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RESEARCH ARTICLE

HIGHLY MONODISPERSE POLYMER-CAPPED ZnS NANOPARTICLES: PREPARATION AND OPTICAL PROPERTIES

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ABSTRACT

In this paper we have reported the synthesis of luminescent nanoparticles of Zinc Sulfide (ZnS) with and without capping agent. Nanoparticles of ZnS are prepared by a chemical precipitation method. The change in optical and morphological properties of ZnS nanoparticles is observed by using organic capping agent. Band gap measurements done by UV-Visible spectrophotometer and excitation spectra shows that band gap increases by introducing capping material. The phase structures and morphologies of the obtained composites were characterized by X-ray diffraction, scanning electron microscope and transmission electronic micrographs. Selected area electron diffraction (SAED) showed that the ZnS has a cubic spherulite structure. The FT-IR shows strong chemical bond between ZnS nanoparticles and host PVP polymer. Photoluminescence studies show that emission intensity increases for capped sample.

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INTRODUCTION

Nanoparticles have been investigated intensively in last many years because of their interesting optical properties due to their size dependent absorption and / or emission (Patolsky *et al.*, 2003). Among the variety of nano – sized semiconductors (zinc sulfide Nanoparticles NPs), a typical II – VI compound semiconductor, with a direct band gap of 3.6 eV at room temperature, refractive index of 2.35 and 40 meV as exciton binding energy is a very good luminescent material, which can be used for detector, emitter, modulator in optoelectronics, and blue emitting laser diode. Also, it can be applied to a transparent dielectric material (Kim *et al.*, 1997; Kim *et al.*, 2006).

Due to high surface area of nanoparticles, surface defects play an important role in their quantum efficiency. The tunability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new composite materials with optimized properties for various applications. However, applications would be restricted due to different nonradioactive relaxations pathways that mean surface-related defects. To overcome the above mentioned difficulties, organic and inorganic capping agents are used to passivate the free QDs (Pavel *et al.*, 2006; Hongjin *et al.*, 2008). The surface passivation owing to fine-particle surface capping also bears significance. Fine particles are vulnerable to surface traps such as broken bonds, oxides and impurities due to a relatively high surface-to-volume ratio, leading to the deterioration of optical characteristics. It has been reported that adequate surface capping can improve the optical characteristics such as PL (Maity *et al.*, 2006; Shiquan *et al.*, 2012).

This synthesis has been accomplished by sol–gel technique , microemulsion synthesis, mechanochemical processing , spray pyrolysis and drying , thermal decomposition of organic precursor (Xiaochuan and Yongxing, 2005; Calandra *et al.*, 1999; Yanbin *et al.*, 2008; Yinyan *et al.*, 2007; Rast and Stanishevsky, 2005), solvothermal route, selfassembling , hydrothermal processing , vapor transport process (Yanan *et al.*, 2011; Ujjal *et al.*, 2005; Byrappa and Adschiri, 2007; Kanemaru *et al.*, 2010), sonochemical or microwave-assisted synthesis , chemical precipitation method (Seung *et al.*, 2008; Manzoor *et al.*, 2003) etc. have employed in the synthesis of zinc sulfide nanoparticles. However, chemical precipitation method is one of the more widely recognized methods due to its several advantage such as easy to handle, demanding no extreme pressure or temperature control and requiring no special or expensive equipment. Therefore, this study aims to achieve the dual objectives of controlling the particle size and improving the optical characteristics by PVP capping for ZnS nanoparticles.

MATERIALS AND METHODS

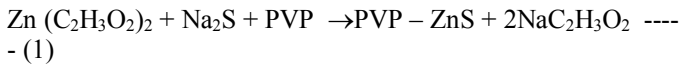
A.R.grade zinc acetate dihydrate, Sodium sulphide nonahydrate, Polyvinylpyrrolidone (PVP- molecular weight (MW) of 360 000 g/mol) and ethanol were procured commercially from nice chemicals and used without further purification.

Synthesis

SHMP capped ZnS nanoparticles were fabricated by chemical precipitation method. Sodium sulfide was added resulting in formation of white precipitate of ZnS nanoparticles that were stabilized with SHMP.

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The same procedure was carried out with different concentration of polymers. All steps of synthesis were performed at 353 K. After stirring for 1h, the solution was filtered to remove most of the solvents. Nanoparticles were washed several times with equal amount of methanol and distilled water for further purification of nanoparticles and then the powder was dried in the oven at 333 K for 12h.

