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Study of variation of band gap with the size of CdSe quantum dots

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Abstract

Herein, we report the synthesis of CdSe Quantum dots of tunable particle size in aqueous phase using freezing temperature injection technique. As prepared CdSe quantum dots were characterized using UV-Vis Absorption Spectroscopy, Photoluminescence Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy. By varying the concentration of cadmium and selenium precursors with thioglycolic acid as the capping ligand, this synthesis method allow us to synthesize Quantum Dots of size ranging from 3.4 to 3.7nm (estimated from optical absorption edge measurements). Absorption spectra of CdSe QDs exhibit a blue shift as compared to its bulk counterpart which is an indication of quantum confinement effect. The photoluminescence (PL) spectra of CdSe quantum dots confirm that the particles are mono-dispersed and possess enhanced luminescent property. Band gap of CdSe quantum dots was found to be decreases with increase in particle size.

Keywords: quantum dots, quantum confinement, spectroscopy, luminescent

1. Introduction

Among the reported semiconductor QDs; CdSe stands out as important material because of wide tuning of emission spectra with particle size^[1], unique photoluminescent properties^[2] and relative mature synthetic techniques. Numerous methods have been reported for the preparation of CdSe nanoparticles, however, synthesis of CdSe NCs can be summarized mainly in two chemical routes, one is nonaqueous trioctyl phosphine/trioctyl phosphine oxide (TOP/TOPO) route, and another is aqueous route that employs use of different thiols, thioacids amides as stabilizing agent^[3]. Organometallic approach^[4-6] has been widely adopted to prepare CdSe colloid nanocrystals with high quality morphology, high quantum yields. Unfortunately, preparation of the NPs in an organic phase is neither cost-effective nor environment-friendly because of expensive processing conditions (inert atmosphere and high temperature above 300 °C to inhibit growth of particles), and as prepared, QDs are hydrophobic and cannot be used directly for biological applications, where an aqueous dispersion of nanoparticles is essential^[4-5]. Recently aqueous route are successfully used to synthesize QDs using various molecules such as thiols, thioacids and amides as capping ligands^[7-9]. The resulting QDs are more stable, water-soluble, and biocompatible but exhibit a low quantum yield (QY) as compared to the QDs obtained via organometallic synthesis^[8]. Herein we report an effective method for the synthesis of CdSe quantum dots using freezing temperature injection technique. As compared to the hot injection and room-temperature injection method, freezing temperature injection method offers longer time for the nuclei reactions, and growth of the CdSe crystals could be easily controlled^[9]. We have investigated the effect on the absorbance spectra and photoluminescence intensity with change in the molarities of Cadmium precursor and discussed the variation of band gap with size.

Materials

CdNO₃, Se Powder and thioglycolic acid (TGA) were purchased from Sigma Aldrich. All other chemicals used were also of analytical grade from Sigma Aldrich. Deionized water with resistivity of 18MΩ cm⁻¹ was used for the preparation of aqueous solutions.

Experimental details

Aqueous solution of Cadmium Nitrate and Thioglycolic acid (HSCH₂COOH) was prepared in the proper ratio and pH of the solution was adjusted to 12 by adding 1 M solution of NaOH. The solution was deaerated using nitrogen gas (N₂) bubbling for 30 minutes. NaHSe solution was prepared by adding Sodium Borohydride and Se powder in 4 mL distilled water in the

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ratio 4:1. The reacting system was cooled to 0°C, in dark. During the reaction, a small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen gas. Addition of NaHSe under vigorous magnetic stirring produced bright-yellow, transparent TGA capped CdSe QDs. QDs were stored at 4 °C to prevent agglomeration no precipitates were observed after 30 days.

