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Highly luminescent CdSe nanoparticles embedded in silica thin films

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Abstract Thin films of luminescent CdSe nanoparticles with and without silica capping were prepared using sol-gel method. The blue shift observed in the optical absorption spectra suggested quantum confinement effect in the prepared films. The films showed photoluminescence emission in the range of 510–590 nm depending upon the particle size of CdSe particles. The emission intensity increased when CdSe particles were embedded in silica matrix. The emission intensity was found to decrease with aging for the films containing CdSe particles without silica capping when they were exposed in relatively humid air (relative humidity 80%). The films containing CdSe nanoparticles embedded in silica matrix showed more stable behavior. The emission intensity practically remained constant with aging in humid atmosphere.

Keywords Nanoparticles · Luminescence · Thin film

1 Introduction

Semiconductor nanoparticles have attracted great interest in both theoretical and applied research areas [1–4] due to their size- and shape-dependent physical properties. CdSe, an important member of luminescent II–VI family having bright luminescence in the visible range of optical spectra, has shown potential to be used in nanocrystalline form in biological field [5, 6], displays [7, 8], diodes and lasers [1], solar cells [9–12] and gas sensors [13–15]. A special class of materials having improved physical properties can be obtained by incorporating semiconductor nanoparticles in a non-conducting (dielectric) matrix [16, 17]. The shell/matrix determines the charge, functionality, and reactivity of the nanoparticle surface and enhance the stability and dispersibility of the core. Encasing the nanoparticles in a shell of different compositions may also protect the core from extraneous chemical and physical changes. Protection can be achieved against agglomeration of the particles caused by strong van der Waals attractive forces and also against nanoparticle degradation as a result of chemical etching by this capping procedure. Collective properties of nanoparticle assemblies are influenced to a large extent by the separation between the particles. Coating the particles with a uniform shell of inert material could control the distance between the particles, which in turn can control the optical, luminescence and electrical properties of this class of materials. Modification in physical properties of the semiconductor nanoparticle due to presence of surrounding dielectric matrix has been studied by different groups [18–24]. Influence of dielectric matrix on third order optical nonlinearity for CdSe nanocrystals embedded in RF-sputtered glass thin films was investigated by Nasu et al. [18]. Mane et al. [19] reported improved properties of dense TiO_2/CdSe coupled thin films synthesized by chemical route at low temperature ($<100^{\circ}$C). Manolis et al. [20] performed photoreflectance study on multilayered structures of nanocrystalline CdSe in insulator matrix like SiO_x and GeS_2. Correa-Duarte et al. [21] reported silica coating to stabilize CdS nanoparticles against

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photo-degradation; however the effect of silica coating on the luminescence property was not reported. Lifshitz et al. [22] studied optical properties of CdSe nanoparticle films prepared by chemical deposition and sol-gel methods. Highly luminescent semiconductor nanoparticles were successfully incorporated in ZrO_2-SiO_2 sol-gel glass film [23]. The chemistry occurring at the CdSe/Si, CdSe/SiO, and CdSe/SiO_2 interfaces has been investigated [24].

In spite of the existence of such large amount of work in this field, very few reports are available that demonstrate the systematic control of physical properties of matrix embedded nanoparticles in thin film form employing sol-gel technique [16]. This study reports sol-gel synthesis of very stable, highly luminescent composite thin films containing CdSe nanoparticles embedded in SiO_2 matrix having controllable optical properties. The films showed significant improvement in material properties compared to the thin films of bare CdSe nanoparticles.

2 Experimental

To prepare the thin films with CdSe nanoparticles embedded in silica matrix, the following method was adopted. A silica sol served as the precursor for the host films was first prepared by dissolving tetraethyl orthosilicate, $Si(OC_2H_5)_4$ (TEOS, Merck) in 2-propanol, $(CH_3)_2CHOH$ (Merck), followed by drying over activated molecular sieve zeolite 4A and adding distilled water. Hydrochloric acid (0.1N, Merck) was used as a catalyst. A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (Merck) mixed with selenourea, NH_2CSeNH_2 (Merck) was prepared in 2-propanol and distilled water to be the source for cadmium and selenium, respectively. The as-prepared solution was slowly added into the silica sol under vigorous stirring and the stirring was continued for 1–2 h after the completion of mixing to obtain the final sol ready for the fabrication of films. The equivalent molar ratio of silica to cadmium selenide was 70:30. To prepare CdSe thin film without silica matrix for comparison, the silica sol was not added to the solution containing cadmium and selenium precursors.

