

Morphological and Optical Investigation of Pure and Triethylamine Modified ZnS[†]

R. ANNIE SUJATHA^{1,*}, M. NAVANEETHAN², P. JOSEPH STALIN³, C. MUTHAMIZHCHELVAN¹ and Y. HAYAKAWA²

¹Department of Physics and Nano Technology, Center for Materials Science and Nanodevices, SRM University, Kattankulathur-603 203, India

²Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8011, Japan

³Department of Physics, Thanthai Hans Roever College, Elambalur, Perambalur-621 212, India

*Corresponding author: E-mail: anniesujatha@gmail.com

AJC-12810

Semiconductor nanoparticles are promising candidates for optoelectronic devices, sensors and display devices due to their size dependent unique properties which can be varied. ZnS a class of wide bandgap II-IV semiconductor (3.65 eV) is a novel class of luminescent material that exhibits excellent physical and chemical properties when reduced to nanodimensions. A facile chemical route of synthesis of pure ZnS and triethylamine capped ZnS is reported. The structural and phase information is obtained from XRD studies. The optical properties of the prepared samples were measured using UV-VIS and photoluminescence spectroscopies. The UV-VIS studies shows a blue shift compared to its bulk counterpart. The photoluminescence signal intensities of doped ZnS shows enhancement compared to undoped samples. The FTIR studies confirm the presence of triethylamine in the synthesized product. The HRTEM images shows sheet like morphology when doped with triethylamine. In this paper we report a general strategy for the synthesis of functional nanomaterials.

Key Words: Morphology, Optical properties, Triethylamine, ZnS.

INTRODUCTION

The unique and potential applications of semiconductor nanocrystals have been of interest because of their size- and shape dependent physical and chemical properties¹. These luminescent nanocrystals have a narrower emission band, broad excitation band and shows characteristic luminescence of the ions which has been doped in them. Manganese doped ZnS is an extensively studied system which has a long lifetime that makes it suitable to be used as opto electronic and display devices such as flat panels, on-linear optical materials *etc.* Earlier reports shows ZnS nanomaterials successfully synthesized into a variety of morphologies, such as nanoparticles², nanowires, nanorods, nanobelts, nanosheets³ and more complicated nanostructures⁴. Manipulation of obtaining desired optical spectra of ZnS nanocrystals is significant for their applications. Here we report on the optical properties of the of ZnS semiconductor nanocrystals doped with Mn impurities⁵. The Mn²⁺ ion *d*-electron states act as efficient luminescent centers while interacting strongly with the *sp* electronic states of the host nanocrystal into which external electronic excitation is normally directed since this electronic interaction provides an effective energy transfer path and leads to high luminescent efficiencies at room temperature. In this work, we propose an

alternative method to synthesize water-soluble ZnS:Mn nanocrystals by using triethylamine as a complexing agent. The introduction of triethylamine can remarkably improve the efficiency and reproducibility of the doping of Mn.

EXPERIMENTAL

ZnS nanoparticles were prepared by wet chemical route⁶. At first, 10 mL each of both zinc nitrate solution and saturated solution of sodium sulfide in methanol are prepared. Zinc nitrate solution is vigorously stirred using a magnetic stirrer up to 1 h and then the solution of sodium sulfide is mixed with the solution of zinc nitrate drop wise. A white precipitate is formed which is separated from the reaction mixture by centrifugation for 5 min at 10,000 rpm and is washed several times with methanol to remove sodium particles. The wet precipitate is then dried up for further measurement and analyses. Manganese doped and triethylamine capped ZnS is then prepared as follows. The analytical grade reagents of zinc nitrate and manganese acetate were used as the precursors. Appropriate amounts were dissolved in ethanol and stirred for few minutes. Then solution of sodium sulphide was added drop wise with addition of triethylamine put into the resulting solution and stirred vigorously for 2 h. The products were washed with ethanol and deionized water for several times

[†]International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

and separated by centrifugation and then dried get white powder. Structural analysis was performed by X-ray diffraction studies using X'per PRO (PANalytical) advanced X-ray Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Optical characterization was done obtained with UV-VIS, photoluminescence and FTIR spectral studies. Electron microscopic analysis were carried out with SEM and TEM analysis. For TEM analysis, the samples were dispersed in ethanol and this dispersion was drop casted on a copper-grid.

