AGING BEHAVIOUR OF CdSe NANOPARTICLES : EFFECT OF STOICHIOMETRY ON CHANGING PHYSICAL PROPERTIES

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We investigate in detail the effect of aging on microstuctural, optical and luminescence behaviour of several sets of colloidal luminescent CdSe nanoparticles synthesized from starting solutions containing stoichiometric excess and deficit of Se. Particle growth with aging followed the Ostwald ripening mechanism in all the samples. No deviation in the nature of optical transition from the bulk material was found in any of the fresh or aged samples. The positions of absorption and emission peaks were red shifted with increasing period of aging. The luminescence intensity decreased with increasing period of aging when the samples were exposed in relatively humid air (relative humidity 80%). The CdSe nanoparticles synthesized from solution having higher Cd to Se molar ratio showed more stability against photo-oxidation.

1. Introduction

Semiconductor nanoparticles are currently being extensively studied in both theoretical and applied research areas [1-4] in the context of their highly size and shape-dependent 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]. The applications in different fields need stable CdSe nanoparticles. Though CdSe nanoparticles capped inside some shell of materials having higher band gaps (e.g. ZnS) exhibit stable properties against physical change. Uncapped CdSe nanoparticles are found to be instable under photo-oxidation [16-18] when they were kept in air for several days. With increasing aging time, they are also found to be vulnerable against the agglomeration to the adjacent particles, changing the particle size as well as the size dependent absorption and emission properties of the nanoparticles. These properties make the bare CdSe not very suitable for device and other practical applications. At this stage, detail study to understand the aging behaviour of bare CdSe may be very useful to control the changing physical properties of CdSe nanoparticles with aging. As a result, stable nanoparticles without any capping may be synthesized for practical applications.

In spite of such importance of the aging behaviour on the material property, almost no systematic work can be found in this field of studying the aging behaviour of uncapped colloidal CdSe nanoparticles in detail. In this communication, we report the study on the effect of aging on microstuctural, optical and luminescence behaviours of the colloidal CdSe nanoparticles having varied composition, synthesized starting solution containing stoichiometric excess or deficit of Se.

2. Experimental details

The nanoparticles were synthesized adopting conventional wet chemical route. All reagents were used as purchased with no additional purification. Cadmium Oxide (CdO, ~ 1

micron, 99.5%, Aldrich) was used as the Cd precursor. Trioctylphosphine Oxide (TOPO, Reagent Plus, 99%, Sigma-Aldrich) and n-Tetradecylphosphonic acid (TDPA, 98%, Alfa Aesar) were used to get better size distribution of the nanoparticles. Selenium powder (100 mesh, 99.5+%, Aldrich) dissolved in Trioctylphosphine (TOP, tech., 90%, Aldrich) was served as the Se precursor. The Cd to Se molar ratio was varied as 1: 0.7, 1:0.9, 1:1, 1:1.1 and 1:1.3 by adjusting the weight of the Cd and Se precursors in the starting solution.

Firstly, TOPO was heated and degassed at 330^0C under Ar flow at a pressure of 1 atm in a three-neck flask. After that, CdO and TDPA were introduced to the TOPO under stirring at 240^0C and the solution was kept in this temperature for 30 minutes. Se powder dissolved in TOP was injected quickly at a time into the flask at that particular temperature. Immediate formation of the CdSe nanoparticles was observed showing change in colour of the solution. The solution was kept at this temperature under stirring for 5 minutes and then cooled immediately. In the next step, the nanoparticles were precipitated in methanol dried over activated molecular sieve and centrifuged several times to wash out the excess TOPO and finally dispersed in Chloroform (anhydrous, 99+%, Aldrich).

For aging experiments, the samples were preserved in 20 ml. disposable glass vials and the vials were kept in general air atmosphere under room light during the tenure of the experiments. Samples were taken from the stock in a regular interval of time (freshly prepared, 1 week, 2 weeks, 3 weeks, 4 weeks and 5 weeks) to study the variation in microstructural, optical and luminescent properties of the samples with aging time.

