

Shifting of Fluorescence Peak in CdS Nanoparticles by Excitation Wavelength Change

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Received: 31 March 2010 / Accepted: 29 December 2010 / Published online: 19 January 2011
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Abstract CdS nanoparticles with different size are prepared by chemical bath deposition method. These particles show strong fluorescence at emission wavelength of 507 nm. It has been observed that this emission peak changes through a range of 147 nm, by varying the excitation wavelengths through 370–480 nm. The emission peak can thus be tuned by varying the excitation wavelengths. This peak emission wavelength shift is due to the selective excitation of vibronic levels in the surface state of the CdS nanoparticles.

Keywords Nanoparticles · Optical absorption · Fluorescence

PACS Code 78.67.Bf · 78.40.-q · 81.07.-b

Introduction

Semiconductor nanoparticles are very important class of materials for the optical studies due to their strong size dependence of spectral properties [1–3]. As a result they are among the best candidates for the applications such as the display devices [4], biological labeling [5], and optoelec-

tronic devices [6] as well as for nonlinear optical studies [7]. In a semiconductor nanoparticle, many physical properties become size dependent, when the size of the nanoparticle becomes comparable to the Bohr radius of the bulk material. The main change in the optical properties is the blue shift of the excitonic peak in the absorption spectrum as the particle size reduces to the nano-level and this is evidently due to the confinement effect occurring in the nano-regime [8]. There is also a shift for the fluorescence emission when the particle size is reduced to nano-level. As the nano-particles are characterized by large surface to volume ratio, they exhibit certain surface state effects and corresponding changes in the emission properties [9]. Thus the optical properties of semiconductor particles become strongly dependent on the effective particle size.

Among II–IV semiconductor family, the CdS nanoparticles are materials which are intensively studied. Optical properties of CdS nanocrystals have been investigated exhaustively; however, there are only few experimental studies related to the excitation wavelength dependent fluorescence emission in CdS nanocrystal. In the nano-regime, of the order of 6 nm in CdS, electronic and optical properties strongly depend on size, shape, and surface properties. In general only a few measurements are carried out to study the excitation wavelength dependent fluorescence in the nano-particles [10, 11]. In the case of CdS/dendrimer nano-composites, J. R. Lakowicz et al. [10] reported peak emission wavelength shift around 40 nm. In the present work, it has been observed that there is much larger shift for the emission peak through a range of 147 nm, when excited through 370–480 nm for CdS nanoparticles. Further by varying the excitation wavelength, the emission peak can be tuned through this fairly wide range of wavelengths.

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Experimental Details

CdS nanoparticles are prepared by precipitation technique from CdSO₄, using thiourea and NH₄OH [12, 13]. All the chemicals are of GR grade from Merck Ltd. In this work, particles of different size are prepared by mixing aqueous solution of CdSO₄ of different concentrations range from 0.1 M to 0.01 M with aqueous solution of thiourea (0.2 M to 0.02 M concentrations). The pH of the mixture solution is kept at 10.5 by adding NH₄OH. The mixture is heated at 70 °C and stirred for 1 ½ hour. The colour of the solution changed to yellow and precipitation occurs. The precipitated CdS particles are filtered, washed and dried. Dimethyl formamide (DMF) is selected as the dispersive medium for the study. The collected particles are dispersed in DMF by ultra sonification and measurement of their light absorption at room temperature is carried out using a spectrophotometer (JascoV-570 UV/VIS/IR). The fluorescence emission from the same is recorded using a Cary Eclipse fluorescence spectrophotometer (Varian). The structural properties of the samples are investigated by X-ray diffraction (XRD) on a Bruker AXS D8 Advance x-ray diffractometer with Ni-filtered Cu K α (1.5406 Å) source.

Results and Discussions

Optical Absorption Studies

The UV-VIS absorption spectrum of the CdS nanoparticles dispersed in DMF is shown in Fig. 1.

