Tuning the Luminescence of CdS Quantum Dots by a Simple Method

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Abstract

In this report, we present a facile approach for the synthesis of luminescent CdS and CdS:Mn^{+2} nanocrystals by reaction of $CdSO_4$ and $Na_2S_2O_3$ in the presence of thioglycerol ($C_3H_8O_2S$) as capping agent. The influence of various experimental variables including, pH values and percentage of dopant, on the growth rate and optical properties of the obtained CdS nanocrystals has been systematically investigated. Experimental results show that by lapsing time and increasing particles size, red shift has occurred in the absorption edge and peak of luminescence. Luminescence of CdS nanoparticles covers 480-650nm of visible range. This luminescence arises from trap states and reaches to its maximum in pH=6 after 5 days. Doping of CdS with Mn^{+2} is found to enhance the photoluminescence (PL) intensity. PL Peak in CdS:Mn^{+2} sample has shifted towards 580nm due to $\left[{}^4T_1 \rightarrow {}^6A_1 \right]$ transition in Mn^{+2} ions.

1. Introduction

Optical properties of semiconductor nanoparticles have been widely studied in recent years [1-3]. In particular, the nanoparticle quantum dots can exhibit extraordinary optical properties that are strongly dependent on their size and shape [4-6].

CdS is an important direct band gap II–VI semiconductor, typically 2.42 eV at room temperature. Due to unique and excellent optical and electrical properties, CdS nanoparticles find wide application in modern technology such as light emitting diodes, solar cells, biological labels, bio sensors and optical devises based on non-liner optical properties [7-10].

Until now, various approaches have been developed to prepare and control the size and shape of CdS nanoparticles [1-6]. Many of researchers have focused on improving and controlling the optical properties of these structures [11-12].

CdS and Mn-doped CdS nanoparticles are conventionally synthesized by thermo-chemical, hydrothermal, sol–gel, reverse micelle, photo-chemical and dark growth method, etc. [7, 13-19]. Among these methods, dark growth method

is simple, inexpensive, high yield producing and is not time consuming. Also this method can be employed at room temperature. In spite of the mentioned advantages of this method, there is no report on doping of CdS quantum dots (QDs) by this technique.

In the present work, we have successfully synthesized not only CdS but also for the first time Mn-doped CdS nanoparticles by simple dark growth method. We have used distilled water as the reaction medium and thioglycerol (TG) as capping agent in order to prevent particle growth and agglomeration.

The photoluminescence and structural properties of CdS and CdS:Mn nanoparticles have been investigated using UV-Vis, photoluminescence (PL) and X-ray diffraction (XRD) spectroscopy methods .

2. Experimental procedure

All the chemical materials containing $3Cd(SO_4).8H_2O$, $Na_2S_2O_3.5H_2O$, $MnSO_4.H_2O$, $C_3H_8O_2S$ and NH_3 were purchased from Merck company. Two separate solutions containing 1mM (mmol/l^{-1}) of $CdSO_4$ and 50mM of $Na_2S_2O_3$ were both prepared in 15ml of distilled water. The two solutions were mixed under vigorous stirring condition and then 20 ml aqueous solution of TG with 0.5 mM concentration was added to the prepared solution as the capping agent. Three different solutions with pH values of 5, 6 and 7 were prepared using diluted solution of NH_4OH.

For preparing Mn-doped CdS nanoparticles, the appropriate amount of $MnSO_4$ (Mn:Cd ratios of 1, 3, 6, and 10%) was added to the aqueous solution of Cadmium and Sulfur and then followed the same procedure.

The solutions were left in dark place at room temperature for a few days and were continuously monitored for transmittance and photoluminescence analysis.

