Available online at www.sciencedirect.com
SCIENCE DIRECT
Physica E 33 (2006) 388–393
PHYSICA E
www.elsevier.com/locate/physe

Colloidal CdSe–ZnS core-shell nanoparticles: Dependence of physical properties on initial Cd to Se concentration

Baibaswata Bhattacharjee[a], Chia-Hao Hsu[a], Chung-Hsin Lu[a,*], Walter H. Chang[b]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC*
[b]*Department of Biomedical Engineering, Chung Yuan Christian University, Chung Li, Taiwan, ROC*

Received 8 February 2006; accepted 21 April 2006

Abstract

Different sets of CdSe–ZnS core-shell colloidal nanoparticles are synthesized from the starting solution containing stoichiometric excess or deficit of metal counterpart (Cd to Se ratio) to study the variation in physical property depending upon the core composition. It is found that the stoichiometric variation in the starting solution affects the microstructure of the nanoparticles and hence the variation in absorption and emission properties. It is found that the band edge emission peak shifted to the lower energy levels with increasing Cd/Se ratio in the starting solution. Broadening of the Photoluminescence spectral shape is found for Cd rich or Se rich samples. The stoichiometric sample shows the brightest emission that can be associated with the lesser defects associated to the nanoparticles in that sample. Tailing of the optical absorption beyond the band edge is found to be least for the stoichiometric sample indicating fewer defects present in the sample.

PACS: 71.55.Gs; 78.67−n; 78.55.−m; 78.67.Bf

Keywords: Nanoparticles; Luminescence; Optical property

1. Introduction

Size and shape dependent optical properties have made semiconductor nanoparticles a very interesting research topic in both theoretical and applied areas [1–4]. Developing synthetic chemistry to get control over the luminescence properties of the colloidal semiconductor nanoparticles has been a major goal since the early days of research in this field. CdSe is an important member of luminescent II–VI family having bright luminescence in the visible range of optical spectra. This material has shown significant potential to be used in biological filed [5,6], displays [7,8], diodes and lasers [1], solar cells [9–12] and gas sensors [13–15] in nanocrystalline form.

The emission intensity of CdSe nanoparticles are found to increase several times when the CdSe cores are capped inside a shell of high bandgap material like ZnS [16] to form CdSe–ZnS core-shell structure. Emission characteristics of CdSe–ZnS core-shell nanoparticles are well known to depend strongly upon the size of CdSe core. Numerous studies can be found to explore size [17–21] and shape change [22–25] to get tunable band edge luminescence from blue to red, a wide range of the visible optical spectra. On the other hand, it is also revealed that the initial Cd to Se molar ratio of the precursor is a determining factor for the microstructure. Change in size and size distribution of the nanoparticles can subsequently change the luminescence and optical properties of the as synthesized nanocrystals [26,27]. In spite of the prospect of this approach, tuning the stoichiometry of the material to change the optical and luminescence properties is relatively a virgin field. Most of the groups worked with initial Cd/Se ratio 1:1 and less number of studies are available [26–28] depicting systematic study in the change of optical properties due to

---

[*] Corresponding author. Permanent Address: Department of Physics, Ramananda College, Bishnupur, Bankura, W.B. 722122, India.

E-mail addresses: baib23@gmail.com (B. Bhattacharjee), chlu@ntu.edu.tw (C.-H. Lu).

1386-9477/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physe.2006.04.007

compositional nonstoichiometry of CdSe core of the CdSe–ZnS nanoparticles.

In this communication, synthesis of colloidal CdSe–ZnS nanoparticles from starting solution containing different Cd/Se molar ratios is reported. Microstructural, optical and luminescence properties of the samples are studied systematically as a function of initial Cd/Se ratio.

2. Experimental details

The core-shell colloidal nanoparticles were synthesized adopting conventional wet chemical route. All reagents were used as purchased with no additional purification. Cadmium Oxide (CdO, ~1 μm, 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 control of the nanoparticles. Selenium powder (100 mesh, 99.5 + %, Aldrich) dissolved in trioctylphosphine (TOP, tech., 90%, Aldrich) was served as the Se precursor. Dimethylzinc (1.0 M solution in heptane, Aldrich) and Hexamethyldisilathiane (Aldrich) dissolved in TOP are used as the sources of zinc and sulfur, respectively, for the shell solution. 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. The amount of shell solution was kept constant for all the compositions.

