

Synthesis, Characterization and Optical Properties of ZnSe Nanoparticles

Anil Yadav^{1,2*}, S. P. Nehra², Dinesh Patidar³

¹Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonapat (Haryana) India.

²Centre of Excellence for Energy & Environmental Studies, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonapat (Haryana) India.

³Department of Physics, Seth G.B. Podar College, Nawalgarh, Jhunjhunu (Rajasthan) India.

*Corresponding Author

Abstract

The chemical co-precipitation method was employed to synthesize zinc selenide (ZnSe) nanoparticles with the help of Selenium powder, sodium borohydride, zinc acetate. Mercaptoethanol was added as capping agent. The XRD, SEM and TEM techniques were employed for the characterization of ZnSe nanoparticles. The average diameter of ZnSe nanoparticles is 15 nm. HR transmission electron microscopy (HRTEM) image displays the crystalline features of ZnSe nanoparticles. The PL emission spectrum indicates a peak centered at 480 nm along with two shoulders at 453 and 520 nm. The blue shift is also observed in the PL emission spectrum of ZnSe nanoparticles as compared to bulk ZnSe due to the quantum confinement, which is caused by direct band to band transition. Raman peaks at 210 cm^{-1} is assigned to the TO phonon modes of ZnSe phase, that correspond with the reported results for ZnSe.

Keywords: ZnSe nanoparticles, X-ray diffraction, Raman Spectroscopy, Photoluminescence

INTRODUCTION

The chalcogenides of II- VI materials viz ZnS, ZnSe, CdS and CdSe etc. are most studied and synthesized semiconductor nano-materials. Out of these, zinc selenide nano-materials are most noticeable due to their tune-ability over the visible range of the spectrum. Chalcogenide semiconductor nanomaterials having commercial interest due to their distinctive properties among the same material in bulk form. Nanomaterials with a defined size and shape have fascinated much interest due to the effect of size on physical, chemical and optoelectronic properties. Size dependent fluorescence spectrum of ZnSe nanoparticles helps to find applications in laser diodes, solar cells etc. It is also observed that engineers are able to manufacture laser diodes using these particles which cover most part of the electromagnetic spectrum.[1]. The nanoparticles of ZnSe was prepared by methods like hydrothermal, sonochemical, sol-gel, solvothermal routes, and vapor-phase, thin films, wet chemical route, and co-precipitation methods. Among these methods, the co-precipitation method is of particular interest because it is relatively simple, inexpensive and convenient.

There are considerable interest in the synthesis and

characterization of ZnSe semiconductors consisting particles of 2-100 nm, which are generally referred as quantum dots and nanocrystals. The interests of the researchers are mainly because of their size-tunable optical, electronic and chemical properties [3,4]. Further miniaturization of optical and electronic devices leads to their commercial applications [1,4-9] are as diverse as solar cells, catalysis, biological labelling, light-emitting diodes. As we know that Size and shape of the nanomaterials are responsible for their properties but synthesis of stable monodispersed nanocrystals is still a great challenge in Nanoscience. The control of shape of nanocrystals is also very important. The correlation exists between the shape and the chemical, electronic, optical, physical, magnetic and catalytic properties of nanoparticles. Crystal growth kinetics controls the shape and size of nanocrystals. Therefore the Synthetic chemistry and crystallography provides plethora of opportunities to explore these interesting problems in nanoscience. In this research, it was proposed to synthesize the nano-particles of ZnSe nanocrystals by chemical route using the kinetically controlled precipitation method. The study of structural and optical properties of these chalcogenide nano-materials were studied.

EXPERIMENTAL DETAILS

Materials

The chemicals mainly used were zinc acetate ($\text{Z}_2\text{C}_4\text{H}_6\text{O}_4$), selenium (Se), mercaptoethanol, ($\text{C}_2\text{H}_6\text{OS}$), sodium borohydride (NaBH_4), and ethanol. All chemicals of high quality (Sigma Aldrich) were used.

Synthesis of ZnSe Nanoparticles

ZnSe nanoparticles were synthesized by the two steps chemical reaction using chemical co-precipitation method. Firstly, zinc acetate ($\text{Z}_2\text{C}_4\text{H}_6\text{O}_4$) was dissolved in distilled water with the help of continuous magnetic stirring, later the mercaptoethanol was added to it. Consequently selenium powder was used to prepare sodium hydrogen selenide (NaHSe) solution with the help of sodium borohydride (NaBH_4) and distilled water. This mixture was continuously stirred to get a colourless solution at low temperature. This solution was added to first solution with stirring and heated to

100 °C maintaining its pH at 10 using KOH solution. This reaction takes place more than 24 hrs at 100 °C. A precipitate was obtained, which was washed many times with ethanol and distilled water. Centrifugation was done at 4000 rpm for 10 min. The vacuum heating at 80 °C for 48 hrs was done to obtain sediment.