RESULTS AND DISCUSSION

In the XRD patterns of the undoped and doped, triethylamine capped samples, three diffraction peaks at 2θ values of 28.61, 47.71 and 56.31 appeared due to reflections from the (111), (220) and (311) planes of the cubic(zincblende) phase of ZnS. The XRD patterns of the sample as shown in Figs. 1 and 2 matches well with JCPDSNos.05-0566. The average crystallite size as calculated using Scherrer's formula⁷ for pure ZnS is around 15 nm and with the doping of Mn and capping with triethylamine the size has been reduced to an average of 6 nm. This shows the role of triethylamine in the size control of the ZnS samples.

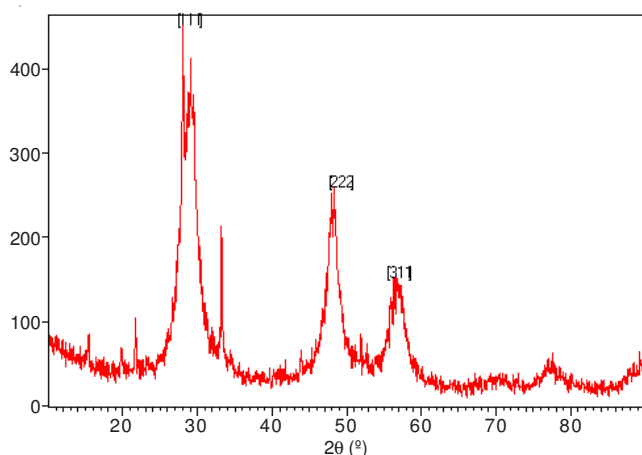


Fig. 1. XRD powder pattern of pure ZnS nanoparticles

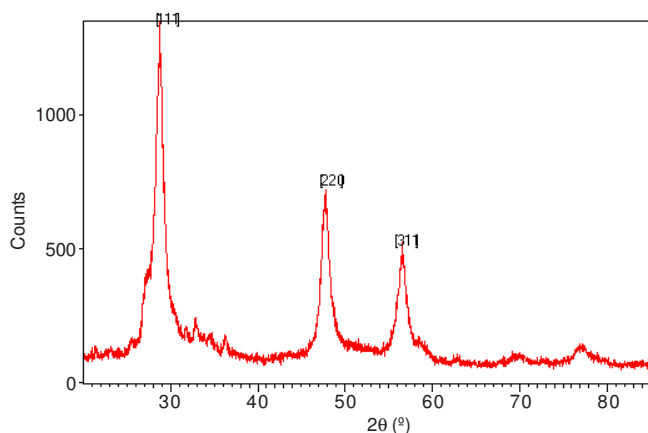


Fig. 2. XRD powder pattern of ZnS:Mn triethylamine capped nanoparticles

The FTIR spectral analysis of undoped and doped ZnS are shown in Figs. 3 and 4. The broad absorption bands in the range of $3500\text{--}3410 \text{ cm}^{-1}$ corresponds to the OH group indicating the existence of water. This may be due to some water

