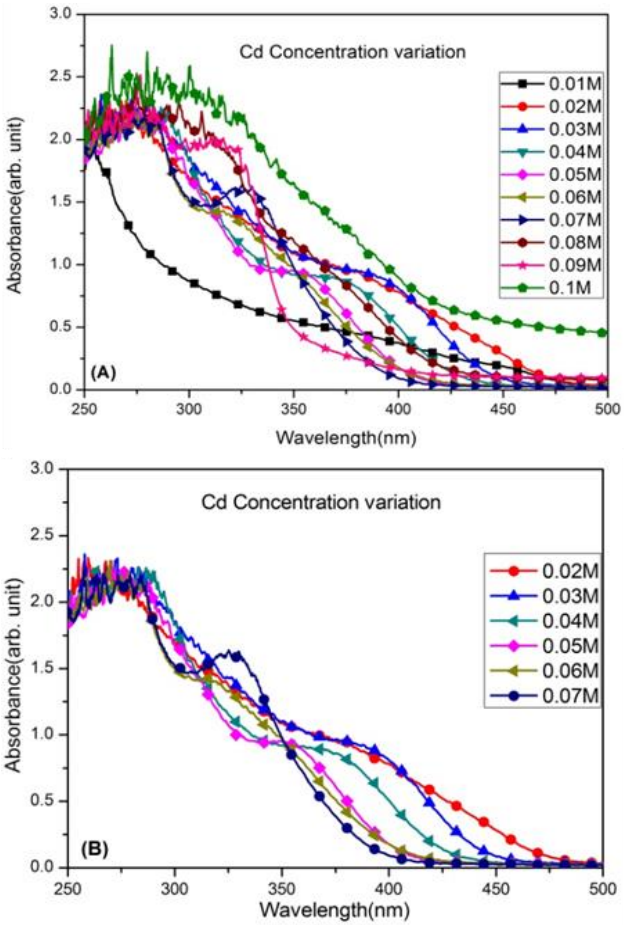

Fig. 3. (A) Absorbance vs. Wavelength plot of 0.01M to 0.1M Cd concentration, (B) enlarged Absorbance vs. Wavelength plot of 0.02M to 0.07M Cd concentration.

This confirms that, these concentration ratios are not preferred for mono sized CdS QDs synthesis. **Fig. 3B** shows enlarged absorption spectra. It depicts that for 0.02M concentration of Cd, there is no profound absorption peak which implies that QDs formed are of non-homogeneous size. The peak for 0.06M concentration also doesn't possess profound peak and shifted to larger extent which is evident in next (0.07M) concentration as well. This variation is due to high concentration of unreacted Cd making 0.06M and above concentrations not to yield mono sized CdS QDs. For Cd concentration 0.03M to 0.05M, the absorption peak is well defined. Due to these facts, Cd concentration of 0.03M to 0.05M is most preferred to get mono sized QDs with MPA and Sulfur concentration of 0.04M and 0.02M respectively.