The mixture of TOPO, CdO and TDPA were heated and degassed under Ar flow at a pressure of 1 atm in a three-neck flask. The mixture was heated at 340 °C until a clear colorless solution was obtained. After that, the temperature was allowed to come down and required amount of Se powder dissolved in TOP was injected quickly at a time into the flask at 240 °C. Immediate formation of the CdSe nanoparticles was observed showing

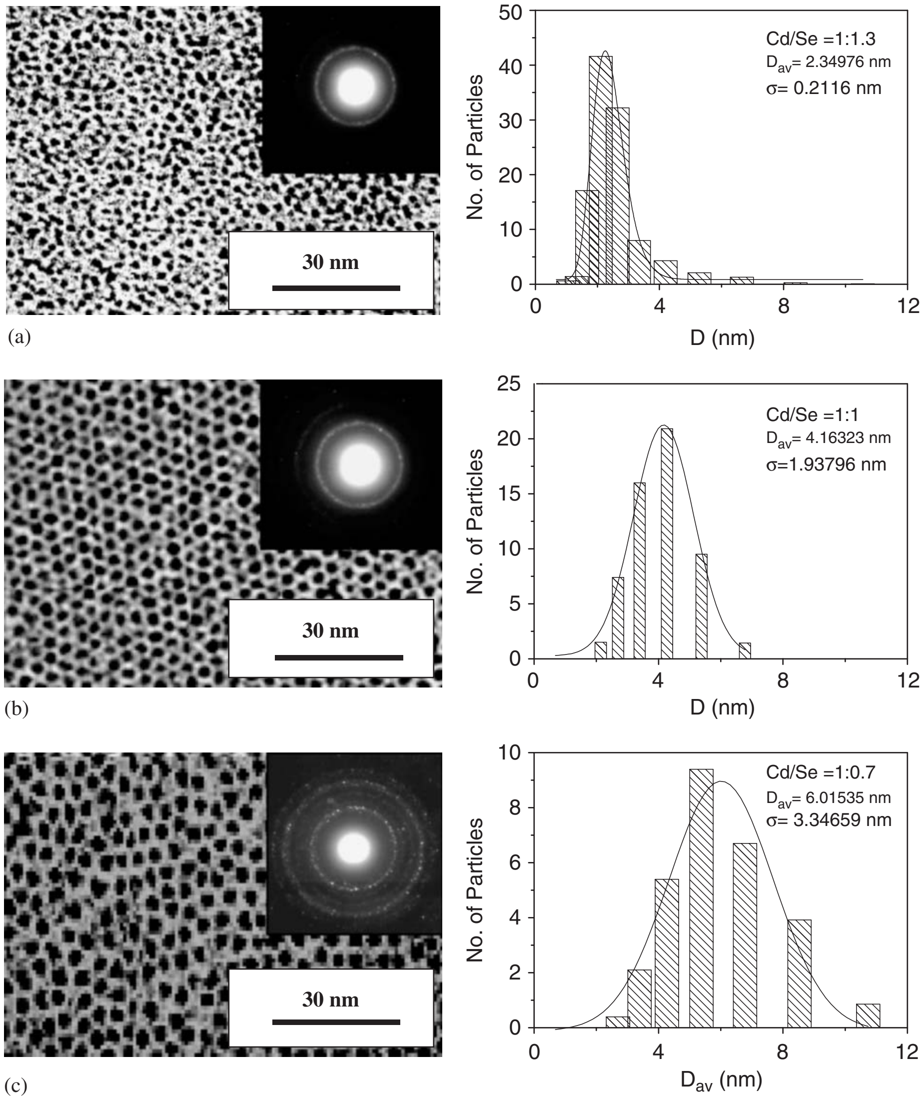

Fig. 1. Transmission electron micrographs (TEM) and particle size analysis (PSA) of CdSe–ZnS colloidal quantum dots synthesized from starting solution containing different Cd to Se molar ratios: (a) 1:1.3, (b) 1:1 and (c) 1:0.7.

change in color of the solution. The solution was kept at this temperature under stirring for 5 min and then the shell solution was injected to the flask and was kept under stirring for another 5 min before removing the flask to a boiling water bath. When the temperature went below 60 °C, the flask containing the solution was cooled at room temperature immediately, using a previously prepared mixture of methanol and acetone. In the next step, the nanoparticles were precipitated in methanol dried over activated molecular sieve and centrifuged to wash out the excess TOPO and finally dispersed in Chloroform (anhydrous, 99 + %, Aldrich).