Results and Discussion

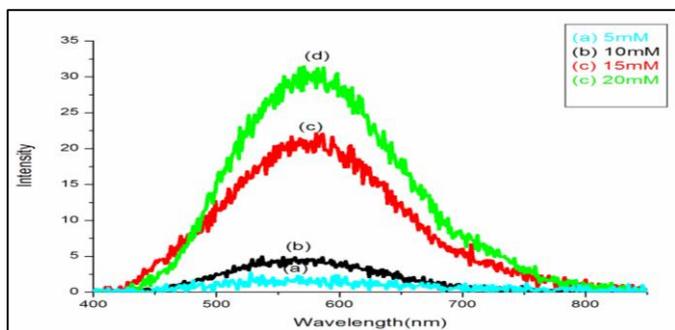


Fig 1: Photoluminescence Spectra of CdSe QDs at different concentration of Cadmium Precursor (Cd²⁺)

Figure 1 shows the Photoluminescence spectra of CdSe QDs. As the precursor concentration increases photoluminescence intensity also increases. The PL intensity is also a strong function of Cd concentration with maximum emission occurring for Cd 20mM concentration. As concentration of Cd precursor increases, a greater proportion of Cd²⁺ atoms are available for surface reaction with the Se²⁻ ions and with capping agent, leading to a situation that favours the stabilization of smaller particles. Lower concentration of Cd precursor results in insoluble precipitate with bulk spectral properties whereas higher concentration results in quenching of photoluminescence intensity (not shown in the graph). Higher concentration of Cd precursor yield molecular clusters, as opposed to nanocrystals with bulk crystal structure. This appears to indicate that surface passivation is best for mid-size (or mid-spectral) CdSe nanocrystals.

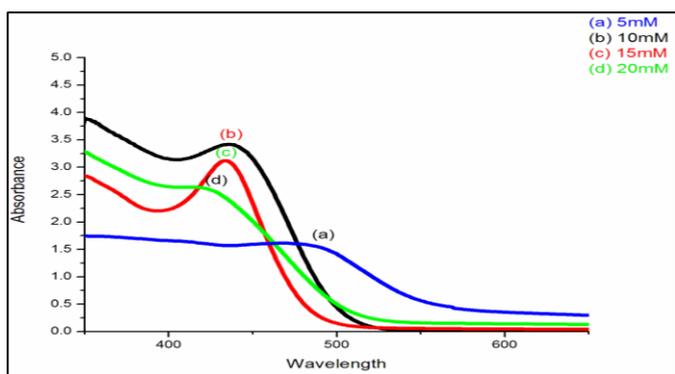


Fig 2: Absorption Spectra of CdSe QDs at different concentration of Cadmium Precursor(Cd²⁺)

Fig (2) shows the absorption spectra of the CdSe quantum dots synthesized with the different concentration of Cd precursor increasing from 5, 10, 15, and 20. It was found that with increase in the concentration of cadmium for a fixed value of selenium and thioglycolic acid there was a blue shift indicating a decrease in the particle size. The range of absorption edge lies in the region between 470 nm to 400nm which is a pronounced blue shift from 712nm of the bulk

CdSe band gap. This result shows quantum confinement effect in CdSe quantum dots. As we increases the concentration of CdNO₃ precursor Cd²⁺ ions are freely available whereas the counterpart Se²⁻ released from NaHSe is much slower. Therefore, the concentration CdNO₃ determines the number of nucleation sites available for the growth of CdSe QDs. Hence for a fixed concentration of selenium precursor, the greater the number of nucleation sites, the smaller will be the size of CdSe QDs. Because of quantum confinement continuous energy bands of a bulk material changes into discrete, atomic-like energy levels [10-12].

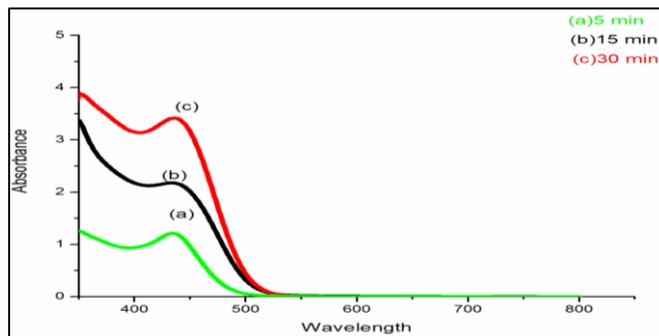


Fig 3: The effect of ageing on the absorption spectra of TGA-capped CdSe QDs. Aliquotes were taken after 5min (a), 15 min.(b), 30min.(c)