Characterization Techniques

XRD measurement was done with the help of Rigaku X-ray diffractometer with Cu-K α ($\lambda = 1.54187\text{\AA}$) radiation and operated at a voltage of 30kV and filament current of 40mA at a scanning rate of 3° per minute between 20 to 70°. The surface morphology of ZnSe nanoparticles was characterized using Carl Zeiss 300 Pro scanning electron microscopy (SEM). The powder sample was positioned on a specimen stub and then gold was deposited on the upper surface of the samples to make it conductive. Tecnai G2 20 S-Twin system was used for TEM measurements. The sample was prepared by mixing of ZnSe nanoparticles in ethanol with the help of ultra sonicator. Mixture drop was placed on the carbon coated copper grid and removed by evaporation before the TEM measurement at room temperature. Wavelength range for recorded photoluminescence (PL) spectrum was from 460 to 600 nm at room temperature. For such measurement ZnSe nanoparticles were dispersed in distilled water and excitation wavelength was 400 nm. Raman spectra of ZnSe nanohybrids was recorded using Laser Raman spectrometer STR-300 at 532 nm excitation wavelength at room temperature in the powder form.

RESULTS AND DISCUSSION

The X-ray diffraction study was carried out for the powder samples. Fig 1 shows typical diffractogram for the prepared ZnSe nanoparticles at room temperature. Peaks at angles (2θ) 27.44° and 47.24° assign to respective (111) and (220) planes.

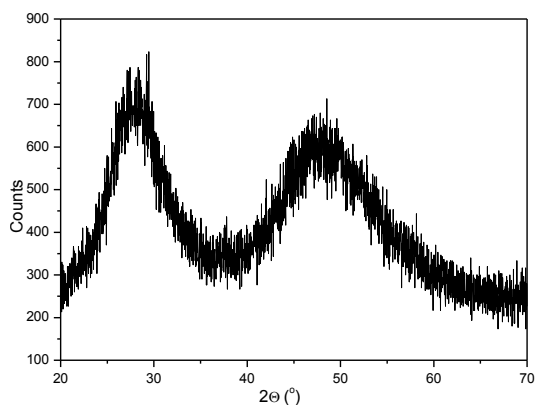


Figure 1: XRD pattern of synthesized ZnSe nanoparticles

Phase of ZnSe nanoparticles was found to be zinc blend structure. Broadening of these peaks as seen in fig. is because of small size of ZnSe particles. In this sample the height of

both peaks was almost same which indicates that growth of crystallites took place in both the directions.

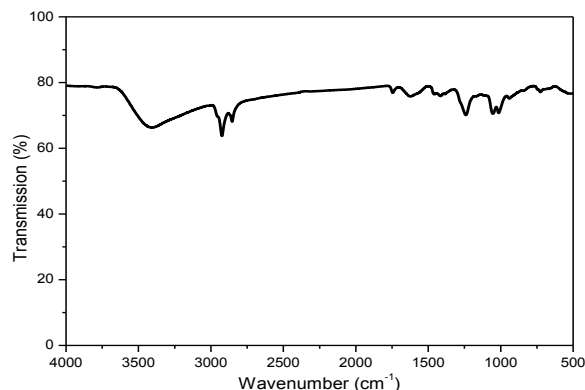


Figure 2: FTIR analysis of synthesized ZnSe nanoparticles

The prepared sample was characterized by Fourier-transform infrared spectroscopy (FTIR) and fig 2 gives illustrations of FTIR spectrum. The peak appears at 3411 cm⁻¹ is OH-stretching, the peak 2917 cm⁻¹ shows CH stretching and CH₂ asymmetric stretching. CH₂ wagging was seen in the peak 1609 cm⁻¹ and 1410.65 cm⁻¹. The characteristic major peaks appearing at 482, 561, 651, 678, 976 cm⁻¹ belong to ZnSe vibrations [10].

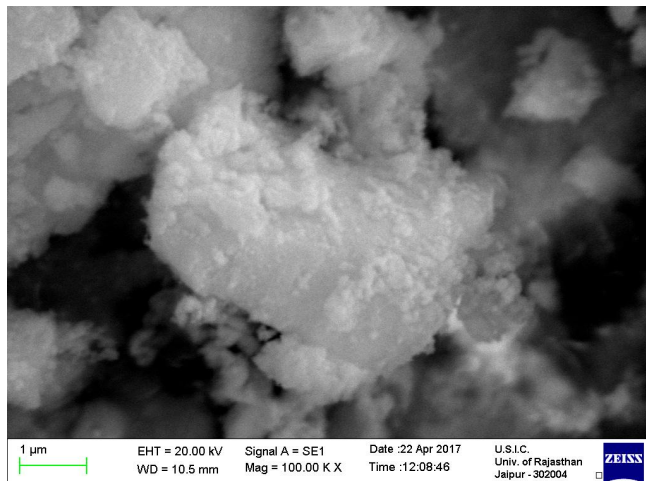


Figure 3: SEM analysis of synthesized ZnSe nanoparticles

The morphological study of ZnSe nanoparticles was also investigated by SEM and TEM. The morphology of the particles were determined from the SEM and TEM images. The SEM image of the synthesized product shown in fig 3 clearly shows that the prepared product is spherical nanoparticles.