Microstuctural studies were performed using Transmission electron microscope (Hitachi H-7100 microscope) and Particle Size Analyzer (Nano-S, Malven, Worcedtershire, UK). Optical absorption spectra were measured using a spectrophotometer (Hitachi-U2010) at the room temperature in the wavelength region 350–700 nm. 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. Commission International d'Eclairage (CIE) color coordinates were measured using a Fluorescence Colormeter (Hong–Ming Technology, MFS-230) as an attachment of Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussion

3.1. Microstructural study

The nucleation and growth of nanoparticles strongly depend upon the initial concentration of precursors. Nucleation takes place rapidly after injection and continues until the monomer concentration drops below a critical concentration, at a fixed temperature. The monomer concentration, which depends upon the initially used Cd/Se molar ratio of the precursors, can change the average particle size, number density and size distribution by "focusing" and "defocusing" the particle growth in the solution [26]. Figs. 1(a)–(c) show transmission electron micrographs with corresponding Electron Diffraction patterns for samples synthesized from starting solution containing different Cd/Se molar ratios, 1:1.3, 1:1 and 1:0.7, respectively. For the Se rich sample (Fig. 1(a)), nucleation of well dispersed quantum dots of nearly same size were observed. This led the particle distribution to narrow one with average particle size ~2.5 nm. For the stoichiometric sample (Fig. 1(b)), the number density of the quantum dots decreased substantially and growth of some particles also found to be started in the same condition. For the Cd rich sample (Fig. 1(c)), the average particle size was large (~6 nm) and the number density was low. In a solution with excess Cd, the nuclei grew very fast and

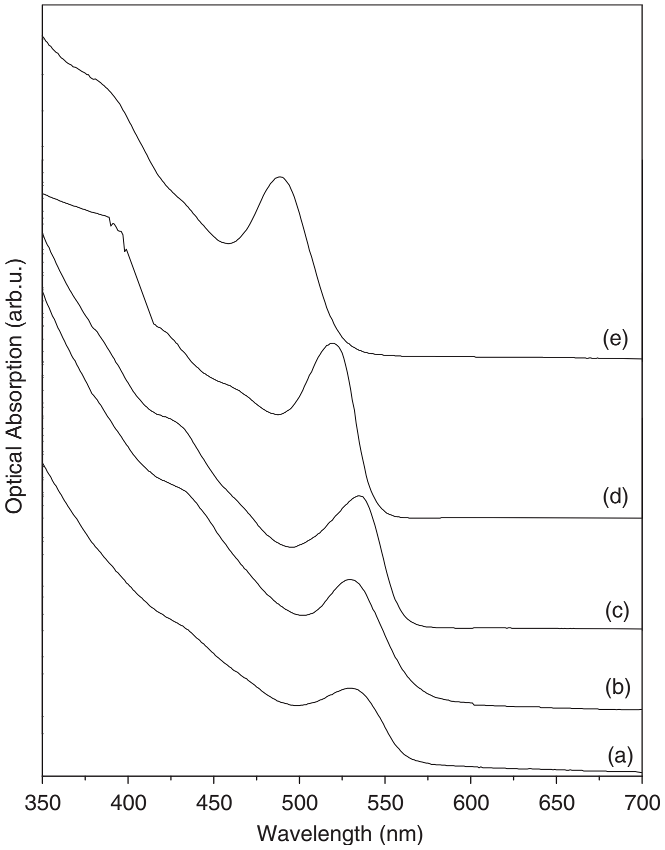

Fig. 2. Room temperature absorption spectra of CdSe–ZnS colloidal quantum dots synthesized from starting solution containing different Cd to Se molar ratios: (a) 1:0.7, (b) 1:0.9, (c) 1:1, (d) 1:1.1 and (e) 1:1.3.