Optical absorption spectra were measured using a spectrophotometer (Hitachi-U3410) at the room temperature in the wavelength region 400-800 nm.   The spectra were recorded with a resolution of $\lambda \sim 0.07$ nm along with a photometric accuracy of $\pm$ 0.3% for the absorbance measurement. Microstuctural studies were performed using Transmission electron microscope (Hitachi H-7100 microscope) and Particle Size Analyzer (Nano-S, Malven, Worcedtershire, U.K.). Photoluminescence (PL) measurement was carried out using a Hitachi F-4500 fluorescence spectrophotometer. The emission spectra were recorded at room temperature using Xe lamp as an excitation source with an excitation wavelength 440 nm.

3. Result and discussions

3.1. Microstructural Study

Fig. 1 (a, b and c) shows the transmission electron micrographs (TEM) and the corresponding particle size analysis data for the CdSe nanoparticles, prepared from the starting solution with stoichiometric composition, aged for different period of times as indicated in the caption. It can be noticed from the micrograph of Fig. 1(a), the freshly prepared sample consists of nanoparticles nearly mono-dispersed in nature with average particle size (d) ~ 3 nm, while the particle size analysis data showed symmetric and narrow size distribution.   All the fresh samples, synthesized from starting solution with different Cd to Se ratio, showed symmetric and narrow size distribution- qualitatively same as the representative sample, only having difference in average particle size (d). The average sizes of the nanoparticles for different sets were found to be depending upon the Cd to Se ratio in the starting solution with a trend of increasing with increasing value of this ratio, when all other experimental conditions were kept fixed.

It was very interesting to study the particle growth process of CdSe nanoparticles, prepared from starting solution containing different Cd to Se ratio, with aging. The formation and subsequent evolution of nanoparticles from the starting solution could be depicted as a combination of nucleation and coarsening of particles in the solution. According to the homogeneous nucleation theory [19, 20] local fluctuation in concentration starts nucleation of the particles in a solution. The primary stage is the nucleation stage. In this stage, new particles form and the number density of the particles increase. When the concentration of the monomers in the solution drops below a critical concentration, nucleation of particles stops and some particles (with radius r > critical value) grow in expense of the smaller ones (r < critical radius). This final stage is known as coarsening or also more popularly as Ostwald ripening. Ostwald ripening is a very general phenomenon occurring in liquids, solids and on solid surfaces. The physical driving force for this process is a decrease in interface energy with increasing the average size, d (t). The ripening at a fixed temperature is usually described by employing a power law [21]

$$d (t) \sim A + Bt^x \qquad (1)$$

where A is a constant introduced to take into account that in the beginning the growth is far from the asymptotic regime, B the constant corresponding to the asymptotic growth, t is the aging time