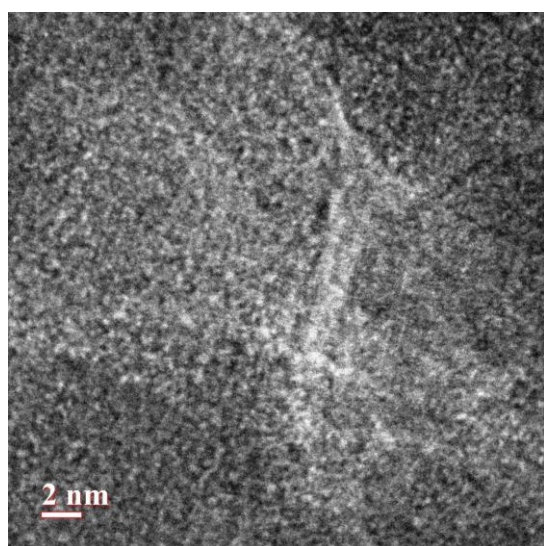
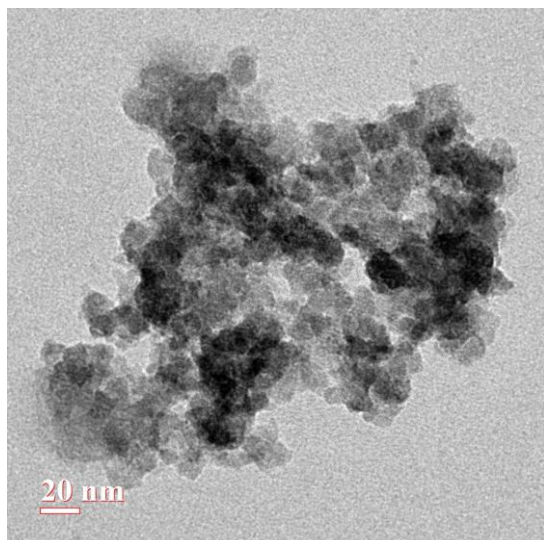


Figure 4&5: HRTEM analysis of ZnSe synthesized nanoparticles

TEM images of ZnSe nanoparticles show that agglomeration of particles was observed in the image which is due to the fact that initial poor re-dispersion of particles in the organic solvent. The agglomeration was also due to high crystallinity of the particles. The particles are stacked over other particles as shown in TEM image. Therefore particles look as a cluster. The average size of ZnSe nanoparticles is approximately less than 15 nm. HRTEM image displays the crystalline features of ZnSe nanoparticles.

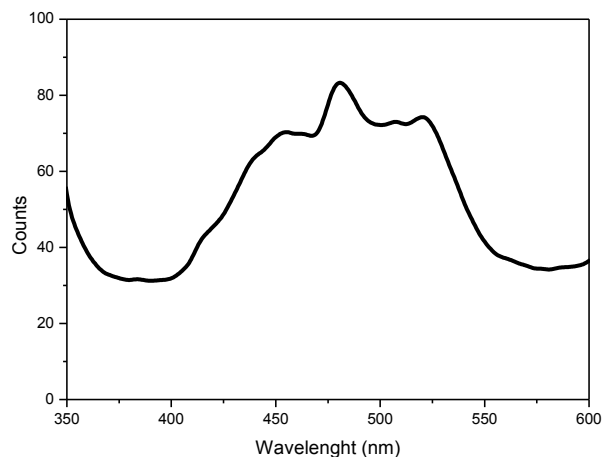


figure 6: PL emission spectra of ZnSe synthesized nanoparticles

F

The photoluminescence (PL) emission spectrum of ZnSe nanoparticles reveals strong emission with exciting of ultraviolet light (325 nm) as appeared in Fig 6. Three emission peaks are observed which are centered at 453 nm, 480 nm and 520 nm. The emission positions of ZnSe nanoparticles are relatively unaltered with changing the excitation wavelength, however emission intensities change.