Fig.3 shows the effect of ageing on the absorption spectra of TGA- capped CdSe QDs, synthesized by the reaction of 15mM Cd(NO₃)₃ with 10mM NaHSe. The absorbance peak shifts shows red shift as the time progresses, indicating agglomeration to larger CdSe QDs on ageing even in the presence of TGA. It seems that TGA is not able to completely stop the aggregation process, but reduces the process to great instant. However in the absence of TGA agglomeration takes place more rapidly resulting in the formation of CdSe precipitate. TGA also aid in restricting the final size of particles to a certain upper limit, depending on the concentrations of reagents used. The similar effect was also observed for other sets of CdSe samples where concentration of CdNO₃ was higher than that of NaHSe

The optical band gap of the CdSe QDs are calculated from the absorption peak using the formula

$$E_g = hc/\lambda \tag{1}$$

Where

h is the Plank’s constant, c is the velocity of light and λ is the wavelength at which, absorption peak is obtained.

The size of quantum dots was evaluated using optical absorption spectra. UV-visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. The particle size of semiconductor particles can be determined using Brus equation [13] based on “effective mass approximation” (EMA)

$$E_g(QD) = E_{bulk} + (1/m_e^* + 1/m_h^*) - 1.786e^2/4\pi\epsilon_0\epsilon_r R \tag{2}$$

Where,

E_g(QD)= band gap energy of quantum dot; E_{bulk} = band gap energy of bulk semiconductor; R = radius of quantum dot; m_e^{*}= effective mass of excited electron; m_h^{*}= effective mass of excited hole;h = Planck’s constant.

It is clear that the particle size reduces as the concentration of Cd precursor increases.

Table 1: Variation of band gap of CdSe QDs with band gap

Sample	Concentration (in mmol)	Absorption Peak (in nm)	Band Gap (in eV)	Size by EMA (in nm)
1.	5	470	2.63	4.07
2.	10	427	2.89	3.6
3.	15	424	2.92	3.5
4.	20	420	2.95	3.4

The difference between excitation and luminescence wavelength is known as Stokes shift which can be explained on the basis of Frank Condon Principle. Electrons are excited from valance band to conduction band by the photons of higher energy (4.1eV). Electrons come back to the bottom of conduction band within 10^{-11} sec dissipating excess energy in the form of lattice vibrations. Then the electron falls in the valance band recombine with hole and emit photon of lower wavelength. Vertical upward transition corresponds to absorption peak and vertical downward transition corresponds to emission peak^[14]. Absorption and narrow luminescence spectra with clear excitonic and emission features indicate the formation of mono-dispersed CdSe QDs.

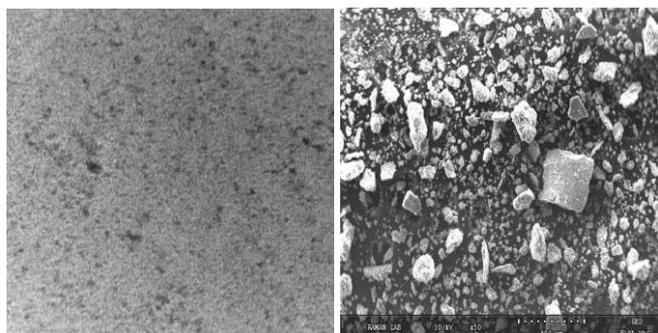


Fig 4: TEM image of CdSe QDs. **Fig 5:** SEM image of CdSe QDs

TEM and SEM measurements were carried out to study the size and morphology of CdSe nanoparticles. Figure 4 gives such picture for concentration 20mM as a representative of other samples. In all cases, the particles are spherical in shape and there is good homogeneity in the particle size distribution

Conclusion

In summary fluorescent CdSe QDs capped with TGA are synthesized by aqueous route using freezing temperature injection technique with narrow size distribution. The average particle size is reduced by increasing the concentration of Cadmium precursor. In absorption spectrum, peak is obtained in UV region and shifts towards lower wavelength by increasing the concentration of Cadmium precursor. This indicates increase in effective band gap. PL spectrum excited by 350 nm shows a Stoke shifted peak in UV region. This peak also shifts towards lower side as the nanocrystal size is reduced. For smaller average size, there is larger distribution of nanocrystalline sizes, causing broadening of PL peak.

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