Using the above sols, spin coated thin films were fabricated on properly cleaned quartz glass substrates (25×25 mm). All the as-deposited films were colorless. The as-deposited films were annealed in vacuum at different temperatures (from 473 to 673 K, with 50 K intervals) for a fixed time of 30 min to study the nucleation and growth of CdSe nanoparticles in SiO_2 matrix. CdSe films without silica capping were annealed under same conditions for comparison with the silica capped particles. The films turned pale orange when annealed above 450 K, and the color was found to be getting darker with increasing annealing temperature. Transmission electron microscopy (TEM) was performed using a Hitachi H-7100 microscope. Films scratched from the quartz substrate were carefully placed on the carbon coated Cu grid for TEM study. Optical absorption spectra were recorded using a spectrophotometer (Hitachi-U3410) at the room temperature with a resolution of $\lambda \sim 0.07$ nm along with a photometric accuracy of $\pm 0.3\%$. Photoluminescence (PL) measurement was carried out using a Hitachi F-4500 fluorescence spectrophotometer. Fourier transformed infrared (FTIR) absorption spectra were recorded by using an IR spectrometer (Nicolet, Magna-IR). X-ray photoelectron spectroscopic (XPS) measurements were performed on commercial VG Microtech (MT-500) machine using Mg K_α radiation.

3 Result and discussions

3.1 Microstructural study

Figures 1(a) and (b) show respectively the TEM and the corresponding electron diffraction patterns of CdSe and CdSe-SiO_2 films, annealed at 673 K for 30 min. Well dispersed nanoparticles with an average particle size of 7.5 nm for

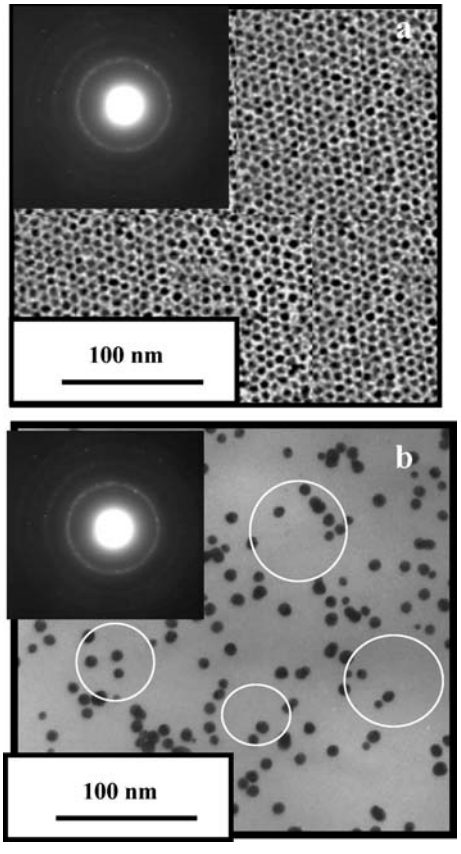

Fig. 1 Transmission electron micrographs (TEM) and corresponding Electron Diffraction patterns of the films annealed at 673 K for 30 min: (a) thin films containing CdSe nanoparticles embedded in silica matrix and (b) thin films containing CdSe nanoparticles without silica matrix. Circles highlight the particle agglomeration (b), which did not occur in the case of silica (a) capping under same experimental conditions

Table 1 Comparison between particle sizes obtained from TEM study and blue shift of optical band gap for CdSe and CdSe-SiO_2 films when annealed at different temperatures for 30 min.

	CdSe films		CdSe-SiO_2 films	
Annealing temperature (K)	Particle size (nm) from TEM	Particle size (nm) from blue shift	Particle size (nm) from TEM	Particle size (nm) from blue shift
473	4.0	3.86	3.5	3.29
523	5.1	5.24	4.0	3.98
573	6.0	5.93	4.5	4.47
623	6.5	6.47	5.1	4.95
673	7.5	7.39	5.5	5.42

CdSe and 5.5 nm for CdSe-SiO_2 films were found under the above mentioned annealing condition. Diffraction patterns showed central halos with concentric ring patterns. Ring patterns showed reflections from (111), (220) and (311) planes, indicating the formation of cubic phase for CdSe in both set of films. Average partcle size changed from 4 to 7.5 nm for the set of CdSe films and 3.5 to 5.5 nm for the set of CdSe-SiO_2 films when they were annealed from 473 to 673 K in a step of 50 K (Table 1). It was clear from the micrographs that the films containing CdSe nanoparticles without silica capping tend to lose their nanocrystalline nature with increasing annealing temperature at a faster rate when compared to the CdSe-SiO_2 films (Fig. 1(b)). In the films containing CdSe nanoparticles embedded in silica matrix, the CdSe particles were completely capped inside the silica matrix (Fig. 1(a)). The distance among the nanoparticles did not favor the possible coalescence with one another through silica barrier. Thus silica capping made the particles more stable against agglomeration when the annealing temperature was increased.