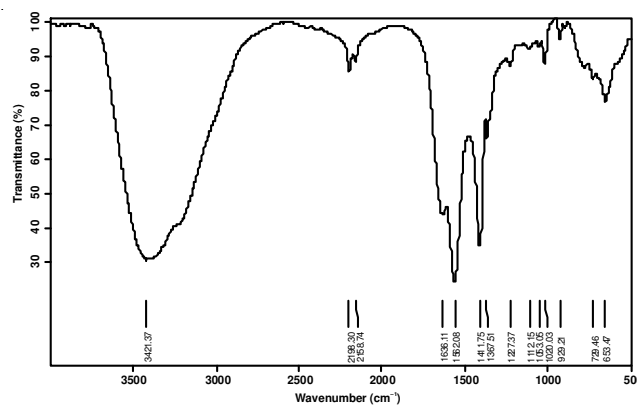


Fig. 3. FTIR of pure ZnS nanoparticles

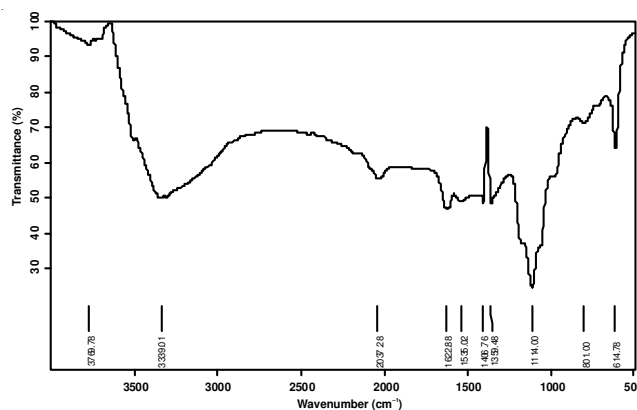


Fig. 4. FTIR of ZnS:Mn triethylamine capped nanoparticles

adsorbed during the FTIR measurements⁸. The absorption at $1650\text{--}1500 \text{ cm}^{-1}$ is due to COO stretching due to absorption of atmospheric CO_2 on the surface of nanoparticles⁹. The bands at 801 and 614 cm^{-1} in figure shows MnS vibrations in which some of the Zn ions have been replaced by means Mn ions in the cationic sites of ZnS particles¹⁰. Triethylamine molecule is identified by the absorption band due to C-N vibrations at 1114 cm^{-1} .

The optical properties of the samples are investigated from the absorption measurements in the range of $280\text{--}700 \text{ nm}$. The UV-VIS studies reveal the optical absorption spectra of the nanocrystalline ZnS and the peak was determined to be at approximately at 240 nm (Fig. 5) and the absorption peak for ZnS:Mn capped with triethylamine was determined to be at 211 nm as in Fig. 6. This is blue shifted when compared to the bulk ZnS (measured at 340 nm)¹⁰. The shift can be explained by quantum confinement effects, consistent with the fact that the size of the synthesized samples is in the nano scale region which can be used as a measure of particle size and size distribution¹¹.

The optical properties of pure ZnS and ZnS:Mn: triethylamine were studied with photoluminescence measurements in Figs. 7 and 8. The photoluminescence spectra measurement showed maximum peak intensity at 417 nm for ZnS pure and maximum peak intensity at 564 nm for ZnS capped with triethylamine. The radiative recombination on the surface of ZnS nanocrystals with sulfur vacancies has been held responsible for defect emission with a maximum at *ca.* 564 nm when Mn ions were incorporated into the ZnS lattice and substituted for host cation sites the mixing between the *s* and *p* electrons of

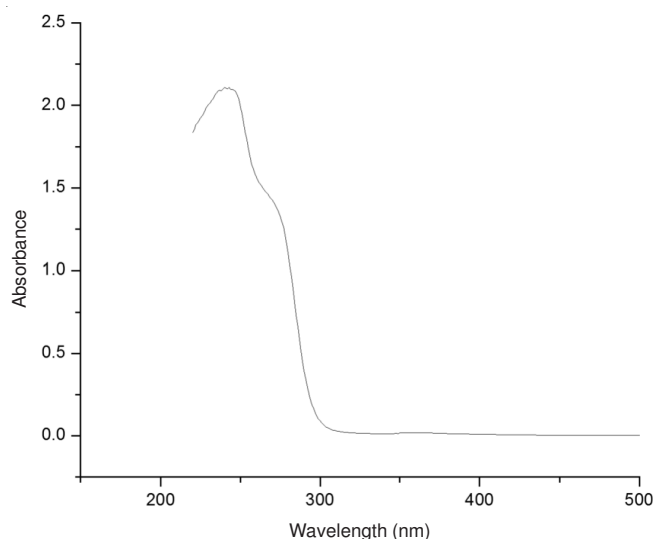


Fig. 5. UV-visible absorption spectra of pure ZnS nanoparticles

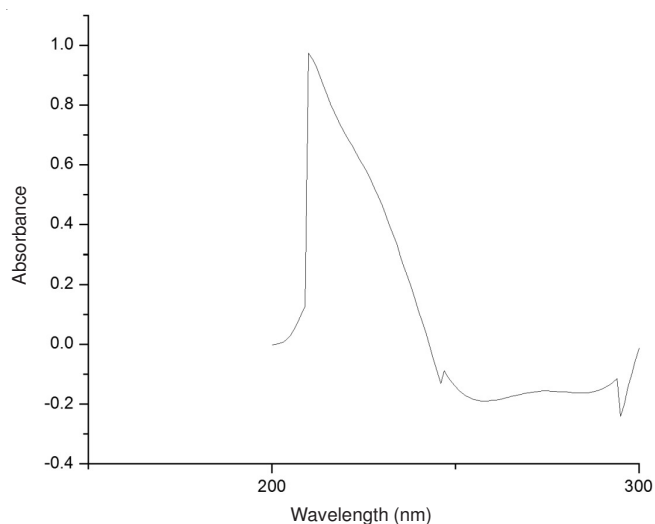


Fig. 6. UV-visible absorption spectra of ZnS:Mn triethylamine capped nanoparticles