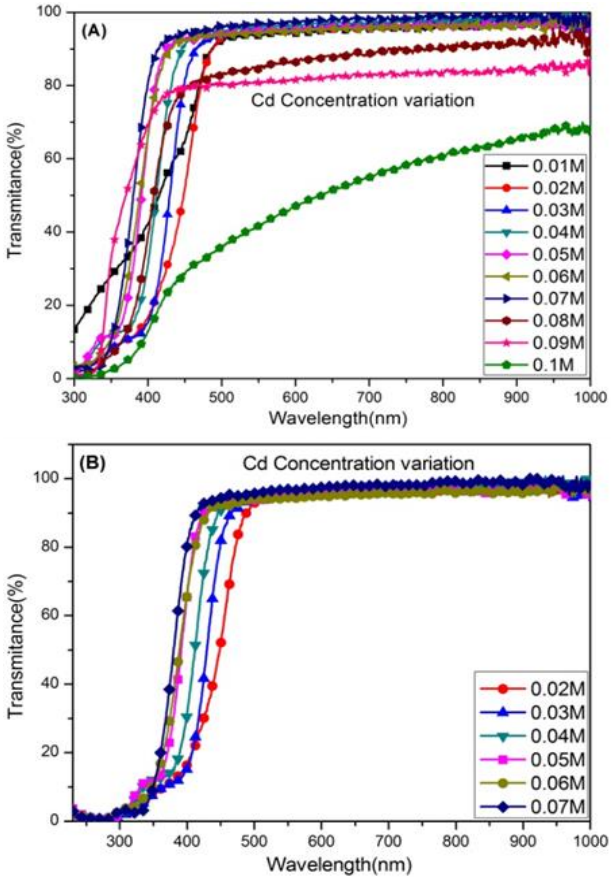

Fig. 4. (A) Transmittance vs. Wavelength plot of 0.01M to 0.1M Cd concentration, (B) Enlarged Transmittance vs. Wavelength plot of 0.02M to 0.07M Cd concentration.

In similar manner, consequences of Sulfur concentration were studied with Cd and MPA concentration as constant 0.04M. **Fig. 5A** and **5B** are absorbance and transmittance plots of CdS QDs having S varied from 0.01M to 0.05M concentration. As S concentration incremented from 0.01M to 0.05M, two important observations were made. First, absorption peak was found to be shifted towards higher wavelength (red shift) due to increase in QDs size as S concentration elevated. Later it was found that, the concentrations 0.01M and 0.03M to 0.05M doesn't have well defined absorption peak. Because, for 0.01M sulfur concentration (S:Cd=1:4), Cd is four times more concentrated leading to very small sized crystals and higher percentage of unreacted Cd. For concentrations 0.03M, 0.04M and 0.05M, Sulfur to Cd ratio is 0.75:1, 1:1, 1.25:1 respectively; this elevated Sulfur concentration result in formation of large sized crystals coated with multiple layers of sulfur. In transmittance spectra **(Fig. 5B)**, sulfur concentration of 0.01M has transmittance decreased below 85% due to increased unreacted Cd. For 0.02M to 0.05M concentration, the transmittance edge has shifted

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from 450 nm to 400 nm. All these observations point that the most suitable sulfur concentration is 0.02M with 0.04M Cd and MPA concentration (Cd:S:MPA= 2:1:2); which has well resolved absorption peak indicating uniform sized QDs and transmittance of about 96% above 400 nm.

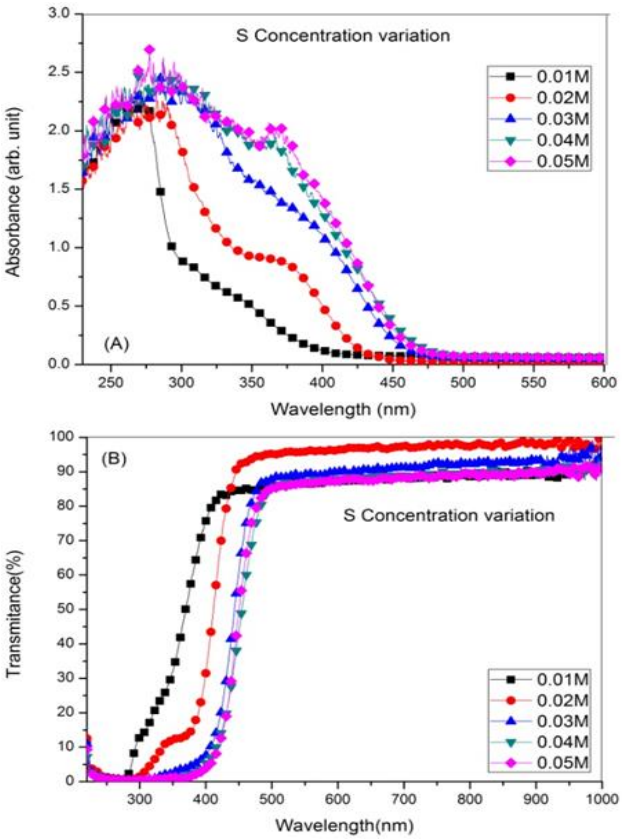

Fig. 5. (A) Absorbance vs. Wavelength plot of 0.01M to 0.05M Sulfur concentration, (B). Transmittance vs. Wavelength plot of 0.01M to 0.05M Sulfur concentration.