3.2 Fourier transformed infra red (FTIR) absorption study

FTIR has been employed to examine the chemical purity of CdSe-SiO_2 films annealed from 473 to 673 K. All the spectra (Fig. 2(a)–(e)) were found to be dominated by three

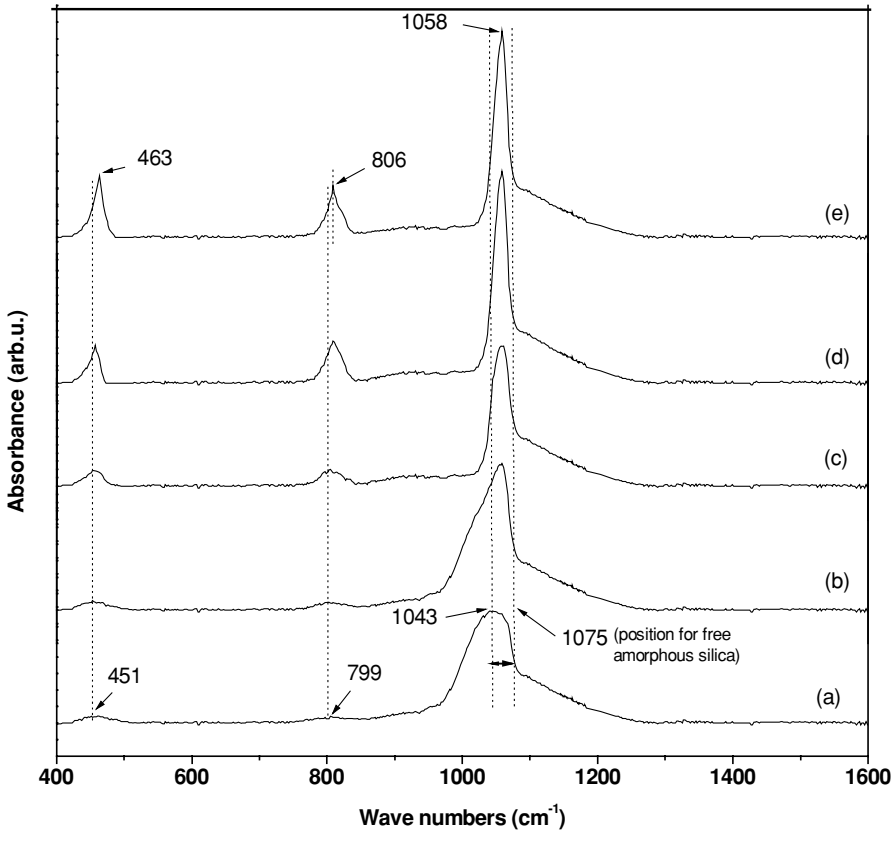

Fig. 2 Fourier transformed infra red (FTIR) absorption spectra of thin films containing CdSe nanoparticles embedded in SiO_2 matrix annealed for 30 min at (a) 473 K, (b) 523 K, (c) 573 K, (d) 623 K and (e) 673 K

absorption bands centered at frequencies about 450, 800 and 1050 cm^{-1}. The absorption peaks near 450, 800, and 1050 cm^{-1}were associated with the Si–O stretching modes [25]. The peak occurred at about 1050 $cm^{-1}$was due to the broad asymmetrical stretch of Si–O–Si and that at about 800 cm^{-1} was due to the symmetrical Si–O–Si stretch [26]. The peak at 1050 cm^{-1} is resulted from the oxygen atom stretching parallel to Si–O–Si and is also called the transverse optical (TO) mode [26]. The peak of the asymmetric stretching mode lied at a frequency lower than that of amorphous SiO_2 ($\sim$1075 cm^{-1}) [27] in all the films. Shifting of the band to the lower frequencies could be attributed to the partial bond formation with the surface Se atoms which eventually passivate the surface of CdSe nanoparticles. The absorption band related to Si—O—Si asymmetric stretching mode was found to become more intense with a narrower bandwidth for the films annealed at higher temperatures. The band was also found to be shifted gradually towards higher frequencies with increasing annealing temperature. Broadening of the band corresponding to the asymmetric stretching mode can be related to a statistical distribution of different bonding arrangements at each silicon atom site, and so to a structural inhomogeneity of the film [28]. On the other hand, the shift toward lower frequencies of the peak intensity can be ascribed to greater film porosity or lower packing density [28–30]. Thus the above observation clearly demonstrates the gradual densification of silica matrix with increasing annealing temperature.