Characterization

The UV-Vis spectra of the samples were explored with the help of Perkin-Elmer Lambda 20 UV-Vis. XRD analysis was studied by Seifert Iso - de bye flex - 2002 X-ray diffractometer using Cu K_α radiation (λ=0.1542 nm) which was operated at 50 kV and 100 mA. TEM analysis was performed with a Hitachi 600 microscope operated at 120 kV. Approximately 150 nanoparticles of each sample were measured for size distribution. The microphotographs of these samples were recorded using Jeolsem model, (Jse - 5610 lv). The semi quantification elemental analyses were investigated to identify the weight percentage of major elements present in the samples using the Oxford Inca energy dispersive X-ray spectrometer (EDX). The FTIR spectra were carried out with help of FTIR spectrometer Perkin - Elmer 330 series in the range of 375 cm⁻¹ to 4000 cm⁻¹ Photoluminescence spectra were recorded at room temperature using Elicosl- 174 fluorescence spectrophotometer.

Optical absorption studies

The UV-Vis absorption spectra show (Figure-1) the prepared PVP capped and uncapped ZnS samples. For measuring the absorption characteristics, the nanoparticles are first dispersed in methanol and taken in a quartz cuvette. The characteristics absorption peaks due to the ZnS nanoparticles appear in the wavelength at 310 nm and this peak position reflects the band gap of the particles. The fundamental absorption, which corresponds to the electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap of the prepared ZnS nanoparticles. For obtaining the absorption characteristics of all the samples, at first the transmittance (T) at different wavelength (λ) are measured and then absorption co-efficient (α) at the corresponding wavelengths (λ) are calculated using the Beer-Lambert's relation

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \text{ ----- (2)}$$

Where d is the path length. The relation between the incident photon energy (h) and the absorption co-efficient (α) is given by the following relation.

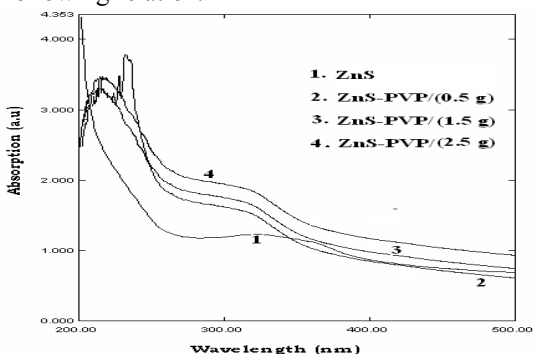


Fig.1 Absorption spectra of different concentration of PVP capped ZnS nanoparticles

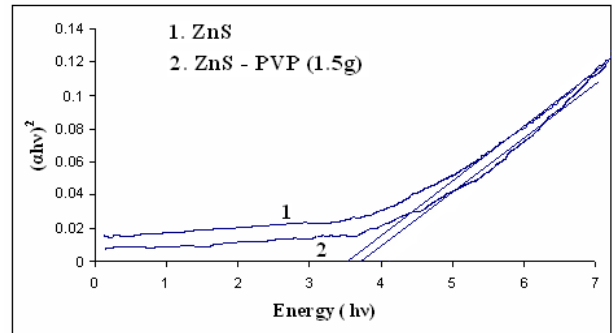


Fig.2: Optical band gap of PVP capped ZnS nanoparticles

$$(\alpha h\nu)^{1/m} = C(h\nu - E_g) \text{ ----- (3)}$$

Where C is a constant and E_g is the bandgap of the material and exponent m depends on the type of the transition. For direct and allowed transition m=1/2, indirect transition m=2 and for direct forbidden m=3/2. For calculating the direct bandgap value, (αhγ)² versus energy is plotted and it is shown in Fig.2.

The obtained values of the bandgap of ZnS nanoparticles are higher than that of the bulk value of ZnS (3.6 eV). This blue shift of the bandgap takes places because of the quantum confinement (Jianfeng *et al.*, 2004). From the value of the bandgap shift and using Brus modes (Brus, 1986), the size of a nanoparticle has been calculated. For example, the calculated diameter for uncapped ZnS is ~3.9 nm.

