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Surface characterization and optical properties of polyphosphate capped ZnS nanoparticles

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ABSTRACT

Polyphosphate capped ZnS nanoparticles have been successfully synthesized by simple aqueous method using thiourea as S^{2-} source. X-ray diffraction (XRD) indicated that the ZnS nanoparticles were 1.38 nm in size with a zinc blende structure. Morphology of the prepared sample was characterized using a scanning electron microscope (SEM). Surface characterization of the nanocrystals has been done by FTIR spectroscopy and it was found that the nanoparticles were sterically stabilized by sodium hexametaphosphate. Absorption spectra have been obtained using UV-Vis spectrophotometer to find the optical band gap. Particle size was calculated by deriving an equation using effective mass approximation (EMA). The results indicated that varying the capping agent concentration could produce stable ZnS nanocrystals with the mean size varying between 3.0 and 4.3 nm.

Key words: ZnS nanoparticles, SHMP, optical properties, powder XRD, Electron microscopy.

INTRODUCTION

Synthesis of materials at nanomaterial scale has become an important research line in the recent years due to strong dependency of the size of the particle over the optical**,** electronic and thermodynamical property [1]. With the decrease of particle size extremely high surface to volume ratio causes the surface states to act as luminescence quenching centers. A large number of surface atoms result in the high surface energy of these nanoparticles, which makes them extremely reactive. Most systems without protection or passivation of their surfaces undergo aggregation [2,3] Much effort has been made to seek the best capping agents to passivate the nanoparticles surface [4-6]. Unfortunately, many organic passivators, such as thiolphenol [7] and mercapto acetate [8] and so on, are toxic, which will pollute the environment if large-scale nanoparticles are produced. Hence it is necessary to modify the nanoparticles surface by using suitable capping agent so that the surface caps will passivates the defect states and dangling bond density. ZnS, as an important group II–VI semiconductor

compound with wide band gap energy of 3.67 eV, has attracted much research interest due to its excellent properties in luminescence and photochemistry [9-14]. There are different processes used to produce ZnS nanoballs and nanoparticles based material by microwave assisted synthesis [15-17], ZnS microspheres and hollow nanospheres by hydrothermal synthesis [18] and ZnS nanoparticles by mechanochemical synthesis [19]. Among the synthesis strategies the wet chemical approach has attracted much more attention due to its distinct advantages in having simple reaction conditions and effective control over the size and shape of nanoparticles by systematically adjusting reactant molar ratio [20].

Here we present the synthesis of polyphosphate capped ZnS nanoparticles using SHMP as capping agent by simple aqueous method that avoids the detrimental organometallic precursors and high temperature. The obtained nanocrystals were characterized for their morphology and structure. Optical studies were also done.

MATERIALS AND METHODS

A.R. grade zinc acetate dihydrate, copper acetate monohydrate, thiourea, sodium hexametaphosphate (SHMP), ethanol were obtained commercially and used without further purification. Double distilled water was used for sample preparation and dilution. In a typical synthesis, 10 g of SHMP was dissolved in 80 ml of water and to it a solution of zinc acetate (10 mmol dissolved in 10 ml of water) was added drop wise with continuous stirring. White precipitate was formed which subsequently dissolved during the stirring process. The mixture was then heated to 80ºC using hot plate. Solution of thiourea (10 mmol dissolved in 10 ml of water) was added slowly to the above mixture along with continuous stirring for 15 minutes. The white precipitate so formed was isolated by centrifugation, washed several times with water and finally with ethanol to remove any impurities and dried in oven at 60ºC. Three different samples were prepared by changing the concentration of SHMP.

Characterization

The prepared sample was characterized by powder XRD using Rigaku Miniflex with Cu Ķα (1.5406Å) radiation in 2θ range of 20° to 80° at step size of 0.02º (2θ). The SEM images and elemental compositions (energy-dispersive X-ray analysis) of the ZnS nanoparticles were analyzed by scanning electron microscope equipped with EDX unit (FEI Quanta 200). The FTIR spectrum was recorded on SHIMADSU FTIR 8400S spectrophotometer. UV-VIS spectra were recorded on a Systronic UV spectrophotometer 119.