The spectra showed no Se-O absorption peaks around 890 cm^{-1} as seen in bulk CdSe that had been oxidized [31]. No absorption peaks from bulk SeO_2or SeO_3 group were

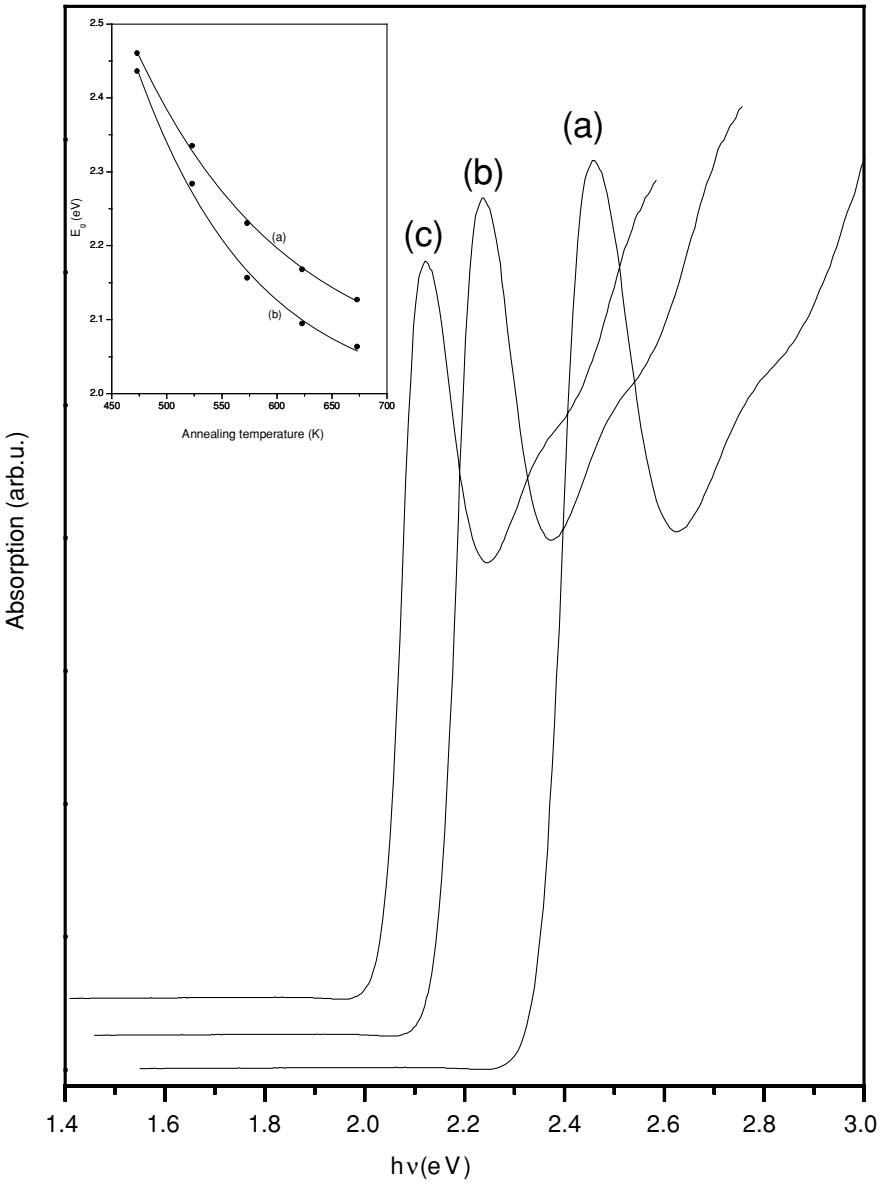

Fig. 3 Optical absorption spectra of thin films containing CdSe nanoparticles embedded in SiO_2 matrix annealed for 30 min at (a) 473 K, (b) 573 K and (c) 673 K. Inset shows variation of optical band gap (E_g) with annealing temperatures for (a) thin films containing CdSe nanoparticles embedded in silica matrix and (b) thin films containing CdSe nanoparticles without silica matrix

observed in the spectra within the range of 680–695 cm^{-1} [32]. These results strongly suggested that CdSe nanoparticles were completely passivated by the silica host and surface oxidation was prevented successfully in all of the capped films. No trace of residual precursors or any other impurities were found in the CdSe-SiO_2 films when annealed at and above 473 K.