and x is the growth exponent. Using the Kelvin equation describing the relationship between the solubility of a particle and its radius, Lifshitz and Slyozov [22] found the value of the exponent x =1/3 in eqn. (1). This indicates that the average particle size should follow a straight-line relation ship with cube root of aging time if the Ostwald ripening governs the particle growth.
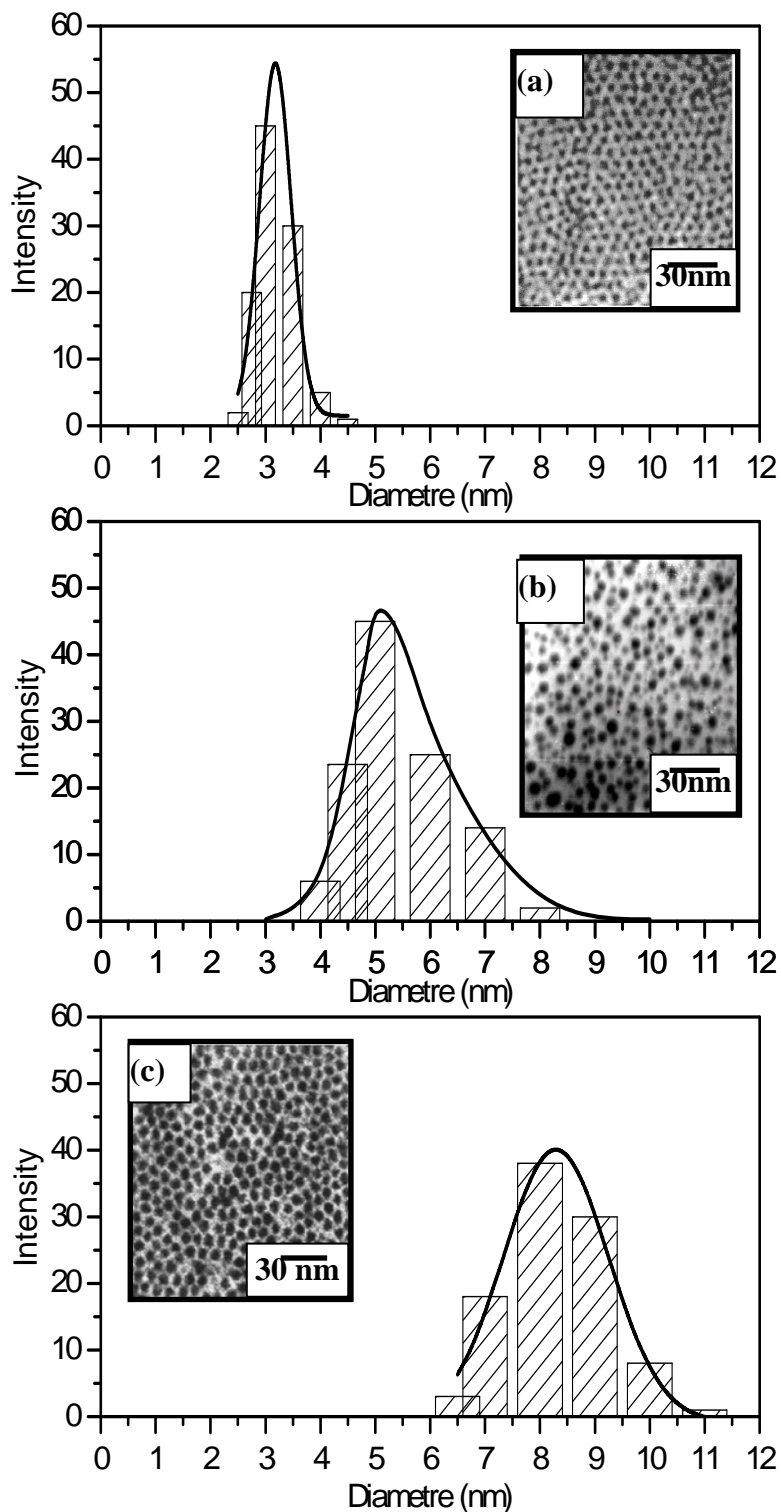

Fig. 1. Transmission electron micrographs (TEM) and Particle Size Analysis data for the CdSe nanoparticles synthesized from starting solution having Cd to Se ratio 1:1 : (a) freshly prepared sample (b) sample after 2 weeks of aging and (c) sample after 5 weeks of aging at air under room light.   Solid lines represent the particle size distribution fittings.

In the present case, it is obvious from the representative micrographs and size distribution data (Fig. 1) that particle size increased and the particle size distribution also traversed through different states during the tenure of five weeks of the aging experiment. The size-distribution data indicate that the average size increased from ~3 nm to ~ 8 nm after aging of 5 weeks.

The micrograph of the freshly prepared sample suggested that the particles were in nucleation stage with narrow size distribution (figure 1a) after it was kept at 240^0C for 5 minutes during the reaction. In the nucleation stage of the particle synthesis process, the particle size distribution should be Gaussian like equation having the form [23]

$$P(R)=(2\pi)^{-1/2}\Delta R^{-1}\exp[-(R-r_{av})^2/2\Delta R^2] \tag{2}$$

where the average radius of particle $r_{av}= 2\sigma/\Delta G_v$, ΔG_v is the bulk free energy decrease per unit volume, σ is the interface free energy per unit area and R is the particle radius. The standard deviation of the particle radius is given by

$$\Delta R=(3kT/8\pi\sigma)^{1/2} = 0.3455(kT/\sigma)^{1/2} \tag{3}$$

where k is the Boltzmann constant.