Determination of optical band gap of CdS QDs

For synthesized CdS QDs of varied Cd and S concentration band gap was calculated using modified form of Tauc plot and size of QDs was calculated using Brus Equation. Band gap is one of the most vital parameter by which we can know QDs electrical conductivity type as QDs band gap changes with its size due to quantum confinement effect. Band gap of QDs is determined by variation of optical coefficient with wavelength, which could be expressed using this equation [**16**].

$$\alpha h\nu = A(h\nu - E_g)^m \quad (1)$$

where, A is optical constant, E_g is Optical Band Gap, h is Planck's constant, ν is Frequency, m gives the transition type which has specific value of 1/2, 2, 3/2 and 3 corresponding to allowed direct, indirect, forbidden direct and indirect band transition respectively, so here m = 1/2 as CdS has direct band transition, α is absorption coefficient determined from transmission spectrum data using the relation.

$$\alpha = \frac{1}{d}\ln\left[\frac{1}{T}\right]$$

where, d is thickness of the cuvette and T is transmittance spectra data. Equation 1 can be rewritten as [**17**],

$$\frac{d(\ln \alpha h\nu)}{d(h\nu)} = \frac{m}{(h\nu - E_g)}$$

Hence, the plot of $\frac{d(\ln \alpha h\nu)}{d(h\nu)}$ vs. $h\nu$ will produce discontinuity at $h\nu - E_g = 0$; using this relation, optical band gap energy can be evaluated.