3.3 Optical study

Optical absorption spectra were recorded for the films annealed at different temperatures (T). Some representative spectra for CdSe-SiO_2 films are shown in Fig. 3. The appearance of absorption peaks at higher energies as compared to the bulk material was indicative of the formation of CdSe nanoparticles. Absorption edges were red-shifted with increasing annealing temperature, indicating growth of the particles at higher annealing temperatures. It could be noticed that the line shape of the absorption spectrum with decreasing photon energy ($h\nu$) at the band edge was sharper for the films baked at higher temperatures, suggesting stronger band-tailing effect in the films containing smaller particles. The optical band gaps (E_g) were calculated using the conventional method by extrapolating the straight line portion of the $(\alpha h\nu)^2$ vs. $h\nu$ curve to $\alpha = 0$ (figure not shown), where α is the optical absorption coefficient derived from the absorption data. The band gaps for different films varied within the range of 2.46–2.12 eV, which were always greater than the bulk value of 1.75 eV at 293 K [33]. The increase in the fundamental band gap of the nanostructured material could be attributed to the quantum size effect [34]. The band gaps in different films varied with the annealing temperature as

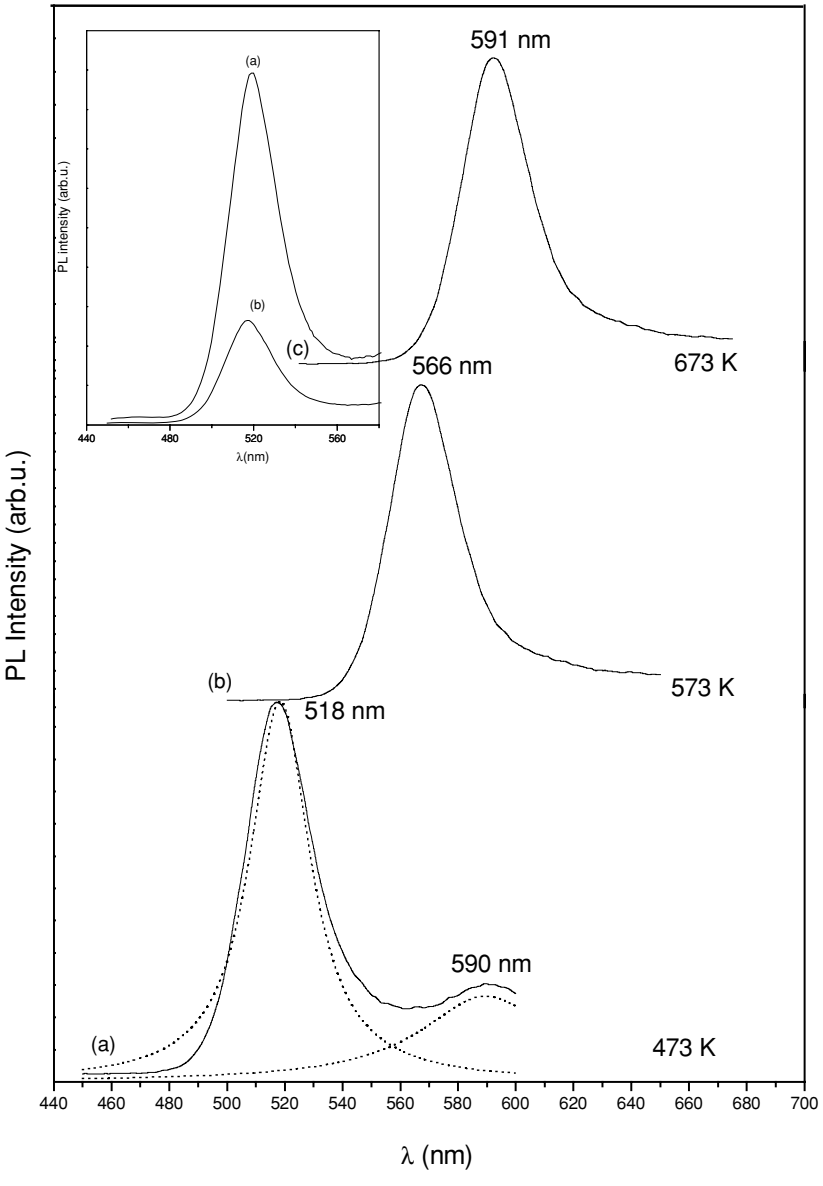

Fig. 4 Photoluminescence (PL) emission spectra of thin films containing CdSe nanoparticles without SiO_2 matrix annealed for 30 min at (a) 473 K, (b) 573 K and (c) 673 K. Inset shows photoluminescence (PL) emission spectra of (a) thin film containing CdSe nanoparticles embedded in silica matrix and (b) thin film containing CdSe nanoparticles without SiO_2 matrix, both annealed at 473 K for 30 min

shown in Fig. 3 (inset). This figure depicted that the band gap progressively decreased with increasing annealing temperature for both CdSe and CdSe-SiO_2 films. This observation is obviously an indication of the increase in particle size with increasing annealing temperature. The average particle sizes of the CdSe nanoparticles in the films with and without silica matrix were determined using the value of blue shift in the optical band gaps. The values obtained via this method match well with that form TEM as the results are shown in Table 1.