As the contentration of the monomer drops below a critical limit, coarsening of particles becomes the dominating process and the particle distribution function at this stage can be described by the Lifshitz -Slyozov function [22]

$$P(u)=3^4 2^{-5/3}eu^2(u+3)^{-7/3}(2/3-u)^{-11/3}\exp[(2u/3-1)^{-1}], \text{ for } u<3/2$$
$$P(u)= 0, \text{ for } u>3/2 \tag{4}$$

Where $u=R/r^*$, R is the particle radius and r^* is the critical radius of the particles. This function produces an asymmetric distribution in R with peak at~ 1.2 r^* and full width at half maxima of ~ 0.5 r^* [25].

In the present study, the size distribution data were fitted with the distribution functions and the results are shown in solid lines in figure 1. The size distribution of the fresh sample fitted well the Gaussian distribution (Fig. 1a) with an average particle size 3.2 nm obtained from best fit. In the sample with 2 weeks of aging, coarsening process was found to be in progress. Due to the existence of particles with wide range of size in this sample, the size-distribution became wider and asymmetric in the larger particle side. The fitting in this case was better with L-S function with the peak at 5.3 nm (figure 1b). The size distribution of the sample aged for 5 weeks was again fitted well with the Gaussian function, rather than the asymmetric L-S distribution, with an average particle size of 8.24 nm (figure 1c). This result could be attributed to the fact that the coarsening process of the CdSe nanoparticles had reached near completion for this sample after 5 weeks of aging.

When the average particle size obtained from the size distribution fittings were plotted against the cube root of aging time in minutes (figure 2a) for the representative sample, a straight line was found confirming the Ostwald ripening in the sample with aging. The plot of Full width at half maxima (FWHM) of the size distribution against aging time (Fig. 2b) shows primary increase indicating the onset of coarsening and finally goes down again for higher aging time, showing a gentle peak at ~ 3 weeks of aging time, depicting the completion of coarsening process.

Change in particle size and size distribution with aging time was found to be qualitatively similar for different set of samples, synthesized from starting solutions having different Cd to Se molar ratio. It was found that rate of change in average particle size with aging were higher for the samples prepared from the solution containing lower Cd to Se ratio. These samples also completed their growth process in a shorter time. The detail mechanism of the composition dependence of the nanoparticle growth with aging is yet to understand and more research should be carried on this area.
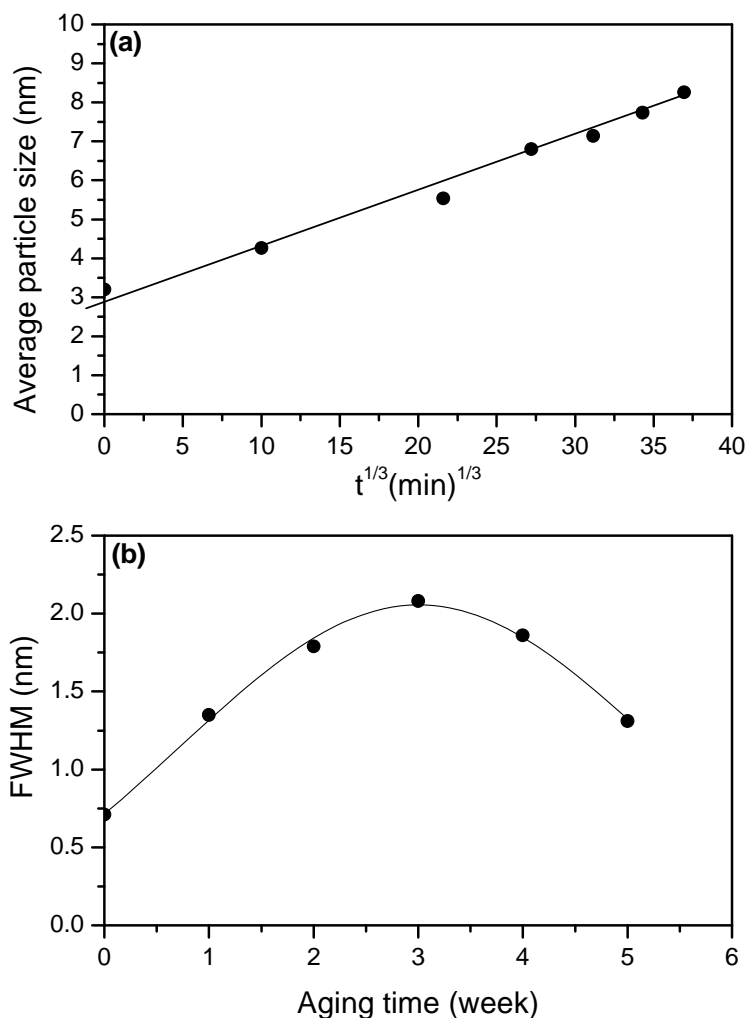
*Fig. 2. Variation of (a) average particle size and (b) Full width at half maxima (FWHM)
of particle size distribution with aging time for the CdSe nanoparticles synthesized from
starting solution having Cd to Se ratio 1:1.*