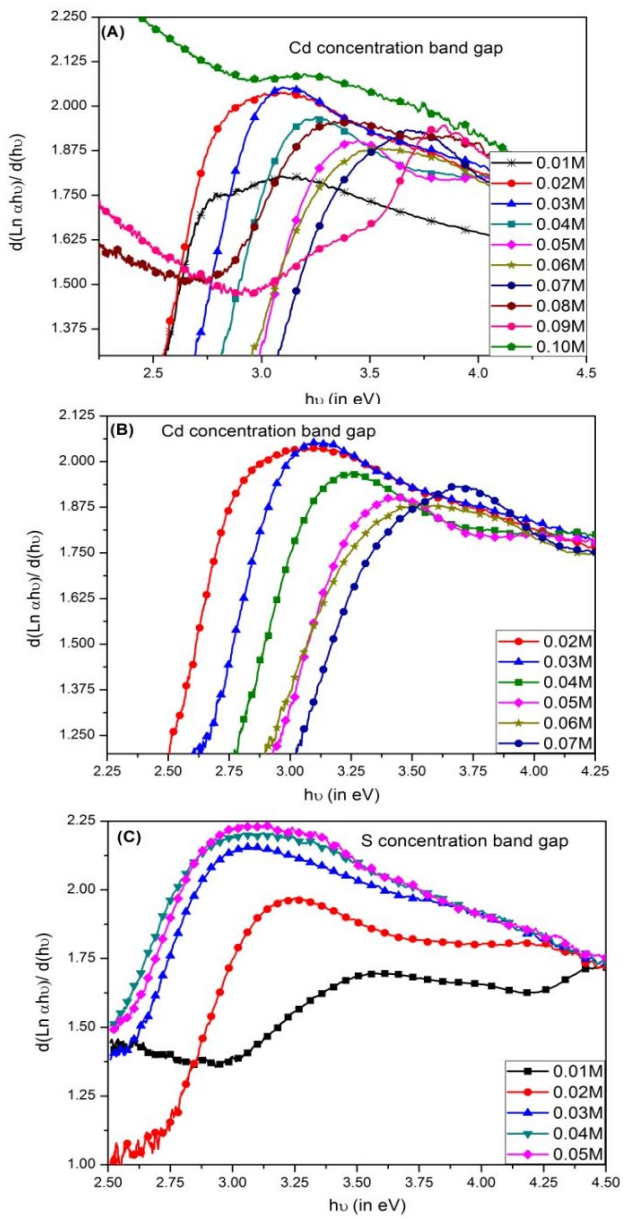

Fig. 6.(A) Band gap plot of 0.01M to 0.1M Cd concentration. (B) Enlarged band gap plot of 0.01M to 0.07M Cd concentration (C) Band gap plot of 0.01M to 0.05M sulfur concentration.

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Fig. 6A, 6B and **6C** are the plots of $\frac{d(\ln \alpha h\nu)}{d(h\nu)}$ vs. $h\nu$, although figure show peak instead of discontinuity position (due to instruments limits), peak position of the plot gives band gap energy and corresponding band gaps are tabulated in **Table 1** and **2**. Band gap of the CdS QDs has increased from 3.1 eV to 3.7 eV for Cd concentration ratio of 0.02M to 0.07M; band gap was not determined for 0.01M and above 0.07M as there was no distinct peak and sifted haphazardly. For 0.01M to 0.05M sulfur concentration variation, band gap decreased from 3.55 eV to 3.034 eV respectively. These results conclude that all CdS Quantum dots are well under strong quantum confinement regime.

Determination of QDs size

Size of QDs can be calculated by comparing their band gap with its bulk material band gap or by calculating quantum confinement energy on QDs. Many researchers have formulated various relations relating bulk material band gap with QDs band gap and Quantum confinement energy; among them Brus equation is the simplest one, expressed as given below for spherical QDs [**1**].

$$E_g^{QD} = E_g^{Bulk} + \frac{h^2}{8R^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] - \frac{1.786\ e^2}{4\pi\epsilon_o\epsilon_r R} \qquad (2)$$

where, E_g^{QD}Quantum dot band gap (eV), E_g^{Bulk} bulk semiconductor band gap (eV), R is Radius of Quantum dot (m), m_e^* is Effective mass of electron, m_h^* effective mass of hole, ϵ_o absolute permittivity, ϵ_r relative permittivity, e is charge of an electron, h is planks constant. The 1st term is characteristic band gap energy of bulk materials, 2nd term gives quantum confinement energy which increases the QDs energy to higher energy level compared to E_g^{Bulk}, directly proportional to R^{-2}, 3rd term stand for Columbic interaction energy of exciton which reduces QDs energy level which is proportional to R^{-1}.With known QDs band gap value the Quantum dot radius can be calculated, rearranging equation 2.

$$r = \frac{-\left[\frac{1.786\ e^2}{4\pi\epsilon_o\epsilon_r}\right] + \sqrt{\left[\frac{1.786\ e^2}{4\pi\epsilon_o\epsilon_r}\right]^2 + \left[E_g^{QD} - E_g^{Bulk}\right]\frac{h^2}{2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right]}}{2\left[E_g^{QD} - E_g^{Bulk}\right]}$$

This equation is obtained by reducing equation 2, to form $aX^2 + bX + c = 0$ and solution to X is given by $X = \frac{-b+\sqrt{b^2-4ac}}{2a}$ neglecting negative value and considering only positive value. The obtained size of CdS QDs is tabulated in **Table 1** and **2**, with respect to its QDs band gap, taking values of constant of CdS as $E_g^{Bulk(CdS)}$= 2.42 eV, ϵ_r= 5.7, $m_e^* = 0.19m_o$, $m_h^* = 0.8m_o$, m_o is absolute mass of electron. The size of CdS QDs, as decreased from 3.22 nm to 2.45 nm as concentration of Cd as increased from 0.02M to 0.07M and similarly size as increased from 2.58 nm to 3.33 nm for Sulfur concentration increased from 0.01M to 0.05M, confirming that optical properties is directly related to size of QDs and their effect as already explained. The radius of all the CdS QDs synthesized is below Bohr radius of CdS (3 nm) [**18**] which confirm the formation of QDs and Blue shift in energy band gap due to strong quantum confinement.