The reported absorption edge for the bulk hexagonal CdS is at 512 nm (2.42 eV) [2]. Comparing with the bulk

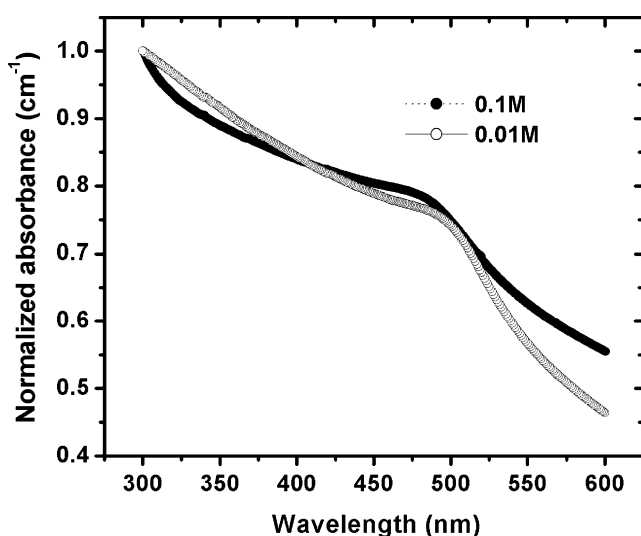


Fig. 1 Absorption spectra of particles obtained from precursor solution of concentration. a 0.01 M & 0.1 M

CdS, it is observed that there is blue shift of absorption edge and it is well-known that the blue shift in the absorption peak is obviously caused by the quantum confinement effect [8]. From Fig. 1, it is clear that there is a slight blue shift in absorption edge of the CdS nanoparticles when the concentration of precursor solution in the preparation changed from 0.01 M to 0.1 M. These results are the manifestations of quantum confinement occurring at nanolevel. The absorption spectra observed here for these particles are the same as those in the literature [14, 15].

The particle size of the CdS particles can be calculated using Brus formula based on the band gap value obtained from the absorption spectra [8]. The calculated bandgap values of these CdS nanoparticles are 2.5 eV and 2.56 eV. The approximate calculated sizes of the particles prepared from different concentrations (0.01 M and 0.1 M) of precursor solution are 9 nm (S1 particles) and 6 nm (S2 particles).

X-Ray Diffraction Studies

A typical XRD pattern of the prepared CdS nanoparticles is as shown in Fig. 2. Three broad peaks at $2\theta = 26.7^\circ$, 44° and 52° belonging to (1 1 1), (2 2 0) and (3 1 1) respectively, which are in agreement with Miller indices of a cubic zinc-blende-type structure (JCPDS file no. 10454). Mixture of hexagonal and cubic phases is routinely observed in nanoparticles of CdS, as the two phases have similar energy and, hence, the transformation from one to another is most feasible [16]. It is reported that the particle size plays an important role in deciding the crystal structure. With reduction in the size, the material goes from the hexagonal wurtzite-type structure to the cubic zinc blende-type structure if the particle size is below 5 nm, above this value, the material will have a mixture of both phases. In the present pattern, the peak located at 26.7° is more symmetric and (1 0 3) peak at 48° of hexagonal phase is absent. This shows that the present nanoparticles exhibit cubic phase due to their small particle size. Using Debye–Scherrer's formula $D = 0.89\lambda/\beta \cos(\theta)$, (where D is the particle diameter, λ is the wavelength of x-ray used, β is the full width half maximum and θ is the scattering angle), the estimated particle size is in the range of 5 nm, which is quite close to the size estimated from optical absorption measurements.

Scanning electron microscopy (SEM) of CdS powder was performed on JEOL Model JSM-6390LV. A gold film was evaporated on the samples before loading on the instrument. SEM of the powder indicated the formation of fine spherical particles of cadmium sulphide and the majority of the particles looked in the range of below 100 nm (Fig. 3).