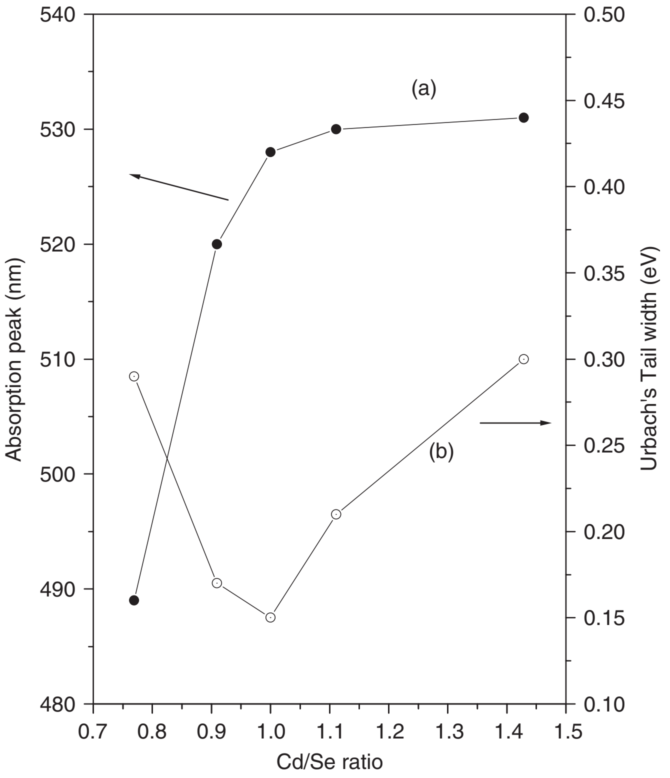

Fig. 3. Variation of (a) first excitonic peak wave length and (b) Urbach's tail width as a function of Cd to Se molar ratio used in the starting solution.

growth was the predominant process over nucleation, which reduced the number density and increased the average particle size under the same experimental condition. This observation was similar with that of Qu and Peng [27]. Increase in average particle size with increasing Cd/Se ratio was responsible for red shift of emission and absorption color of the nanoparticles as reported in the following sections. Diffraction patterns showed central halos with concentric ring patterns. Ring patterns showed reflections from (1 1 1), (2 2 0) and (3 1 1) planes indicating formation of cubic phase for CdSe in all the samples.

3.2. Optical study

Fig. 2 shows the optical absorption spectra of the samples prepared from starting solutions containing different Cd to Se ratio. The absorption edges are found to be blue shifted with respect to their bulk counterpart [29] indicating quantum confinement effect [30] in all the CdSe–ZnS core-shell quantum dots. There was a trend of red shifting of the absorption edge with increasing Cd amount in the starting solution (Fig. 3(curve a)) indicating existence of larger particles in the samples having greater Cd/Se ratio.

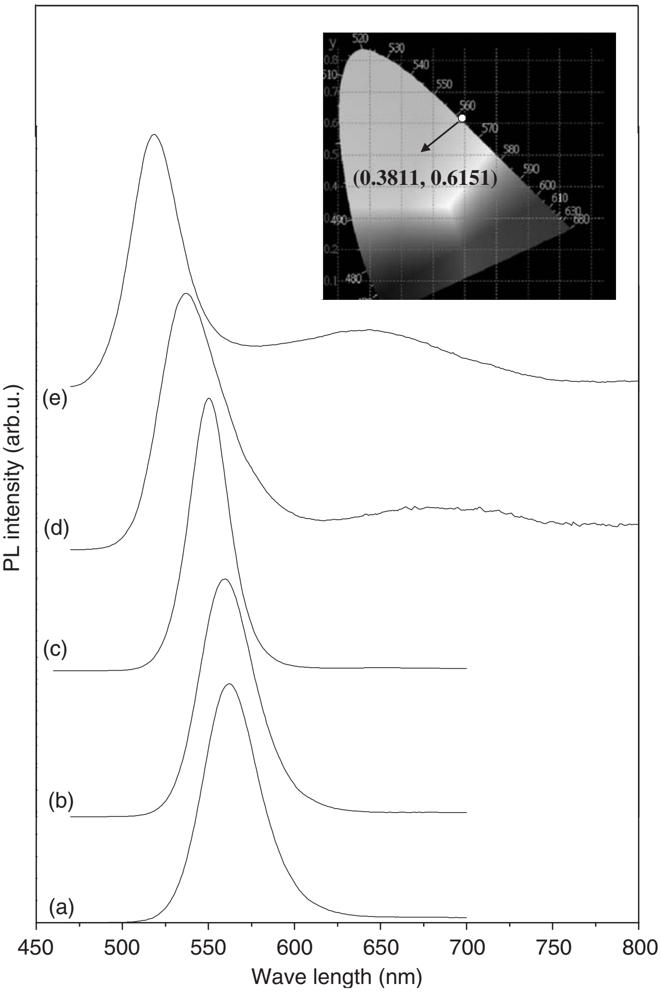

Fig. 4. Room temperature photoluminescence (PL) spectra of CdSe colloidal quantum dots synthesized from starting solution containing different Cd to Se molar ratios: (a) 1:0.7, (b) 1:0.9, (c) 1:1, (d) 1:1.1 and (e) 1:1.3. Inset shows CIE color co-ordinate analysis of a representative sample.