RESULTS AND DISCUSSION

Grain size studies

Figure 1 shows the measured XRD pattern of SHMP capped ZnS nanoparticles. Three broad peaks corresponding to the (111), (220) and (311) planes were observed. The pattern is well matched with the cubic ZnS sphalerite structure, no second phase can be observed. The peak broadening clearly indicates that small nanocrystals are present in the sample.

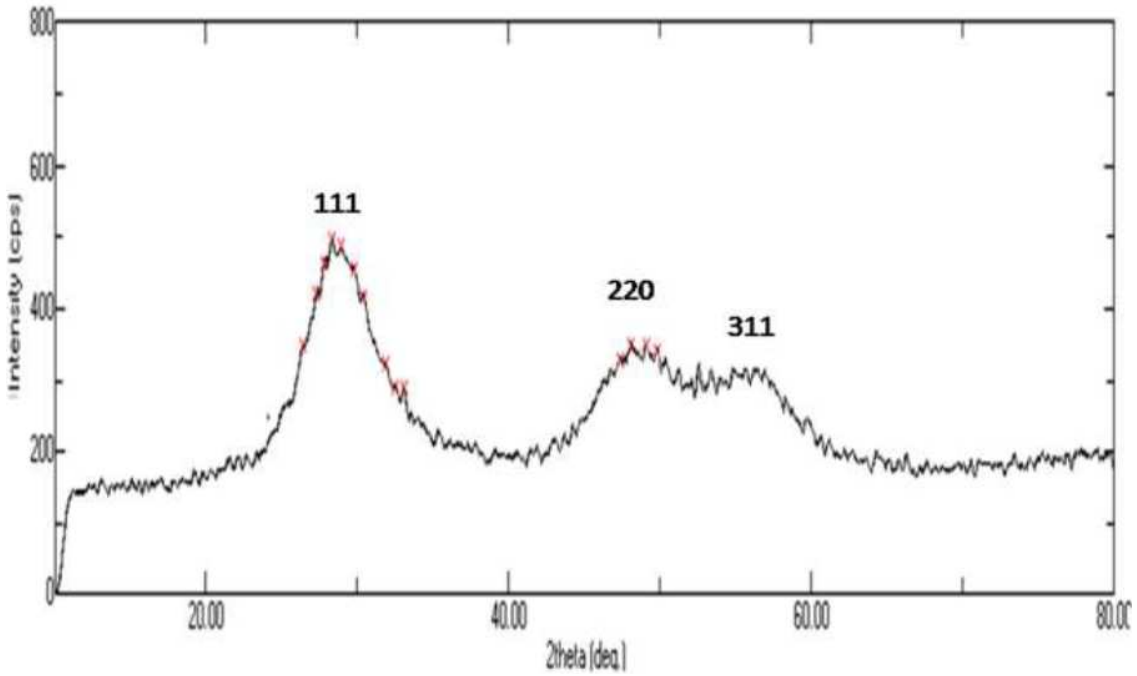

Figure 1. XRD diffraction pattern of SHMP capped ZnS nanocrystals

Crystallite size of capped ZnS nanocrystals was calculated by following Scherrers equation [21].

$D = K \lambda / \beta \cos \theta$ (1)

The average size calculated from the above formula is 1.38 nm.

Electron microscopy

The microstructure of the nanocrystals was examined by scanning electron microscopy (SEM) and the elemental composition of the nanoparticles formed were confirmed by energy dispersive x-ray (EDX) analysis as shown in figure 2 (a) and (b). It can be seen that the surface of the particles appears smooth and spherical.