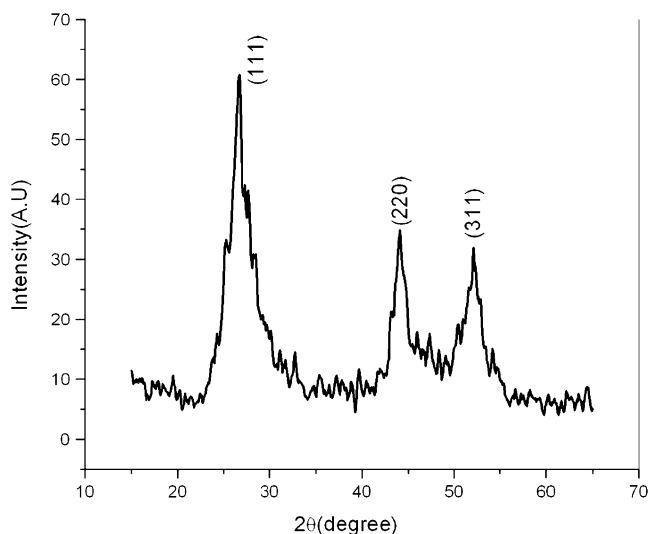


Fig. 2 A typical XRD pattern of CdS nanoparticles S2

Fluorescence Studies

Figure 4 shows the PL spectrum of S1 particles when excited with wavelength 380 nm. It shows two bands of emissions one around 423 nm and other around 520 nm when excited with 380 nm wavelength. There is a small emission peak at 486 nm. 423 nm and 486 nm emissions are assigned to the excitonic emissions.

As CdS has a broadband absorption, excitation spectrum is very significant in finding the optimum excitation wavelengths at which it has maximum emission intensity. Figure 5 shows the excitation spectrum for an emission peak of 423 nm and 520 nm. For 423 nm emission, the excitation spectrum shows peaks at 274 nm and 376 nm. Also for 520 nm emission wavelength, there exists a peak at 274 nm and another peak at 380 nm that is a shift of 4 nm to the later peak with respect to the 423 nm emission. The fluorescence spectra of CdS nanoparticles under