The emission band at 480 nm is typically viewed as band to band emission of ZnSe [11]. The peaks at 453 nm and 520 nm are typically doled out to self-activated luminescence that occurs due to donor- acceptor pairs, which are identified to interstitial states and Zn/Se vacancy [12,13]. These outcomes propose that the optical properties of ZnSe nanoparticles were very delicate to the exploratory conditions.

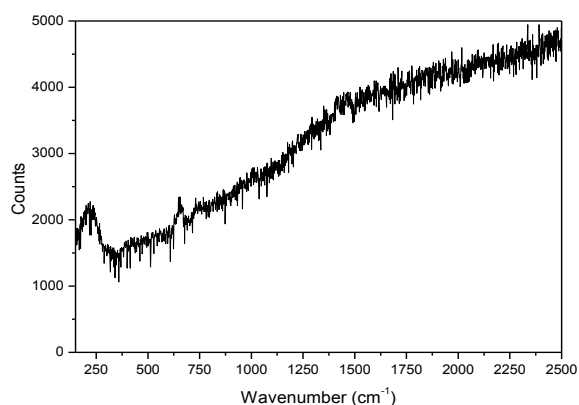


Figure 7: Raman spectrum of the ZnSe synthesized nanoparticles

The Raman spectrum of the ZnSe nanoparticles was recorded using excitation wavelength of 532 nm from an argon-ion laser. Fig.7 shows Raman spectrum of as-grown ZnSe nanoparticles. The Raman peak at 210 cm^{-1} can be assigned to the TO phonon modes of ZnSe nanoparticles [14].

CONCLUSION

ZnSe nanoparticles were successfully synthesized through co-precipitation method with capping of mercaptoethanol. The phase of ZnSe nanoparticles is zinc blend with an average size 15 nm. The emission spectrum indicates band to band emission of ZnSe as well as self-activated luminescence due to interstitial states and Zn/Se vacancy.

ACKNOWLEDGEMENTS

The authors are highly thankful to Deenbandhu Chhotu Ram University of Science & Technology, Murthal for providing financial assistance under University Grants Commission minor research project scheme to do this research work. Authors are also thankful to Department of Physics and Central Instrumentation Laboratory for XRD and FTIR measurements.

REFERENCES

- [1] Wang ,X., Zhu, J.J., Zhang, Y.G., Jiang, J.G., Wei S.B., (2010) *Appl. Phys. A* 99: 651.
- [2] Peng ,Q., Dong ,Y.J., Deng ,Z.X., Y.D. Li, (2002), *Inorg. Chem.* 41: 5249.
- [3] L.H. Qu, X.G. Peng, (2002) *J. Am. Chem. Soc.*, 124 2049-2055.
- [4] Xi , B.J., Xiong, S.L., Xu, D.C., Li ,J.F., Jhou, H.Y. x, Li, J.Y., Qian, Y.T., (2008) *Chem. Eur. J.* 14: 9786.
- [5] Zhai, T.Y., Zhong, H.Z., Gu ,Z.J., Peng ,A.D., Fu ,H.B., Ma ,Y., Li, Y.F., Yao ,J.N., (2007) *J. Phys. Chem. C* 111:2980.
- [6] Wang ,H.T., T. T, Yan ,S.C., Huang ,N.P., Xiao ,Z.D., (2009) *J. Cryst. Growth* 311:3787.
- [7] Zhou ,W.C., Liu ,R.B., Tang, D.S., Wang ,X.X., Fan ,H.M., Pan A.L., Zhang ,Q.L., Wan ,Q., Zou , B.S., (2013) *Nanotech.* 24: 055201.
- [8] Senthilkumar ,K., Kalaivani ,T., Kanagesan, S., Balasubramanian, V., J., Balakrishnan, (2013) *J. Mater. Sci.* 24: 692.
- [9] Wang ,X., L. L, Lin ,Y., Zhu ,J.J., (2013) *J. Ceramics. Inter.* 39: 5213.
- [10] Ahamed ,A. J., Ramar ,K., Kumar ,P. V. , (2016) *J. Nanosci. Tech.* 2: 148–150.
- [11] Panda ,B.A.B., Acharya, S., Efrima, S., (2005) *Adv. Mater.* 17: 2471.
- [12] Wang ,H.T., T. T, Yan, S.C., Huang ,N.P., Xiao, Z.D.,(2009) *J. Cryst. Growth* 311: 3787.
- [13] Wei, J., Li ,K.Z., Chen, J., Zhang, J.Z., Wu ,R.H., (2012) *J. Alloys Compd.* 531: 86.
- [14] Kumar ,P., Singh ,J., Pandey ,M.K., C.E., Jeyanthi, Siddheswaran , Paulraj, R., M., Hui ,K.S., (2014) *J. Mater. Res. Bull.* 49: 144.