3.2. Optical study

The absorption peaks of all the samples, synthesized from different Cd to Se ratio in
starting solution, occurred at relatively higher energy compared to its bulk counter part.
Representative optical absorption spectrum of the sample with Cd to Se ratio 1:1 at the starting
solution is shown in figure 3 (spectrum a). The absorption bands were not also very sharp
indicating band tailing effect occurred in the process of optical absorption in these nanoparticles.
A trend of red-shifting of the absorption edge of the samples with increasing Cd to Se ratio in the
starting solution was observed (data not shown), which could be attributed to the increase in
average particle size with increasing Cd to Se ratio in the starting solution, as indicated in the
previous section.

The optical band gap (E_g) were estimated from the plot of $(\alpha h\nu)^{1/m}$ vs. $h\nu$, by
extrapolating the straight line portion of the graph to $\alpha=0$, where m indicates the nature of
optical transition in the material. For bulk semiconductors the value of m is ½, 2, 3/2, and 3
corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect
transitions [24] respectively. In a nanocrystalline material with compositional nonstoichiometry,
the nature of optical transition may be different from that of its bulk counterpart. Therefore, to
avoid any presumption, the values of m for all the samples under consideration were determined as
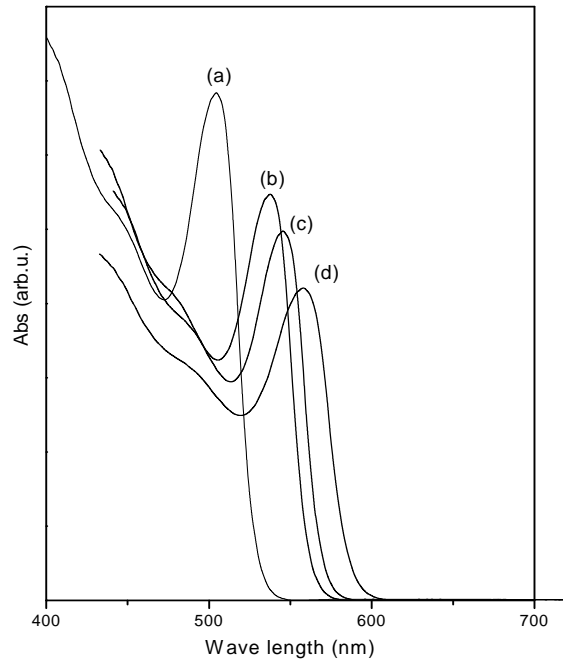discussed below.

Fig. 3. Optical absorption spectra of CdSe nanoparticles synthesized from starting solution having Cd to Se ratio 1:1, when aged for different period of times: (a) freshly prepared, (b) 2 weeks, (c) 3 weeks and (d) 5 weeks.

The optical absorption coefficient (α) at the absorption edge is expressed as [25]

$$\alpha = (A/h\nu)(h\nu - E_g)^m \qquad (5)$$

where A is a constant dependent on the nature of the optical transition and E_g is the optical band gap. Now Eq. (6) can be written as follows

$$d\{\ln(\alpha h\nu)\}/d(h\nu) \quad = \quad m/(h\nu - E_g) \qquad (6)$$

So, there should be a discontinuity in $d\{\ln(\alpha h\nu)\}/d(h\nu)$ vs $h\nu$ plot at the bandgap energy. A representative plot of $d\{\ln(\alpha h\nu)\}/d(h\nu)$ vs. $h\nu$ for the fresh sample with Cd to Se ratio 1:1 in the starting solution is presented in figure 4 (inset a), showing a divergence at $h\nu = E_g$. Using the value of E_g (2.37 eV) thus obtained, we can determine the value of m and hence, the nature of transition. Again, from Eq. (6) we can get