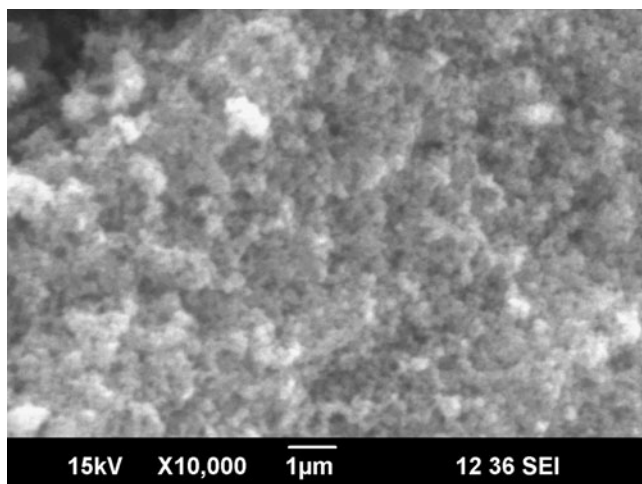


Fig. 3 SEM of S1 particles

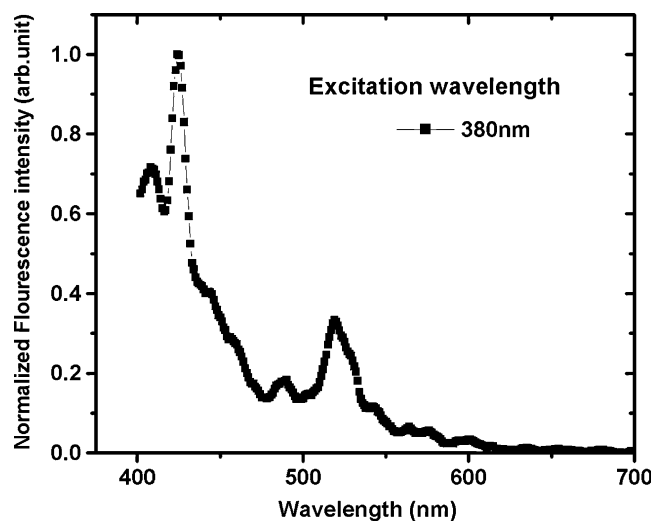


Fig. 4 Emission spectra of S1 particles when excited with excitation wavelength of 380 nm

different excitation wavelengths of 274 nm, 376 nm and 380 nm are shown in Fig. 6. Results show that at the excitation of 274 nm, there is an emission at 492 nm and a broad emission band around 540 nm. Also at excitation of 376 nm and 380 nm, the emission peaks at 516 nm and 520 nm occur. That is, when excitation wavelength is changed from 376 nm to 380 nm, the emission peak at 516 nm is shifted to 520 nm, i.e., a shift of 4 nm, which indicates an excitation wavelength dependent shift. This observation indicates the effect on this emission peak under different excitation wavelengths. Hence the fluorescence spectra for different excitation wavelengths could lead to interesting results. The fluorescence spectrum of S1 particles for different excitation wavelengths is shown in Fig. 7.

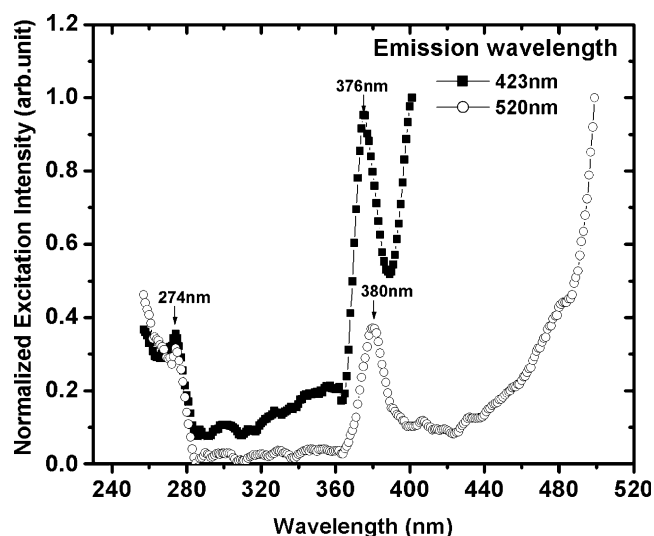


Fig. 5 Excitation spectra for emission wavelengths 423 nm and 520 nm of S1 particles

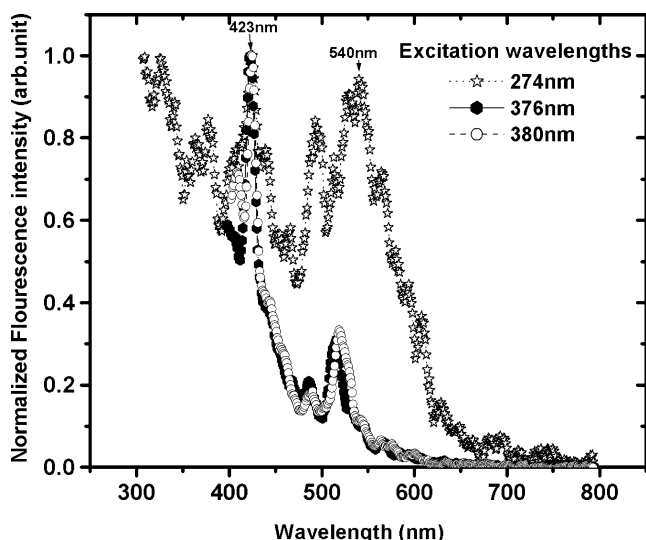


Fig. 6 Emission spectra of S1 particles when excited with excitation peaks of 274 nm, 376 nm and 380 nm