3. Results and discussion

3.1 Optical properties of CdS nanoparticles

Room-temperature UV-Vis absorption spectra of the samples were obtained using a Shimadzu UV-1650PC UV-Vis spectro-photometer. Figure 1 presents the UV-Vis spectra of the colloids in different times after synthesis. Radius of the semiconductor QDs was calculated using the effective mass approximation method [20]. The nanoparticles diameter was found initially 2.5nm on average and kept increasing by lapsing time. Our observation also showed that the particles size in the first day after reaction reached to 4.1nm with the highest growth rate. After 1 month the particles reached their bulk size, i. e., 6nm. It is seen that the absorption edge is blue shifted with decreasing size due to quantum confinement effect.
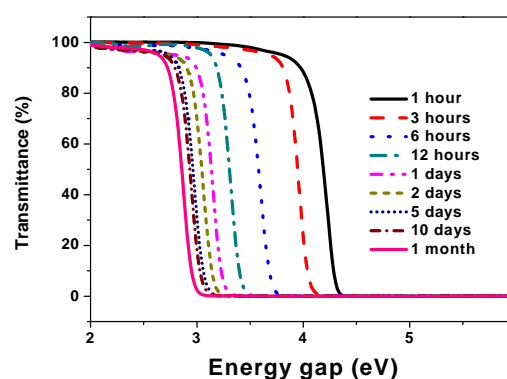

Fig. 1. UV-Vis spectra of CdS QDs after 1, 3, 6 and 12 hours and after 1, 2, 5, 10 and 30 days from synthesis.

Also the color of the initial solution turned slightly yellow after ten days which is another

indication of increment in the size of CdS nanoparticles due to lapse of time.

3.2 PL Spectra

3.2.1 Investigation on photoluminescence time dependent properties

PL emission was collected through an optical fiber and measured using an Avantes spectrometer (AvaSpec-2048 TEC). The evolution of PL spectrum of the particles during 10 days is shown in Fig. 2. The samples were excited with 365nm UV light. The prepared CdS nanoparticles exhibit PL emission covering almost in the whole visible range of 450–650 nm wavelength of the spectrum, originating from the recombination of surface states.

PL peak of obtained CdS QDs was found to gradually shift from 480 to 570nm. This red-shift of PL peak is due to the increasing of QDs size as expected. It can be seen that the intensity of PL increased by lapsing time and reached to its maximum value after 5 days.
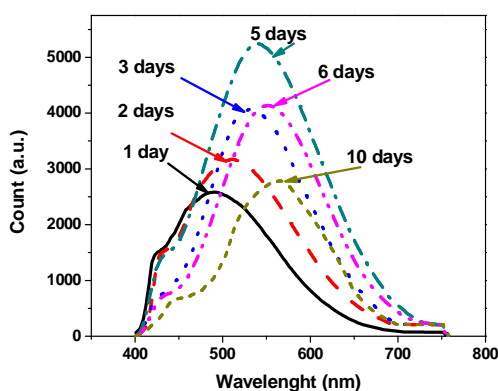

Fig. 2. photoluminescence spectra of CdS QDs 1, 2, 3, 5, 6 and 10 days after synthesis.

Surface trap states allow radiative recombination and enhance luminescence. Broad low energy PL spectrum is usually attributed to

trap state emissions arising from surface defect sites [21]. Thus the emission band observed in the sample could be assigned to the electron-hole recombination at surface traps for CdS QDs.

3.2.2 Influence of pH value on PL emission

In order to investigate the influence of pH value on the PL of CdS QDs, three aqueous solutions with pH values of 5, 6 and 7 were prepared. Evolution of PL intensity and position of these solutions 5 days after synthesis is given in table 1. It is found that the PL peak is shifted toward the shorter wavelengths upon increasing pH value and the maximum of PL intensity was obtained at pH=6.

In fact, the reaction rate in the solution with pH equal to 6 is so slow that the particles have enough time to arrange in appropriate positions and QDs with high crystallinity are obtained. Also these QDs showed better emission than the solutions with other pH value.