$$\ln(\alpha h\nu) = \ln A + m \ln(h\nu - E_g) \qquad (7)$$

The value of m was determined from the slope of the plot of $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$. The slope in Fig. 4 (inset b) gives the values of m for the same representative sample. Using this method, the m values for different samples synthesized from starting solution with varied Cd to Se ratio (1: 0.7, 1:0.9, 1:1, 1:1.1 and 1:1.3) were evaluated. These values were found within the range of 0.47-0.52 having no specific co-relation with Cd to Se ratio. These values of m were comparable to that for direct transition occurred in the bulk material (m=0.5). This observation suggested that no change in the nature of optical transition at the band edge occurred from the bulk in these CdSe nanoparticles despite their higher surface area as well as compositional nonstoichiometry. No change in the nature of optical transition was also noticed for any of the compositions with increasing aging time.
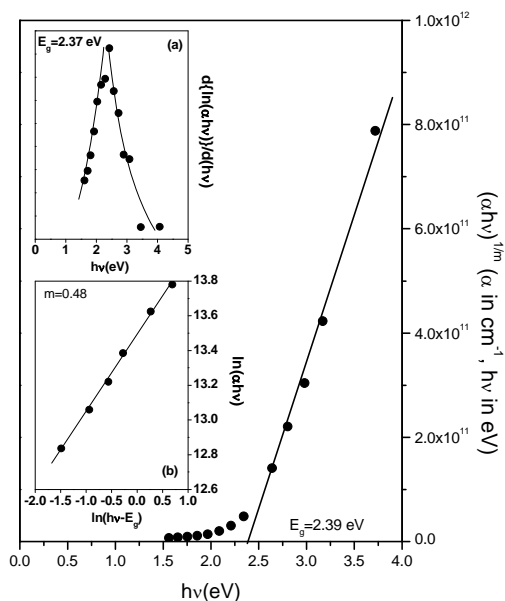
Fig. 4. Plot of (αhυ)$^{1/m}$ vs. hυ for a representative sample; Inset (a) shows the plot of d{ln(αhυ)}/d(hυ) vs. hυ; Inset (b) shows plot of ln(αhυ) vs. ln (hυ-E$_g$).

The Plots of (αhυ)$^{1/m}$ vs. hυ with the corresponding m values for different samples gave the exact value of the optical band gaps in the samples as shown for the same representative sample in figure 4. The band gaps for different samples varied within ~ 2.6-2.29 eV as a function of increasing Cd to Se ratio in the starting solution and these values were always greater than the bulk value (1.75 eV at 293 K) [26]. This increase in the fundamental band gap of nanostructured material could be attributed to the quantum size effect. Decrease in optical band gap value as a result of particle growth with increasing aging time was found for all set of samples prepared from starting solutions having different Cd to Se ratio.
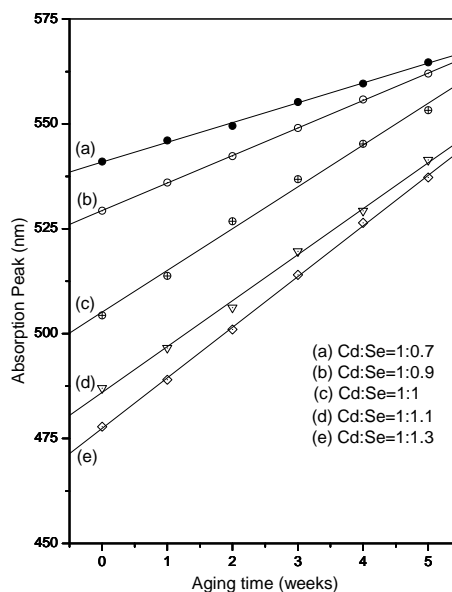

Fig. 5. Red-shift of Absorption peaks with aging time for samples prepared from starting solution having different Cd to Se ratio.