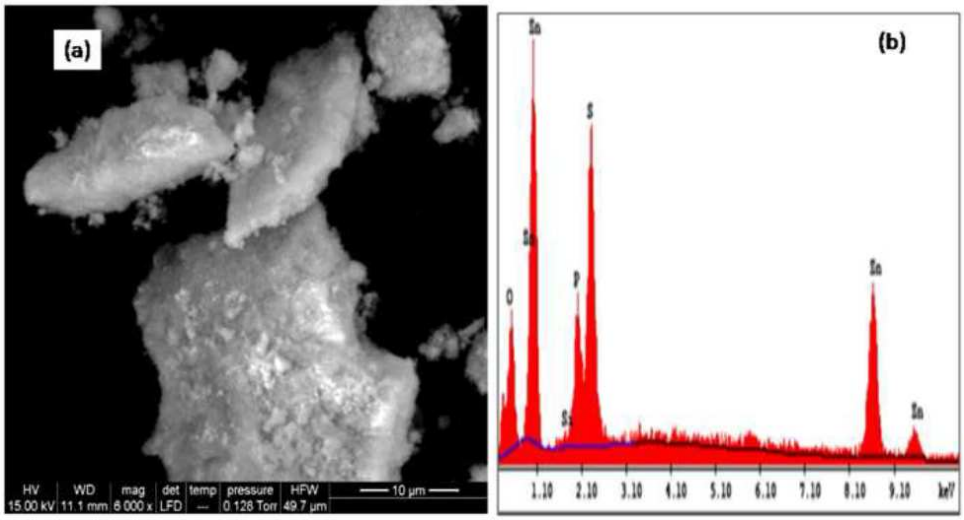

Figure 2 (a) SEM image of SHMP capped ZnS nanocrystals and (b) EDX spectrum of SHMP capped ZnS nanoparticles

FTIR spectra

Passivation of the surface of ZnS the nanoparticles by the stabilizing agent is inferred from FTIR spectra as shown in Figure 3.