The variation of absorption coefficient (α) with photon energy ($h\nu$) at the band edge was found to be not very sharp-which indicated band-tailing effect in these colloidal nanoparticles. With decreasing photon energy, just below the band edge, the absorption coefficient can be expressed by [31]

$$\alpha = \alpha_0 \exp[\sigma(h\nu - E_0)/kT] = \alpha_0 \exp[(h\nu - E_0)/\varepsilon], \quad (1)$$

where E_0 and α_0 are the characteristic parameters of a material, σ is the steepness parameter, k is the Boltzmann constant and $\varepsilon = KT/\sigma$. Eq. (1) suggests that the inverse-slope of the plot of $\ln\alpha$ vs. $h\nu$ would give the tail width ($E = 1/\varepsilon$). The Urbach's tail width is the measure of the band tailing of the samples. This parameter was calculated for different samples to investigate the effect of composition on the line shape of the absorption band and the result is shown in Fig. 2(curve b). The band tailing is found to be least for the stoichiometric sample indicating fewer defects associated with this sample.

3.3. Photoluminescence study

Fig. 4 shows the PL emission spectra of different CdSe–ZnS samples prepared from starting solution

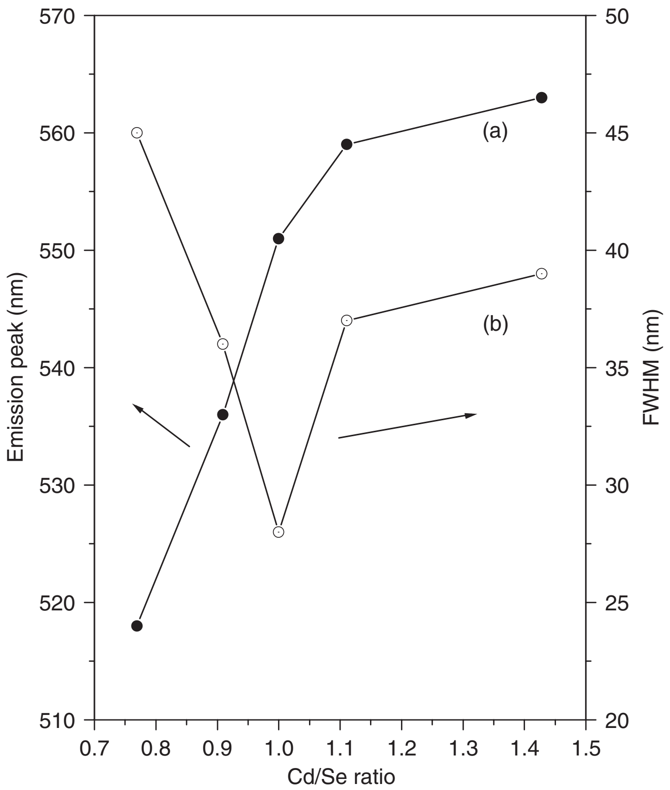

Fig. 5. Variation of (a) photoluminescence (PL) emission wavelength and (b) full width at half maxima (FWHM) as a function of Cd to Se molar ratio at the starting solution.