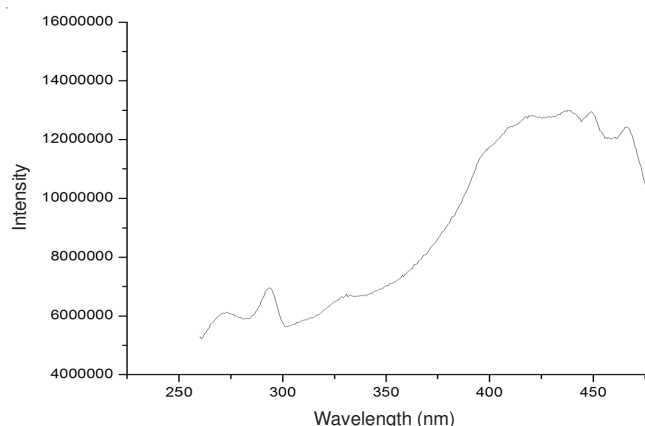


Fig. 7. Photoluminescence of pure ZnS nanoparticles

the host ZnS and the electrons of Mn occurred and made the forbidden transition of $4T_1-6A_1$ partially allowed, resulting in the characteristic emission of Mn¹². The difference between the absorption edge (211 nm) and emission peak (417 nm) was around 106 nm. This is due to the trap state emission in

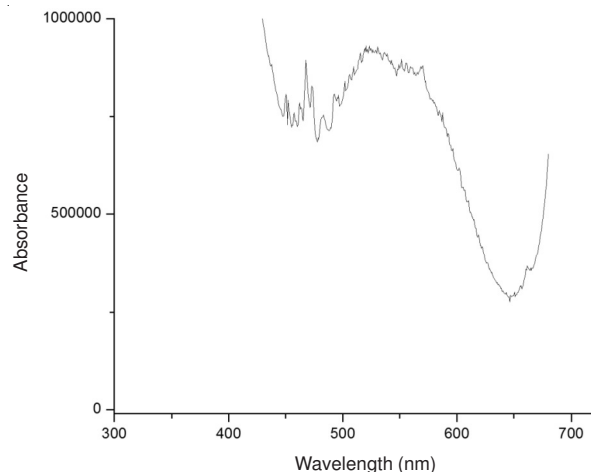


Fig. 8. Photoluminescence of ZnS:Mn triethylamine capped nanoparticles

the smaller size of the particles¹³. Also, the emission width of the nanoparticles indicates the formation of crystallites with electronic sites attributed to the electronically passivating of the capping molecules to the semiconductor nanoparticles. This shows that the triethylamine molecules effectively capped the surface of the ZnS nanoparticles. Also this may be attributed to the reduction in the number of dangling bond density and thus the number of surface trap sites for nonradiative recombination due to the addition of triethylamine and improving the photoluminescence intensities.

The TEM and SEM images of ZnS and ZnS:Mn capped with triethylamine nanoparticles showed that these nanoparticles are agglomerated¹⁴. The Figs. 9 and 10 shows the SEM image of pure ZnS and ZnS:Mn capped with triethylamine which exhibits particle and sheet like structures, respectively.

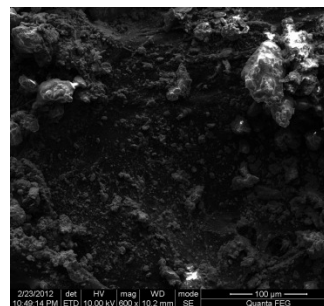


Fig. 9. SEM image of pure ZnS nanoparticles

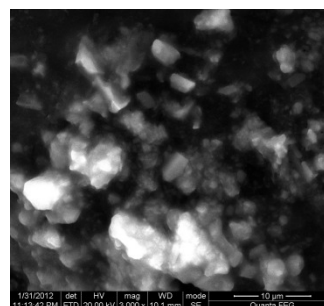


Fig. 10. SEM image of ZnS:Mn triethylamine capped nanoparticles

Figs. 11 and 12 shows the TEM images ZnS:Mn capped with triethylamine which shows a two-dimensional sheet like morphology¹⁵.