Fig. 3 shows the absorption spectra of the CdSe nanoparticles synthesized from the starting solution having stoichiometric composition, after different period of aging. The shift of the absorption band to the lower energy can be associated with the ripening/coarsening and subsequent growth of the particles with aging. The position of the absorption band with increasing period of aging for samples of different sets with different Cd to Se ratio was shown in figure 5. It can be found that rate of change in the absorption peak position with aging were higher for the samples prepared from starting solution containing lower Cd to Se ratio. Origin of the greater sensitivity to aging for the samples prepared from Se rich starting solution primarily can be associated to the higher growth rate of the particles in those solutions as indicated in the previous section. Thus, the change in the optical property of the nanoparticle with aging in turn depends upon the composition of the starting solution.

3.3 Photoluminescence Study

Fig. 6 shows the emission spectra of the sample, prepared from the starting solution containing stoichiometric molar ratio of Cd to Se, after different period of aging. The PL peaks were smooth, symmetric and narrow, not broad. The Stoke-shift of the emission generated from different samples was small (~20-30 nm), indicating that the emissions occurred from the samples were band edge emissions.
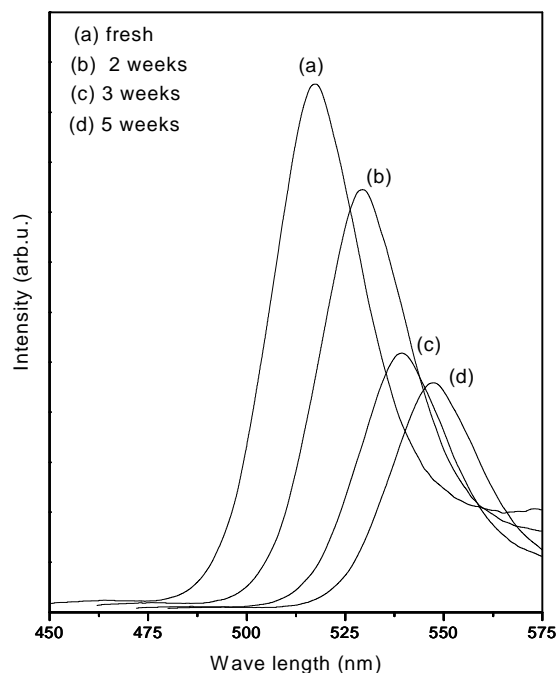

Fig. 6. Emission spectra of CdSe nanoparticles synthesized from starting solution having Cd to Se ratio 1:1, when aged for different period of times: (a) freshly prepared, (b) 2 weeks, (c) 3 weeks and (d) 5 weeks.

It can be noticed from figure 6, that there are two general features in emission spectra with increasing aging time, viz. red shift of the emission band and gradual decrease in intensities. The red shift of the emission band with increasing period of aging for samples with different Cd to Se ratio in starting solution is shown in figure 7. It can be found that rate of change of emission peak wavelengths with aging were higher for the samples prepared from the solution having lower Cd to Se ratio. The red shift could be attributed to the coalescence and subsequent growth of the particles with aging. Origin of the greater sensitivity of luminescence peak to aging for the samples prepared from Se rich starting solution primarily can be associated to the higher growth rate of the particles, as indicated earlier. Thus, the change in the luminescence property of the nanoparticles with aging also depends upon the composition of the starting solution.
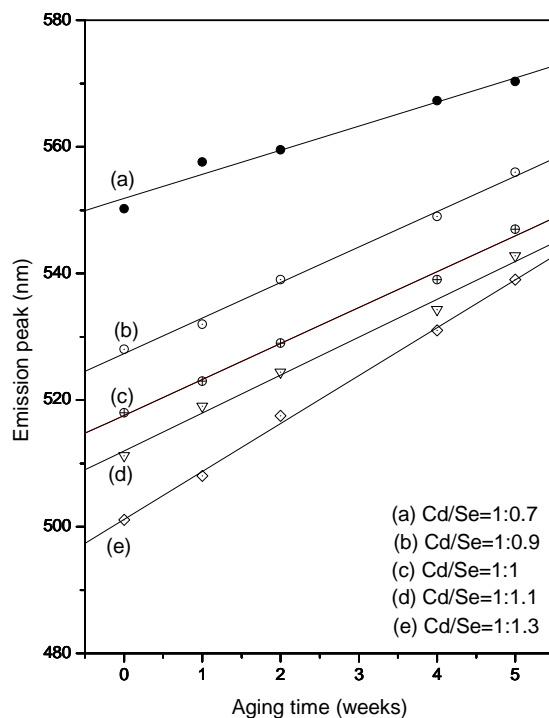
Fig. 7. Red-shift of emission peaks with aging time for samples synthesized from starting solutions having different Cd to Se ratios.