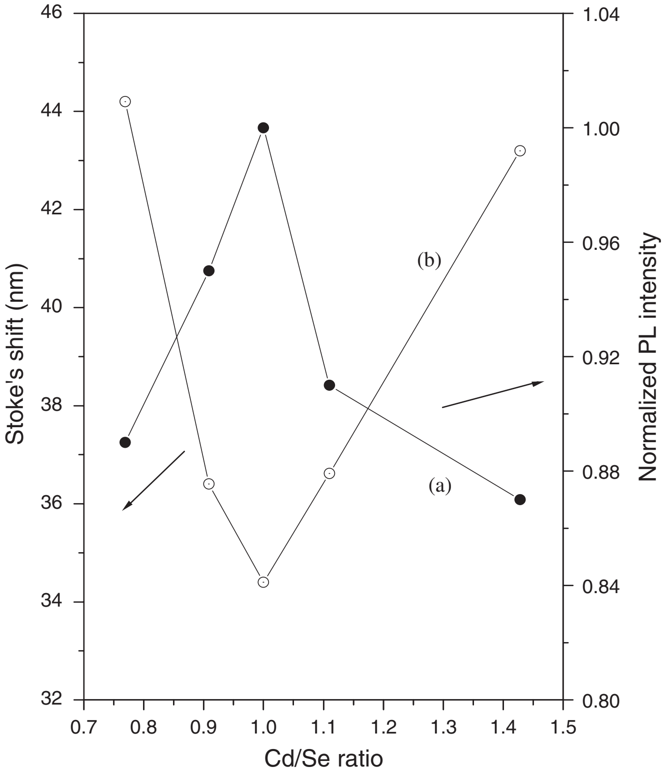

Fig. 6. Variation of (a) normalized photoluminescence (PL) intensity and (b) Stokes' shift of Photoluminescence (PL) emission as a function of Cd to Se molar ratio at the starting solution.

containing different Cd/Se molar ratio.The band edge emissions were intense with smooth, symmetric and narrow line shape for all the samples. In addition to the band-edge luminescence, the samples having lower Cd/Se ratio showed a weak and broad emission band at relatively lower energy. This PL band was originated owing to higher surface area of the particles due to their smaller particle size in those samples. However, this band from surface states was quite insignificant compared to the band edge luminescence and did not appear for stoichiometric or Cd rich samples. CIE color coordinates measurement for a representative sample is shown in Fig. 4(inset).

The emission properties of semiconductor nanoparticles can be characterized by the fundamental emission parameters like the emission color and color purity. Fig. 5 shows the results on the study of band edge luminescence with respect to these parameters as a function of Cd to Se stoichiometry in the starting solution. PL emission wavelength showed a trend of red shift (Fig. 5(curve a)) with increasing Cd amount in the starting solution. This red shift of the emission color can be associated with increasing average particle size of the samples synthesized from the solution with increasing Cd/Se ratio as discussed in some detail in Section 3.1. The full width at half maximum (FWHM) of the emission peak is the measure of the color purity of the emission. Less value of FWHM indicates more pure emission. Fig. 5(curve b) shows the variation FWHM of the emission peaks. It is found that the PL peaks are narrow having the FWHM values around 24–45 nm at room temperature for different Cd/Se ratio. These values are comparable to the values around 27–40 nm at room temperature reported by other groups [32,33]. The stoichiometric sample showed least value of FWHM (~24 nm), which is even comparable to emission observed by single dot spectroscopy (typically <20 nm) [34] indicating better homogeneity in the emission properties from the nanoparticles in the present case. The change in FWHM with Cd/Se can be attributed to the changing particle distribution due to presence of different ratio of precursor in the starting solution. PL intensity normalized to the value of the stoichiometric sample was plotted as a function of Cd to Se stoichiometry in the starting solution (Fig. 6(curve a)). The PL intensity was found to be highest for stoichiometric sample and decreased for both Cd rich and Se rich samples. The highest intensity of the stoichiometric sample could be attributed to the less number of defects associated with this sample which subsequently reduced the non radiative recombination pathways. The Stokes' shift of the emissions also showed (Fig. 6(curve b)) least value for the stoichiometric ratio and the value increased for both Cd rich and Se rich ratio.

4. Conclusions

Optical properties of colloidal CdSe–ZnS core-shell nanoparticles were successfully controlled by changing the Cd/Se molar ratios in the starting solutions. Optical absorption and emission spectra both showed gradual red shift with increasing Cd to Se ratio. The sample prepared from stoichiometric solution showed most bright emission with least broadness. The optical absorption also showed least band tailing for this sample. This observation was associated with gradual increase in average particle size with increasing Cd/Se ratio in the starting solution.

Acknowledgement

One of the authors (B. Bhattacharjee) would like to thank Ramananda College, Bishnupur, India for providing leave to participate in this research work.