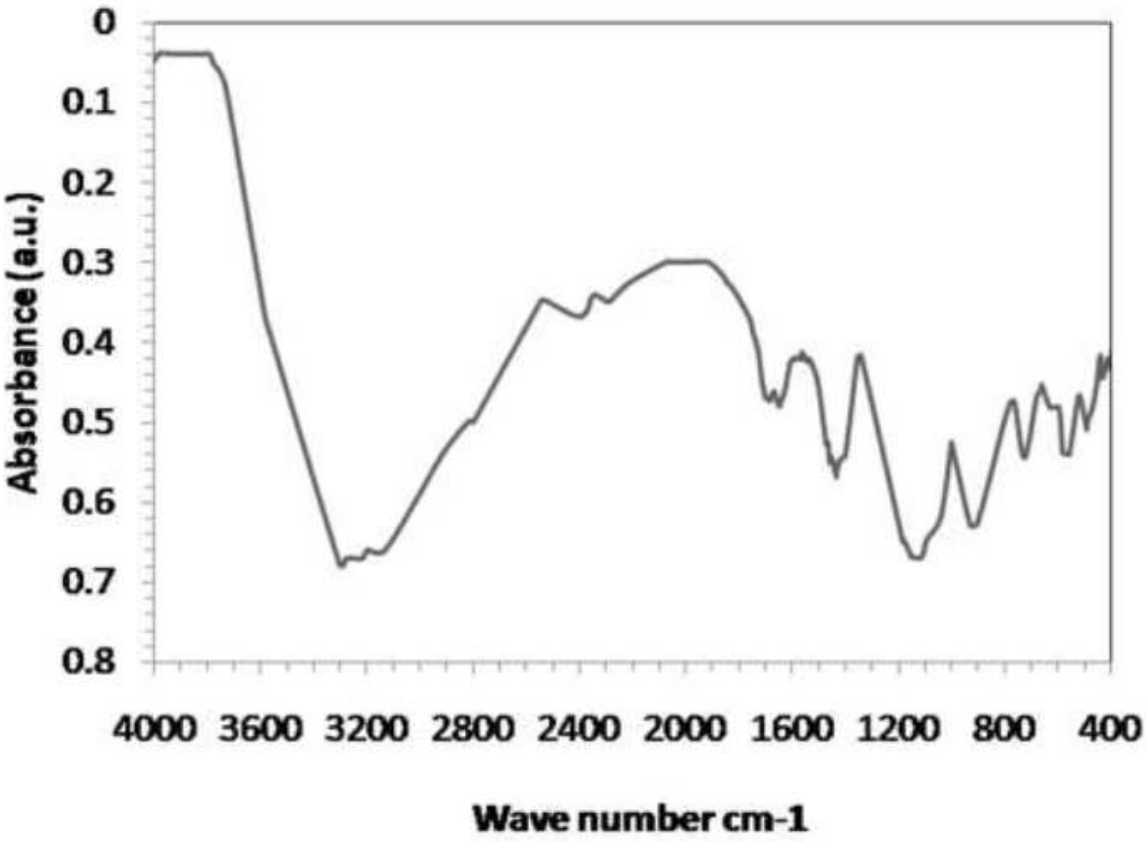

Figure 3. FTIR spectrum of SHMP capped ZnS nanocrystals

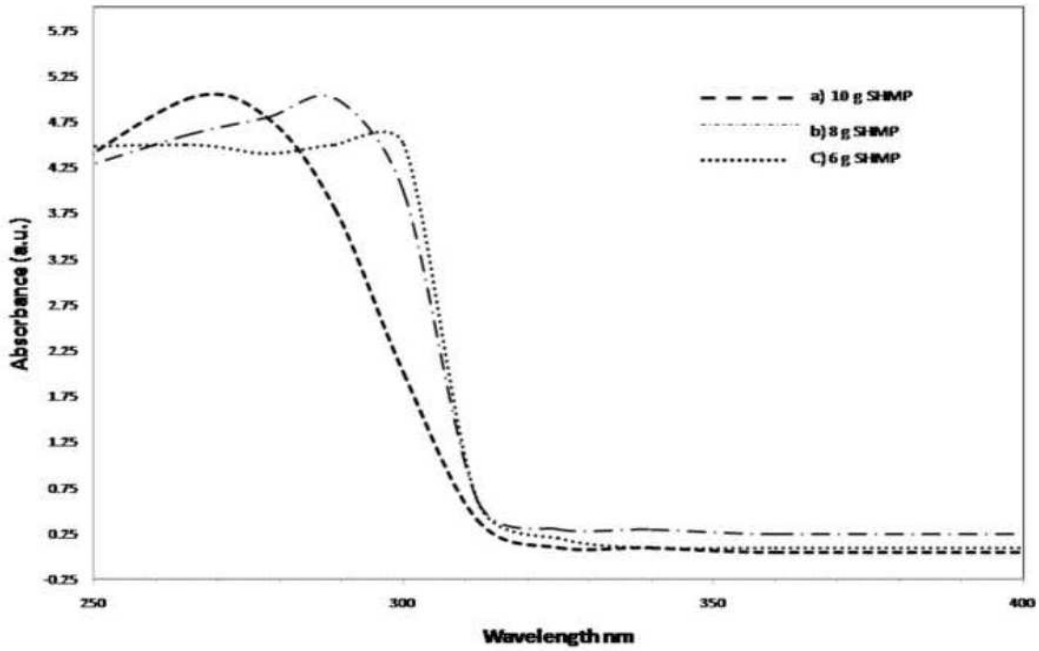

Figure 4. Optical absorption spectra of SHMP capped ZnS nanocrystals with different concentration of capping agent. (a) 10 g SHMP (b) 8 g SHMP (c) 6 g SHMP

The peak at 659 cm^{-1} and 725 cm^{-1} is due to bending vibration of P-O bond while the peak at 927 cm^{-1} is due to P-O stretching. The band between 1089 cm-1 to 1179 cm-1 may be due to the asymmetric P-O stretching vibration of the PO_4 group present in the SHMP.

Optical absorption studies

Absorption spectrum of SHMP capped ZnS nanoparticles have been studied by dispersing 0.001 g of the samples in 1 ml of water as shown in Figure 4.

The spectrum reveals that the intensity increases toward shorter wavelength. Optical excitation of electrons across the band gap is strongly allowed transition thus it causes an abrupt increase in the absorbance at wavelength corresponding to gap energy. Blue shifting of absorption peak (bulk 345 nm) is due to quantum confinement of the excitons present in the sample resulting in a more discrete energy of the spectrum of individual nanoparticles. The average particle size present in the nanoparticles can be determined by using the mathematical model of effective mass approximation.22 The following equation was derived and the particle size (r, radius) was calculated as a function of peak absorbance wavelength (λp) for ZnS nanocrystals.

$$r\ (\text{nm}) = \{-0.2963+\sqrt{(}\ -40.1970+13620/\lambda p)\} / \{-7.34+2481.6/\lambda p\} \qquad (2)$$

Absorption spectra of ZnS nanoparticles at various concentrations of capping agent have been studied in the present investigation. It is clear from the spectra (figure 4) that sudden increase in absorption occurred at 265 nm, 289 nm and 300 nm for sample a, b and c respectively. The absorption edge was found at shorter wavelength with decreasing particle size. As the capping agent concentration increases the optical band gap is found to increase which was calculated using the absorption peak [23]. The size of the particles calculated from the derived equation is shown in table 1.