The luminescence peak intensity relative to that of the freshly prepared samples was investigated as a function of aging time in different set of samples and the results are shown in figure 8. A loss in luminescence intensity with increasing aging time was noticed in all the CdSe samples. The luminescence intensity was found to dwindle down nearly 65 % of its initial value for the CdSe sample prepared from stoichiometric starting solution when kept at humid air (relative humidity 80%) for 5 weeks. Several groups have reported changes in fluorescence of II-VI semiconductor nanoparticles over time [27-30] and they had associated the changes with the interaction of the surface defect sites with oxygen that occurred when the nanoparticle solution was aged. The loss in luminescence as well as absorption intensity could be explained by the instability of CdSe due to photo-oxidation [16-18]. Upon exposure to visible light, superficial CdSe is oxidized to selenate. In turn, this oxide leaves the surface as a molecular species, leaving Cd and a freshly exposed layer of CdSe behind. Surface of the nanocrystals of CdSe exposed to air and light are effectively destroyed by this redox cycles within a few days and results in a reduction in the PL intensity.
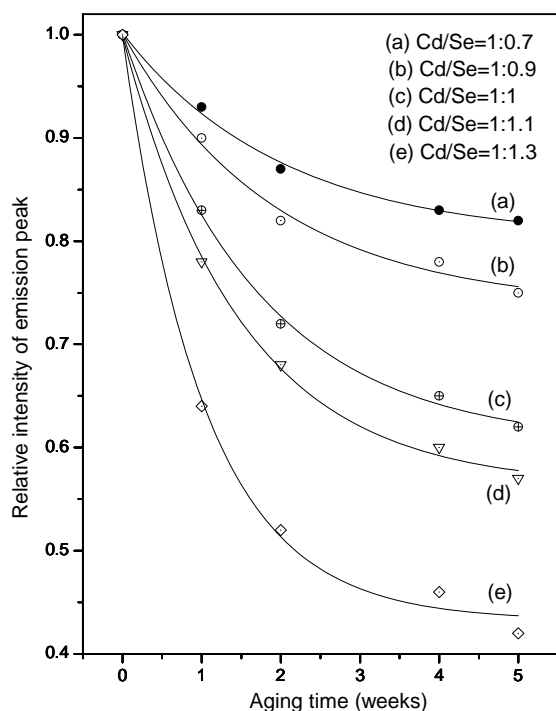
Fig. 8. Change in relative intensity of emission peak with aging time for samples synthesized from starting solutions having different Cd to Se ratios.

It can be noticed that the decrease in relative intensity in luminescence spectra nearly followed the first order exponential decay law, which indicated the subsequent stabilization of photo-oxidation process for a relatively long time of aging. It can be also noticed from Fig. 8, that the slope of the degradation curves are steeper for the samples synthesized from Se rich starting solution and this slope became gradually gentler for the samples prepared from starting solution having increasing Cd amount. The particles synthesized from Se rich starting solution had smaller size with greater surface area. This made them more sensitive to surface photo-oxidation process. As a result, the luminescence degraded at a faster rate than the samples prepared from Cd rich solutions having larger particle sizes.

4. Conclusions

Wet-chemical method was adopted to synthesize colloidal CdSe nanoparticles with different Cd to Se ratio. All of the samples exhibited quantum-size effects. The increase in particle size was observed with increasing period of aging of the samples at a humid atmosphere. The rate of increase in particle-size with aging time was found to increase for the samples prepared with decreasing Cd to Se ratio in the starting solution. The emission intensity was found to decrease with aging for the samples. The optical and luminescence behaviours of CdSe nanoparticles against aging were also found to be depending upon the Cd to Se ratio used in the starting solution.

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