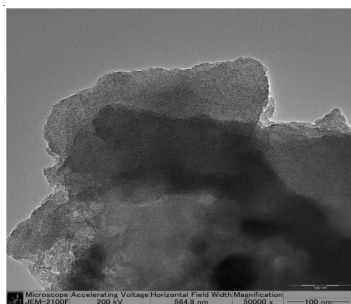


Fig. 11. TEM image of pure ZnS nanoparticles

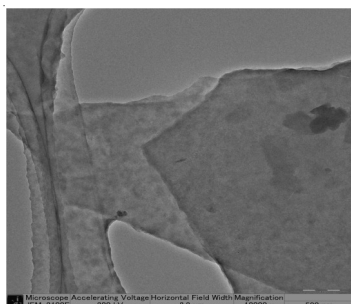


Fig. 12. TEM image of ZnS:Mn triethylamine capped nanoparticles

Conclusion

Pure and manganese doped zinc sulphide (ZnS:Mn^{2+}) nanoparticles are prepared using triethylamine as a surface passivator by wet chemical method at room temperature. The XRD measurements yielded the particle size in the range of 6-15 nm. It has been observed that with the addition of triethylamine the absorption peak of the ZnS:Mn shifts towards shorter wavelength. Room temperature photoluminescence spectrum of the undoped sample exhibit a blue emission peaked

at 417 nm under UV excitation whereas the Mn^{2+} doped sample exhibits a yellow emission peaked at 564 nm under same UV excitation. The enhanced photoluminescence intensity is due to triethylamine, this is achieved by eliminating the surface defects, in which surface passivator plays an important role. The SEM and TEM images show the morphology of pure ZnS which is dispersed particles and triethylamine capped ZnS which shows a sheet like structure.

REFERENCES

1. X.G. Peng, L. Manna, W.D. Yang, J. Wickham, E. Scher, A. Kadavanich and A.P. Alivisatos, *Nature*, **404**, 59 (2000).
2. S.H. Choi, K. An, E.G. Kim, J.H. Yu, J.H. Kim and T. Hyeon, *Adv. Funct. Mater.*, **19**, 1645 (2009).
3. X.S. Fang, C.H. Ye, L.D. Zhang, Y.H. Wang and Y.C. Wu, *Adv. Funct. Mater.*, **15**, 63 (2005).
4. X.S. Fang, Y. Bando and D. Golberg, *J. Mater. Sci. Technol.*, **24**, 512 (2008).
5. A.A. Bol and A. Meijerink, *J. Lumin.*, **87-89**, 472 (2002).
6. T. Isobe, T. Igarashi, M. Konishi and M. Senna, *Mater. Res. Soc. Symp. Proc.*, 383 (1999).
7. J. Eastoe, G. Fragneto, B.H. Robinson, T.F. Towey, R.K. Heenan and F.J. Leng, *J. Chem. Soc. Faraday Trans.*, **88**, 461 (1992).
8. W.Q. Peng, G.W. Cong, S.C. Qu and Z.G. Wang, *Nanotechnology*, **16**, 1469 (2005).
9. M.A. Gondal, Q.A. Drmash, Z.H. Yamani and T.A. Saleh, *Appl. Surf. Sci.*, **256**, 298 (2009).
10. P. Calandra, M. Goffredi and V.T. Liveri, *Colloid Surf. A*, **160**, 9 (1999).
11. P. Vinotha Boorana Lakshmi, K. Sakthi Raj and K. Ramachandran, *Cryst. Res. Technol.*, **44**, 153 (2009).
12. R.N. Bhargava, D. Gallagher, X. Dong and A. Nurmikko, *Phys. Rev. Lett.*, **72**, 416 (1994).
13. N. Pradhan, D. Goorskey, J. Thessing and X.G. Peng, *J. Am. Chem. Soc.*, **127**, 17586 (2005).
14. W.Q. Peng, S.C. Qu, G.W. Cong and Z.G. Wang, *J. Cryst. Growth*, **282**, 179 (2005).
15. Y.L. Soo, Z.H. Ming, S.W. Huang and Y.H. Kao, *Phys. Rev. B*, **50**, 7602 (1994).