It is observed that the emission peak wavelength for these S1 particles differ with the variation in the excitation wavelengths from 370–480 nm. Figure 7a shows the variation of peak shift for shorter range of excitation wavelengths (370–420 nm). When S1 particles are excited with 370 nm, there are three peaks at 421 nm, 485 nm, 507 nm and a shoulder at 454 nm in the fluorescence spectrum. 507 nm peak is shifted to 545 nm, when excitation wavelength is changed to 400 nm. This peak at 545 nm is again shifted to 575 nm when the excitation wavelength is changed to 420 nm. For all excitation wavelengths from 380 nm to 420 nm, there is a weak peak present at 486 nm. In Fig. 7b, the emission peak at 575 nm is shifted to 601 nm for the excitation wavelength of 440 nm. The above trend in the emission peak shift is continued up to the excitation wavelength of 480 nm, at which the emission peak occurs at 654 nm. For excitation wavelengths longer than 480 nm, the emission peak intensity is very weak and further peak shift can not be verified. Thus it is found that among four spectral peaks (421 nm, 454 nm, 486 nm, 507 nm), the shift occurs only for 507 nm peak, when excited with different wavelengths. The emissions at 421 nm, 454 nm and 486 nm are from the excitonic levels [17–19]. The emissions at 421 nm, 450 nm and 486 nm are not shifted for these particles, which indicates that the change in the particle size does not affect the emission band associated with the nanocrystallite core [7, 8].

In the present case, the emission peaks at 423 nm, 450 nm and 486 nm are assigned to the excitonic emissions. The emission peak at 507 nm is shifted with the change in excitation wavelengths. These shifting emission peaks occurring at larger wavelengths with respect to the band

edge emission are attributed to the quasi-free recombination at the absorption band edge, the shallow-trap state near the absorption band edge, the deep-trap band far below the band edge, and a combination of these effects, are called the surface state emissions. Surface state is generally localized within the band gap of the semiconductor and they can trap the excited state electrons and lead to red-shifted emissions. The quasi free recombination and shallow trap emission could be overlapping due to broad size distribution. In this experiment, the possible trapped states may come from the anion (S^{2-}) or cation (Cd^{2+}) vacancy defects. If the trapped states were generated by the cation vacancy, such trapped states would have located at 1.5 eV above the valance band [9]. Recombination from conduction band to such trapped