3.4 Photoluminescence (PL) study

Figure 4 shows photoluminescence (PL) emission spectra for three CdSe films recorded at room temperature using an excitation wavelength of 445 nm. The line shapes of PL peaks were smooth, symmetric and sharp in all cases. The Stoke-shifts of the emission were small (∼20–30 nm). No shift in peak position was observed with changing excitation energy, indicating band edge emissions. For the sample synthesized at 473 K, a less intense broad peak was observed at 590 nm in addition to the intense band-edge luminescence at 518 nm (Fig. 4(a)). Origin of this peak at lower energy could be attributed to the luminescence coming from the surface states. As this film was annealed at lower temperature, smaller particle size culminated higher surface to volume ratio of the nanoparticles present in this film giving rise of this Stoke shifted broad luminescence band. The films synthesized at elevated temperatures did not show luminescence

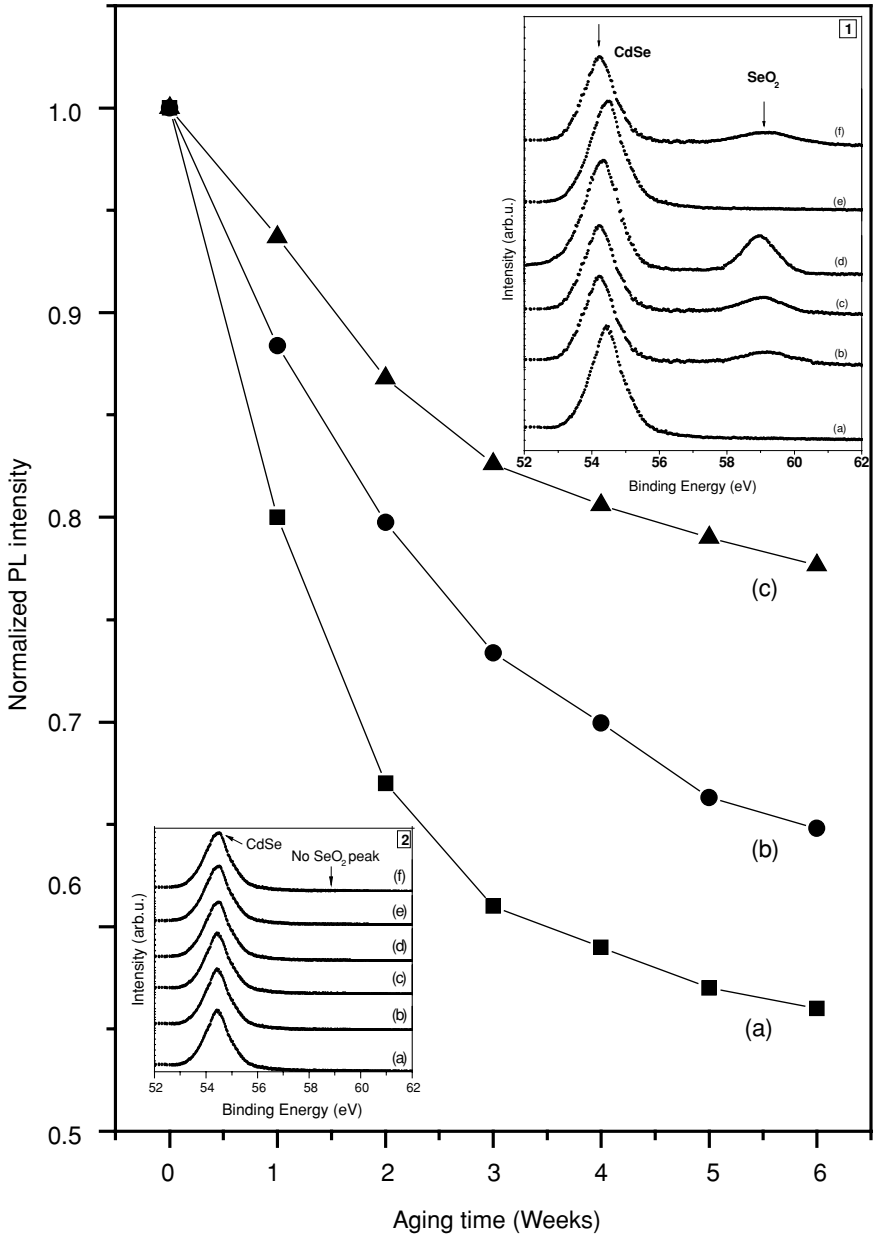

Fig. 5 Change in normalized intensity of emission peak with aging time (degradation curves) for CdSe films synthesized at different annealing temperatures: (a) 473 K, (b) 573 K and (d) 673 K. Inset 1 shows the X-ray Photoelectron spectra of Se 3d core level of a representative film (annealed at 573 K) containing bare CdSe nanoparticles after different period of aging: (a) freshly prepared, (b) 2 days, (c) 4 days, (d) 6 days, (e) 8 days and (f) 10 days. Inset 2 shows X-ray Photoelectron Spectra of Se 3d core level of a representative film (annealed at 573 K for 30 min) containing CdSe nanoparticles embedded in SiO_2 matrix after different period of aging: (a) freshly prepared, (b) 2 days, (c) 4 days, (d) 6 days, (e) 8 days and (f) 10 days