References

[1] V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. Malko, J.A. Hollingsworth, C.A. Leatherdale, H.–J. Eisler, M.G. Bawendi, Science 290 (2000) 314.
[2] H. Mattousi, J.M. Mauro, E.R. Goldman, G.P. Anderson, V.C. Sundar, F.V. Mikulec, M.G. Bawendi, J. Am. Chem. Soc. 122 (2000) 12,142.
[3] G. Markovich, C.P. Collier, S.E. Henrichs, F. Remacle, R.D. Levine, J.R. Heath, Acc. Chem. Res. 32 (1999) 415.
[4] M. Nirmal, L. Brus, Acc. Chem. Res. 32 (1999) 407.
[5] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Science 281 (1998) 2013.
[6] W. Chan, S. Nie, Science 281 (1998) 2016.
[7] V. Colvin, M. Schlamp, A.P. Alivisatos, Nature 370 (1994) 354.

[8] B.O. Dabbousi, M.G. Bawendi, O. Onotsuka, M.F. Rubner, Appl. Phys. Lett. 66 (1995) 1316.
[9] D. Cahen, G. Hodes, M. Gratzel, J.F. Guillemodes, I. Riess, J. Phys. Chem. B 104 (2000) 2053.
[10] R.P. Raffael, S.L. Castro, A.F. Hepp, Prog. Photovolt.: Res. Appl. 10 (2002) 433.
[11] M. Gratzel, Nature 414 (2001) 338.
[12] K. Schwarzburg, F. Willing, J. Phys. Chem. B 103 (1999) 5743.
[13] D. Moris, R.G. Egdell, J. Mater. Chem. 11 (2001) 3207.
[14] K.M. Lin, C.H. Keng, C.Y. Tung, Nanostruct. Mater. 9 (1997) 747.
[15] N. Kumazawa, M.R. Islam, M. Takeuchi, J. Electroanal. Chem. 472 (1999) 137.
[16] M.A. Hines, P. Guyot-Sionnest, J. Phys. Chem. 100 (1996) 468.
[17] C.B. Murray, D.J. Noris, M.G. Bawendi, J. Am. Chem. Soc. 115 (1993) 8706.
[18] J.E. Bowen Katari, V.L. Colvin, A.P. Alivisatos, J. Phys. Chem. 98 (1994) 4109.
[19] B.O. Dabbousi, J.R. Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, M.G. Bawendi, J. Phys. Chem. B 101 (1997) 9463.
[20] Y. Chen, Z. Rosenzweig, Nano. Lett. 2 (2002) 1299.
[21] D. Xu, G. Guo, Y. Guo, Y. Zhang, L. Gui, J. Mater. Chem. 13 (2003) 360.
[22] L. Manna, E.C. Scher, L.S. Li, A.P. Alivisatos, J. Am. Chem. Soc. 124 (2002) 7139.
[23] Q. Peng, Y. Dong, Z. Deng, Y. Li, Inorg. Chem. 41 (2002) 5249.
[24] S.D. Bunge, K.M. Krueger, T.J. Boyle, M.A. Rodriguez, T.J. Headley, V.L. Colvin, J. Mater. Chem. 13 (2003) 1705.
[25] R.B. Kale, C.D. Lokhande, Semicond. Sci. Technol. 20 (2005) 1.
[26] X. Peng, J. Wickham, A.P. Alivisatos, J. Am. Chem. Soc. 120 (1998) 5343.
[27] L. Qu, X. Peng, J. Am. Chem. Soc. 124 (2002) 2049.
[28] J. Taylor, T. Kippey, S.J. Rosenthal, J. Clus. Sci. 12 (2001) 571.
[29] L. Bornstein, in: O. Madelung (Ed.), Numerical Data and Functional Relationships in Science and Technology, vol. 22a, Springer, Berlin, 1987, p. 204.
[30] Y. Kayanuma, Phys. Rev. B 38 (1988) 9797.
[31] F. Urbach, Phys. Rev. 92 (1953) 1324.
[32] V.C. Sundar, J. Lee, J.R. Heine, M.G. Bawendi, K.F. Jensen, Adv. Mater. 12 (2000) 1102.
[33] D.V. Talapin, A.L. Rogach, A. Kornowski, M. Haase, H. Welter, Nano Lett 1 (2001) 207.
[34] J. R. Heath (Ed.), Acc. Chem. Res. (1999) (Special issue for Nanostructures, review articles relevant to colloidal nanocrystals).