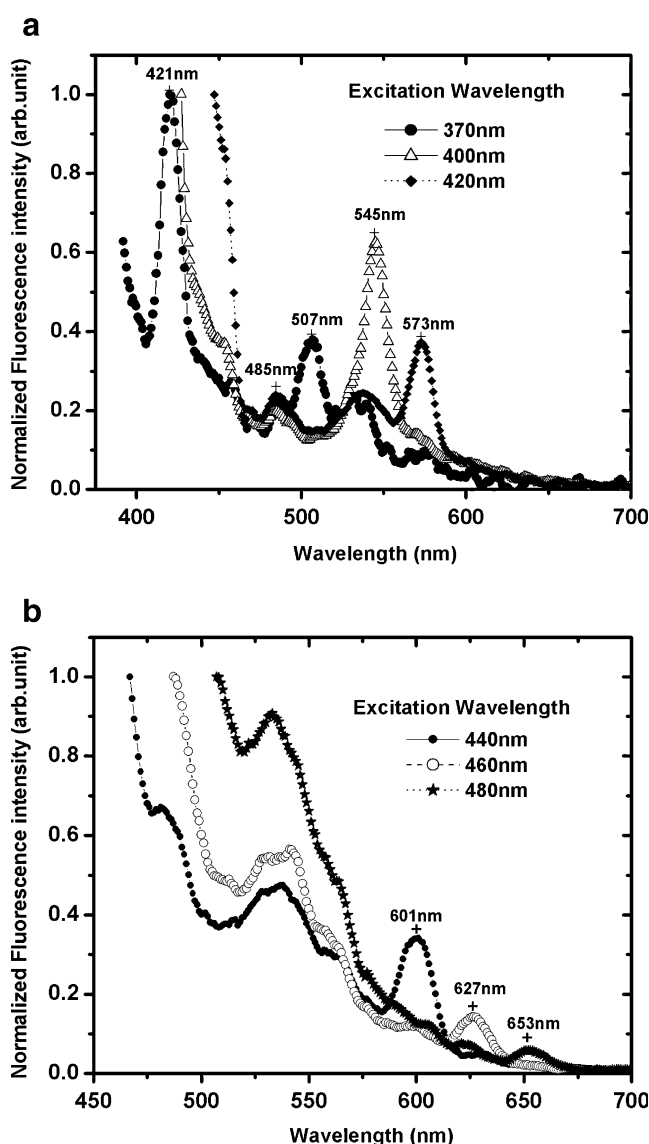
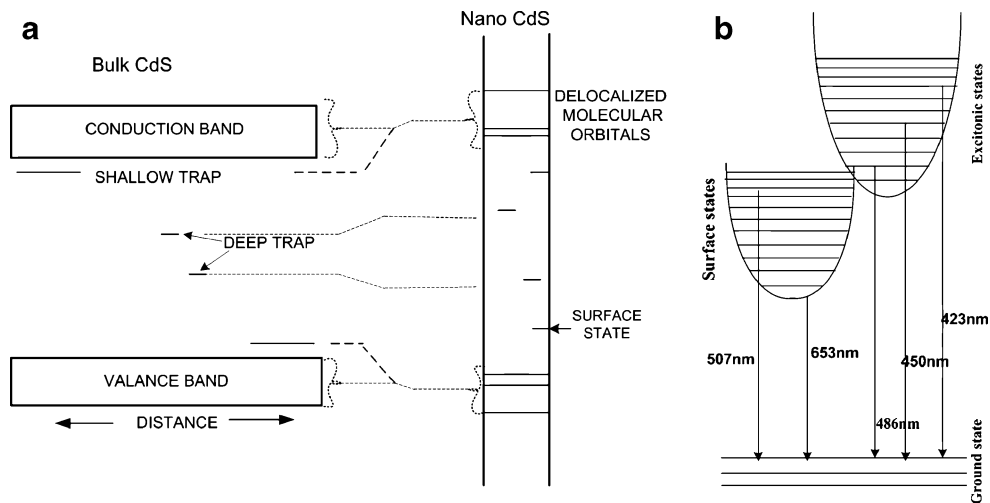


Fig. 7 Emission spectra of S1 particles when excited with **a** lower wavelengths (370–420 nm) and **b** higher wavelengths (440–480 nm)

Fig. 8 **a** Spatial electronic state correlation diagram **b** Emissions in two wells of CdS nanoparticles



states would have resulted in a weak emission with a wavelength of 700–760 nm, in both samples which was not observed. So these emissions can be assigned to the shallow trapped states recombination formed by sulphur vacancy defects. It is reported that S^{2-} vacancy defect in CdS nanoparticles are located at about 0.6 eV–0.7 eV below the conduction band. That is, if an electron is trapped by this anion vacancy defect, one can expect a photoluminescence blue shift with respect to the E_g as the band gap in the CdS nanocrystals are size-dependent [9, 21]. A typical spatial electronic state for CdS nanoparticles is shown in Fig. 8a. From Fig. 8a it is clear that when dimension of the CdS nanoparticles approach the shallow trap diameter, the shallow trap wave function overlaps strongly with the corresponding valence or conduction band wave function [21].