Table 1. Particle size calculation of SHMP capped ZnS from optical studies

Sample	λ_p(nm)	band gap bulk (eV)	band gap nano (eV)	particle size derived from optical studies(nm)
(a)	300	3.67	4.1	4.3
(b)	289	3.67	4.3	3.8
(c)	265	3.67	4.7	3.0

CONCLUSION

In this paper we have reported the synthesis of SHMP capped ZnS nanoparticles by simple aqueous method. The optical properties get modified dramatically due to confinement of charge carriers within the nanoparticles. The optical absorption studies show that the absorption edge shifts towards blue region as the capping agent concentration is increased indicating that the effective band gap energy increase with decreasing particle size. The results indicated that varying the capping agent concentration the mean size of the ZnS nanocrystals varied between 3.0 to 4.3 nm.

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REFERENCES

[1] T. Igarashi, T Isobe , M. Senna, *Phys. Rev. B*, **1997**, 56, 6444.
[2] A. Ulman, *Chem. Rev.,* **1996**, 96, 1533.
[3] R. Wang ,J. Yang, Z. Zheng, M.D. Carducci, J. Jiao, S. Seraphin, *Angew. Chem. Int. Ed*., **2001,**40, 549.
[4] K. Manzoor, S.R. Vadera , N. Kumar, T. R. N. Kutty, *Solid State Commun.,* **2004,**129**,** 469.
[5] J.E. Kim, C.S.Hwan, S.Yoon, *Bull. Korean Chem. Soc*.,**2008**, 29, 1247.
[6] M.H.Ullah, II Kim, Chang-Sik Ha, *Mater. Lett.,* **2007**, 61, 4267.
[7] T.R. Ravindran, A.K. Arora, B. Balamurugan , B.R.Mehta, *Nanostruct. Mater.,* **1999**,11, 603.
[8] S.M. Liu, F. Q Liu, H. Q. Guo, Z. H. Zhang, Z. G. Wang, *Solid State Commun.***, 2000,** 115, 615.
[9] J. Nanda, S. Sapra, D. D. Sarma, N. Chandrasekharan, G. Hodes, *Chem. Mater.,* **2000,** 12, 1018.
[10] M. Tan,W. Cai W, L. Zhang, *Appl. Phys. Lett.,* **1997,** 71, 3697.
[11] N.A. Dhas, A. Zaban, A. Gedanken, *Chem. Mater.,* **1999,** 11, 806.
[12] S.B. Qadri, E.F. Skelton, A.D. Dinsmore, J.Z. Hu, W.J. Kim, C. Nelson, B.R. Ratna, *J. Appl. Phys.,* **2001,** 89, 115.
[13] S.S. Qadri X, E.F. Skelton, D. Hsu , A.D. Dinsmore , J. Yang, H.F. Gray, B.R. Ratna, *Phys. Rev. B,***1999,** 60, 9191.
[14] B. Bhattacharjee, D. Ganguli, S. Chaudhuri, A.K. Pal, *Mater. Chem. Phys.,* **2002**, 78, 372.
[15] Y. Zhao, J.M. Hong, J. Zhu, *J. Cryst. Growth*, **2004,** 270, 438.
[16] H. Yang, C. Huang, X. Su, A. Tang, *J. Alloys Comp.* **2005,** 402, 274.
[17] S.S. Manoharan, S. Goyal, M.L. Rao, M.S.Nair, A. Pradhan, *Mater. Res. Bull.,* **2001,** 36, 1039.
[18] C. Jiang, W. Zhang, G. Zou, W. Yu, Y. Qian *Mater. Chem. Phys.,* **2007,** 103, 242.
[19] T. Tsuzuki T, P.G. Mccormick, *J. Nanostruct. Mater.,* **1999,** 12, 75.
[20] M. de Dios, F. Barroso, C. Tojo, M. C. Blanco, M. A. Lopez-Quintela, *Colloids and Surfaces A:Physicochem. Eng. Aspects*, **2005,** 270, 83.
[21] B.D.Cullity, Elements of X-Ray Diffraction, second ed., Addison-Wesley publishing, Massachusetts, **2003.**
[22] L.E. Brus, *J. Phys. Chem.,* **1986**, 90, 2555.
[23] S.D. Bompilwar, S.B. Kondawar, V.A. Tabhane *Arch. Appl. Sci. Res.* **2010,** 2(3)**,** 225.