Table 1. Evolution of PL intensity and position of CdS QDs prepared at 5, 6 and 7 pH values

pH value	5	6	7
PL intensity (a. u.)	4628.9	5243.6	3601.9
PL Position (nm)	555.9	540.6	532.7

3.2.3 Influence of Manganese impurity

In order to investigate the influence of impurity on PL characteristics of the samples, aqueous solutions with different Mn^{+2} mole percent of 1, 3, 6, and 10% as dopant were prepared. Photoluminescence spectra of samples are shown in figure 3 and data of this spectrum are given in the table 2.
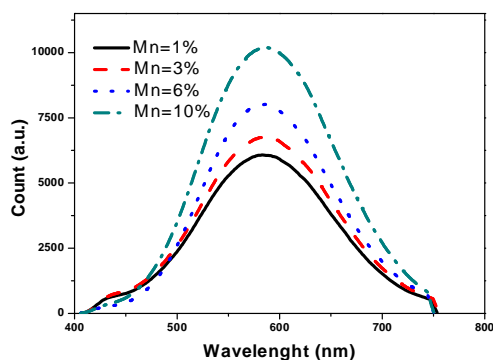
Fig. 3. PL spectra of CdS:Mn^{+2} QDs with 1, 3, 6 and 10 mole percent of manganese 5 days after synthesis.

Table 2. PL evolution CdS:Mn^{+2} QDs with different mole percent of Mn^{+2}

Mn	1%	3%	6%	10%
PL intensity (a. u.)	6076.7	6753.6	8016.6	10187
PL Position (nm)	583.1	584.8	585.9	587.1

Orange emission peak was found around 580nm in Fig. 3 which is originated from $^{4}T_{1} \rightarrow ^{6}A_{1}$ transition of Mn^{+2} ions in the CdS host [12, 13]. The presence of broad emission peak indicates that there is also emission from shallow trap states. Enhancement of the band emission could be due to the possible chemical binding between CdS surface and hydroxyl group.

4. Structural studies of CdS nanoparticles

The X-ray diffraction (XRD) analysis of the centrifuged and extracted CdS nanoparticles from the solution was performed using a X́ Pert MPD system with Cu-Kα with 0.154 nm wavelength. Figure 4 demonstrates the XRD patterns of CdS and CdS:Mn QDs.
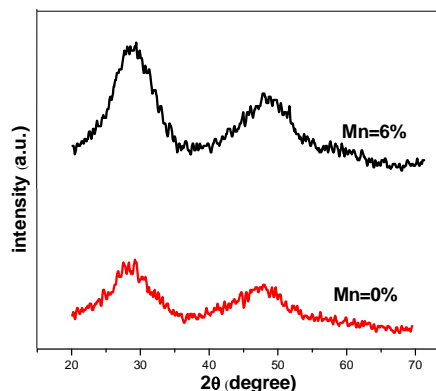

Fig. 4. XRD patterns of CdS and CdS:Mn QDs.

The above figure shows two clear peaks at 28° and 47° that respectively correspond to (101) and (103) planes of hexagonal phase of CdS nanoparticles which are consistent with the values in the standard JCPDS database.

5. Conclusion

Photoluminescent CdS and Mn^{+2} doped CdS QDs have been synthesized by simple dark growth method. We have presented absorption and PL spectra for CdS and CdS:Mn^{+2} nanoparticles. PL of CdS QDs covered almost the whole visible range (480-650nm) of spectrum that originated from recombination of electron-hole at surface trap states. Doping of CdS with Mn^{+2} is found to enhance the PL intensity. PL emission of CdS:Mn^{+2} nanoparticles observed at 580nm is attributed to $^{4}T_{1} \rightarrow ^{6}A_{1}$ transition. It is found that pH and percentage of Mn^{+2} ions play important roles in controlling the PL intensity and position of nanoparticles. PL has altered by lapsing time and reached to its maximum 5 days after synthesis for the solution with pH=6.

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