The peak emission shift is manifested above the emission wavelength of 507 nm which is found to be the band edge emission of these nanoparticles and it is blue-shifted from bulk emission of 520 nm due to the quantum confinement effect. This emission peak shift can be explained on the basis of a double well model which incorporates the surface states to account for the excited electronic states [20] in the CdS nanoparticles as shown in Fig. 8b. Here one of the wells accounts for the excitonic or intrinsic core state emission and the second well is for the surface state emission. These two wells overlap when the dimensions of CdS nanoparticles become close to the shallow trap diameter.

This peak emission wavelength shift is due to the selective excitation of vibronic levels in the surface state of the CdS nanoparticles. The trapping process is reported to be fast (hundreds of femtosecond) and consequently the spontaneous fluorescence cannot compete with it [20]. So the energy transfer between the upper vibrational level and lower vibrational level of the excited

state of the particle becomes inefficient due to this shortening of life time, which leads to the excitation wavelength dependent emission characteristics of these nanoparticles.

There is a band structure around 532 nm, which ranges from 517 nm to 572 nm, for the excitations from 440 nm to 480 nm. This broad band luminescence can be attributed to the midgap states and this occurs normally with low intensity [19].

The fluorescence spectrum of S2 particles also shows a similar shift of emission peaks as shown in Fig. 9.

From Fig. 9, it is clear that the main peak observed for S2 particles is at 421 nm which is same as that of the S1 particles, when excited with 370 nm. The second prominent emission peak is at 506 nm which is 1 nm blue shifted when compared to that of S1 particles. This peak emission

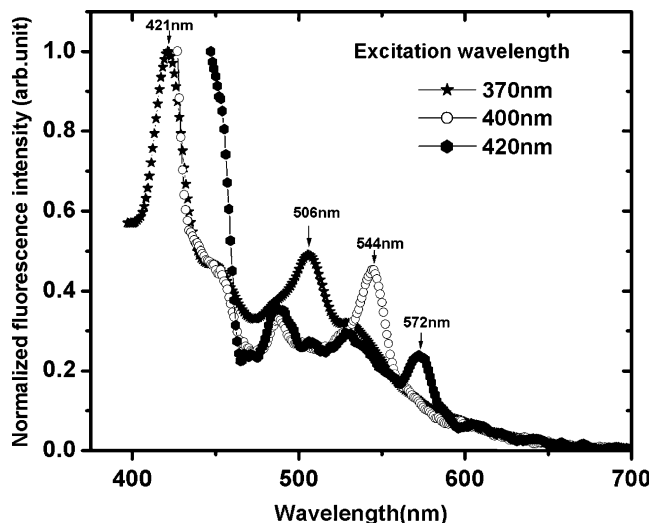


Fig. 9 Emission spectra of S2 particles for excitation wavelengths (370–420 nm)

wavelength is shifted from 506 nm to 572 nm when the excitation wavelength is changed from 370 nm to 420 nm. For 440 nm excitation wavelength, the emission peak is very weak. Thus, it can be stated that the peak emission wavelength shift is not observed from excitation wavelength of 440 nm onwards.

The size dependence of photoluminescence (emission around 520 nm) with respect to S1 and S2 particles reveals that trapped carriers at the surface states are also confined by the spatial-confinement effect. The energy of surface state can also be modified through quantum size effect, which is similar to the case of the exciton confinement.

Conclusion

In this work, we observed that the fluorescence behaviour of the CdS nanoparticles, prepared by precipitation technique, depends on excitation wavelength. It is found that the peak emission wavelength can be shifted by as much as 147 nm by varying the excitation wavelengths and the reason for this phenomenon is the selective excitation of the surface states in the nanoparticles. This provides certain amount of tunability for the emission which results from surface states. Also a strong emission of bluish-green wavelength is observed for the smallest particles prepared.

Acknowledgments MS acknowledges CELOS (funded by UGC-Govt. of India) for research fellowship. SAJ is thankful to UGC for financial assistance. The authors are grateful to CELOS for the experimental facilities.

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