related to surface states, indicating particle growth and relatively lower surface-to-volume ratio in these films. The PL peaks were red-shifted with increasing annealing temperature as shown in the figure, revealing particle growth in the films. The full width at half maxima (FWHM) of the emission peaks were found to increase with increasing annealing temperature. Broadening trend of PL line shape could be related to the broadening of the particle size distribution with raising reaction temperature.

CdSe-SiO_2 films showed substantially higher luminescence compared to CdSe films prepared under the same experimental conditions (Fig. 4, inset). The increase in the luminescence intensity could be attributed to the surface passivation (supported by FTIR study) and subsequent reduction in the non-radiative recombination in the thin films containing CdSe nanoparticles embedded in silica matrices. The emission from CdSe-SiO_2 films also experienced red-shift with increasing annealing temperature, but at a slower rate compared to CdSe films.

3.5 Study on the effect of aging on luminescence property

The films were kept in air under the exposure of room light during the tenure of the aging experiments. The luminescence peak intensities normalized to the freshly prepared samples were investigated as a function of aging time in both sets of films with and without silica matrix. A loss in luminescence intensity with prolonging aging time was noticed in all of the CdSe films. The luminescence intensity was found to dwindle down to nearly 56% of its initial value for the CdSe film annealed at 473 K for 30 min when kept in humid air (relative humidity 80%) for 6 weeks (Fig. 5(a)). The loss in luminescence intensity for the bare CdSe films could be explained by the instability of CdSe due to photo-oxidation [35–37].

Figure 5 (inset 1) shows the XPS spectra of Se 3d core level of a representative CdSe film (annealed at 573 K for 30 min) recorded at different aging times. The formation of SeO_2 peak at energy (∼59 eV) higher than the main Se peak (∼54