Table 1. Cd Concentration related Band gap and Radius of QDs.

S.I.	Molarities Concentration	CdS QDs Band gap (eV)	Size of QDs (in nm)
1	0.02	3.09	3.22
2	0.03	3.09	3.19
3	0.04	3.25	2.94
4	0.05	3.40	2.74
5	0.06	3.55	2.57
6	0.07	3.69	2.45

Table 2. S Concentration related Band gap and Radius of QDs.

S.I.	Molarities Concentration	CdS QDs Band gap (eV)	Size of QDs (in nm)
1	0.01	3.55	2.58
2	0.02	3.25	2.94
3	0.03	3.06	3.27
4	0.04	3.04	3.31
5	0.05	3.03	3.33

The synthesized CdS QDs have absorption in UV region and good transmittance in visible region, which make them as efficient candidate as window layers for solar cells. This can be used as UV absorbing active layer along with other materials so that a wide band of solar energy of light can be utilized. The absorption peak is narrow which can be used as UV filters. CdS QDs exhibits green luminescence which can be used as coating material to UV tubes to produce green light. CdS quantum dots were synthesized in aqueous medium so this can be also used in biological application.

Conclusion

CdS Quantum dots were synthesized using double injection aqueous method in ambient atmosphere. To optimize the Cd:S ratio, concentration study of Cadmium from 0.01M to 0.1M with constant 0.04M MPA and 0.02M Sulfur was carried out. The Cd of 0.03M to 0.05M was found as best optimized concentration for which the mono sized QDs were obtained. Similarly, 0.02M sulfur was found most appropriate in 0.01M to 0.05M keeping MPA and Cd concentration at 0.04M. Band gap of CdS quantum dots obtained is 3.1 eV to 3.7 eV for Cd concentration of 0.02M to 0.07M with size varying from 3.22 nm to 2.45 nm. For Sulfur concentration of 0.01 M to 0.05 M, band gap is 3.55 eV to 3.034 eV respectively with size ranging from 2.58 nm to 3.33 nm. As Cd concentration is increased there is profound blue shift due to decrease in QDs size and as Sulfur concentration is increase there is Red shift due to increases in QDs size.

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All the CdS QDs are under strong quantum confinement regime and the best Cd to S ratio i.e. cation to anion ratio is 2:1 to obtain mono sized CdS Quantum dots. The Concentration Optimization by Optical Spectra (COOS) method illustrated in this work is simplest experiment method. This uses absorption and transmittance spectra as a qualitative tool, to get the optimum concentration ratio of cation to anion to synthesis mono sized QDs of any species.

Author's contributions

Conceived the plan: Performed the expeirments: Jai Kumar B. Data analysis; Wrote the paper:Jai Kumar B, Sumanth Kumar D, Mahesh H. M. Authors have no competing financial interests

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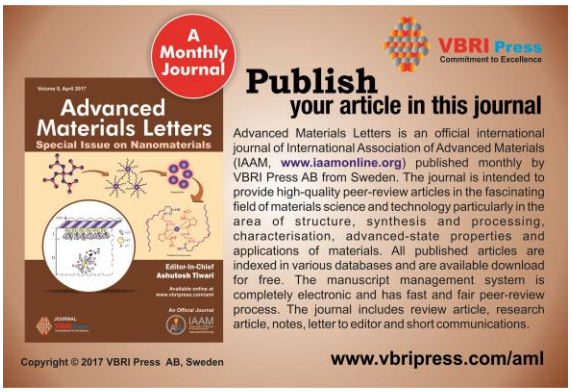
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