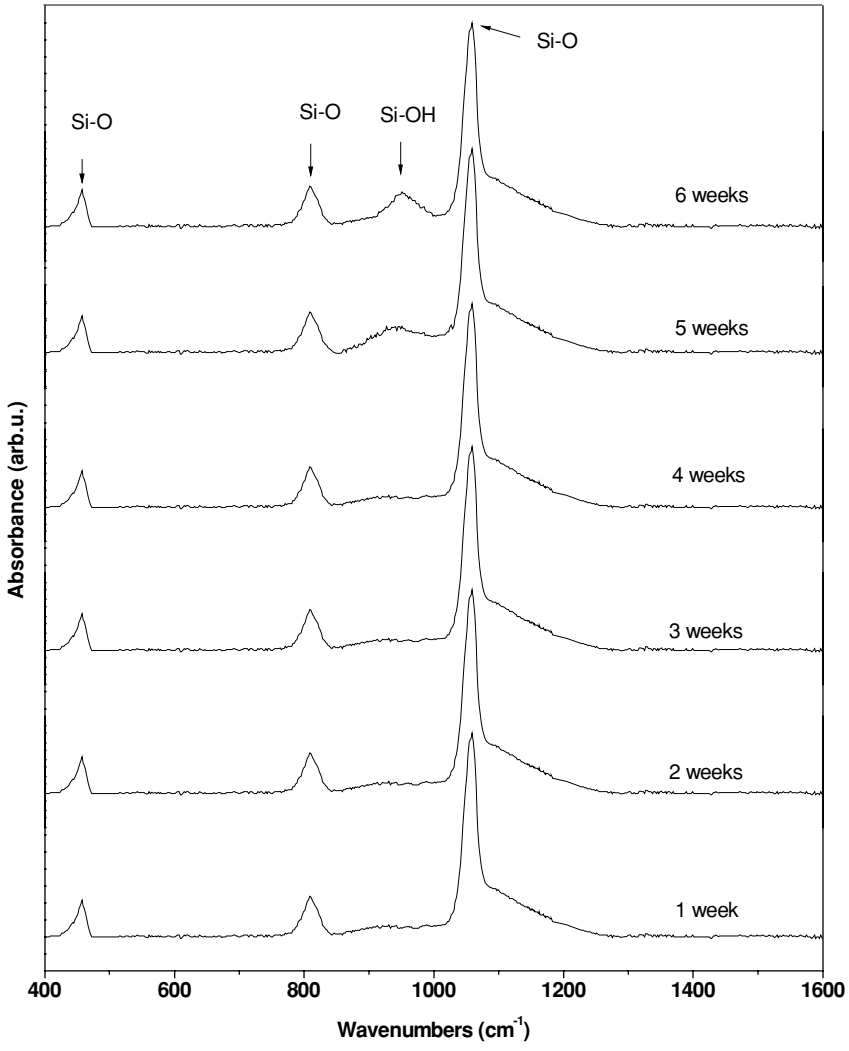

Fig. 6 Fourier transformed infra red (FTIR) absorption spectra of a thin film containing CdSe nanoparticles embedded in SiO_2 matrix annealed at 573 K 30 min at different periods of aging times

eV) after two days was an indication of the surface oxidation of the nanoparticles when it was exposed to visible light in normal humid atmosphere. It was interesting to note the temporal behavior of the SeO_2 peak with increasing aging time. After initial rise of the oxide peak, the peak decayed and then rose again. Oscillations continued over the period of several weeks indicating that the oxide leaves the surface as a molecular species, leaving Cd and a freshly exposed layer of CdSe behind. During the period of decaying the oxidized peak, the Cd/Se ratio was found to rise, confirming the loss of Se from the nanoparticles. Surface of the nanocrystals of CdSe exposed to air and light was thus effectively destroyed by these redox cycles within a few days and resulted in the reduction of PL intensity [35]. It can be noticed from Fig. 5, that the slope of the degradation curves were steeper for the films synthesized at lower annealing temperature and the slope gradually became gentler for the films prepared with increasing annealing temperature. The films synthesized at lower temperature contained smaller nanoparticles with greater surface area. This made the particles more sensitive to surface photo-oxidation process, leading to a faster degradation compared to the films prepared at higher temperature having larger particle sizes. No such evidence of surface oxidation was found (Fig. 5, inset 2) for the films containing CdSe nanoparticles embedded in SiO_2 matrix due to the effective silica capping on the CdSe nanoparticles. This resulted in much more stable luminescence behavior of the CdSe-SiO_2 films (luminescence intensity practically remains constant throughout the period of aging experiments) compared to that of the films containing CdSe nanoparticles without silica capping.

The overall quality of the CdSe-SiO_2 films during aging was studied using FTIR data colleted at different stages of aging and the results for the film annealed at 573 K for 30 min are shown in Fig. 6. No significant change was observed in the FTIR spectra, depicting stable and effective silica capping of CdSe nanoparticles. After 5 weeks of aging, a broad and weak band appeared around 935 cm^{-1} in the spectrum. The intensity of this additional band was increased slightly when the film was aged for 6 weeks. No further increase in the intensity of this band was found beyond 6 weeks of aging. The presence of a band peaking at $\sim$935 cm^{-1} in the FTIR spectrum has been ascribed to the vibrational stretching mode of Si─OH groups [38]. Appearance of this weak band could be attributed to the absorption of small amount of water vapor on the outer surface of the SiO_2 matrix after the films were being aged for a long period of time (at least 5 weeks) in the humid environmental conditions. However, this process remained confined to the outer surface of the silica matrix and did not attack the nanoparticle surface. Prevention of surface oxidation was revealed from the absence of any Se─O band in FTIR spectra and also from XPS study. As a result, the luminescence intensity remained practically unchanged with aging in the CdSe-SiO_2 set of films.

4 Conclusions

Sol-gel technique was adopted to synthesize thin films containing CdSe nanoparticles with and without silica capping. All of the films exhibited quantum-size effects. The increase in particle size was observed with increasing annealing temperature. The emission intensity was found to increase when CdSe nanoparticles were encapped in silica matrix. The emission intensity was found to decrease with aging for the films containing CdSe nanoparticles without silica capping. CdSe-SiO_2 films showed more stable luminescence behavior and less degradation against aging.

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