From the band gap energy (E_g), the calculated size of PVP capped ZnS nanoparticles is ~3.6nm. ZnS nanoparticle has Zinc-blende structure with the effective mass of the electron ≈ 0.25 m_e and hole ≈ 0.59m_h. The particle size was determined using effective mass approximation method (Hamid, 2011).

$$E_n = E_b + \left(\frac{h^2}{8R^2}\right)\left(\frac{1}{m_n} + \frac{1}{m_e}\right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r R} \text{ ----- (4)}$$

where h is the Planck's constant, R the radius of the particle and ε the dielectric constant of the material. This suggests that the excitation at 3.8 eV (310 nm) is due to the band to band transition of electrons in ZnS nanoparticles.

Phase characterization

The vertical bars indicate a standard cubic bulk ZnS peak position from JCPDS No. 77-2100. It is obvious that all of the XRD peaks of the nanoparticles can be indexed as the cubic zinc blende structure (Ranjani *et al.*, 2004), which is consistent with the values in the standard card. It can be seen that XRD patterns are broadened with three main peaks corresponding to the (111), (220) and (311) planes reflections corresponding to the 28.2°, 47.6° and 56.7° respectively. For all these four samples the above mentioned three planes are alone present. This point out the non-entry of the caper molecules (PVP) inside the crystal lattice but just grazed the molecules.

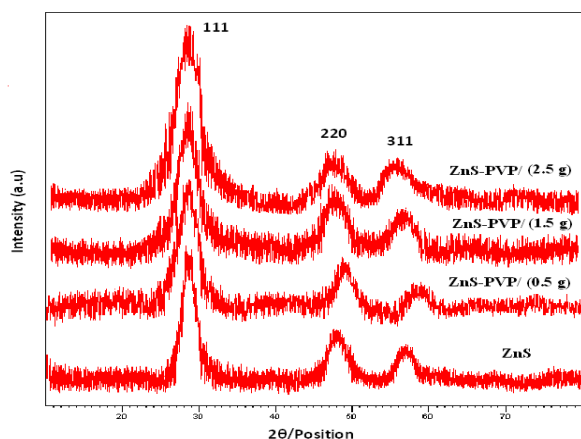


Fig. 3 XRD patterns of PVP capped ZnS nanoparticles

In addition, the broadening of the diffraction peaks for without and with capped nanoparticles (PVP) was due to the characteristic of a nanoparticle. The mean crystallite sizes of the without and with capped nanoparticles were determined by using the Debye - Scherrer's

$$D = \frac{k\lambda}{\beta \cos\theta} \text{----- (5)}$$

Where k is a constant, (shape factor, about 0.9) λ is the X-ray wavelength ($\lambda=1.544 \text{ \AA}$), β is the full width at half maximum (FWHM) of the diffraction line and θ is diffraction angle. Based on the full width at half maximum of the reflection from (111) plane in Zinc blende structure, the mean crystallite sizes were estimated as 4.54nm and 3.93nm corresponding to ZnS, PVP – ZnS respectively. The change of particle size is due to the coordination of surfactant and which plays an important role in the preventing formation of agglomerate (Gopa *et al.*, 2006).

Morphology Studies

The TEM image of ZnS-PVP nanoparticles along with selected area energy dispersion (SAED) of ZNS-PVP and fig.(4a) indicates that nanoparticles are high homogeneously dispersed in the host polymer matrix. The particle size is in the range of 4 - 5 nm. The SAED pattern of a typical nanoparticle is shown in fig.(4b) which consists of concentric rings which revealed the purity and grain size of the PVP capped ZnS nanoparticles (Gayou *et al.*, 2008).

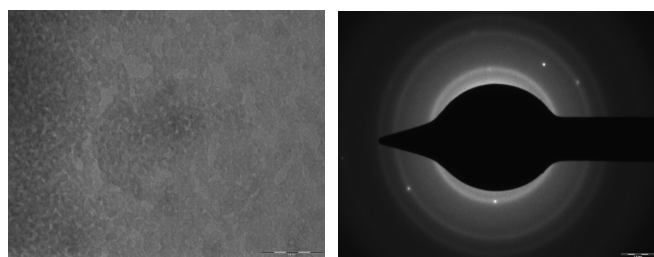


Fig.4 (a&b): TEM and SAED image for SHMP capped ZnS nanoparticle

Scanning Electron Microscope analysis

Fig.5 (a&b) show PVP capped ZnS nanoparticles at low and high magnification SEM images for PVP capped ZnS nanoparticles, which reveal that the particle size is <100 nm (Xinjun *et al.*, 2008). Fig.6 shows the EDX spectrum of PVP

capped ZnS nanoparticles. It indicates the existence of polymer molecules on the ZnS nanoparticles.

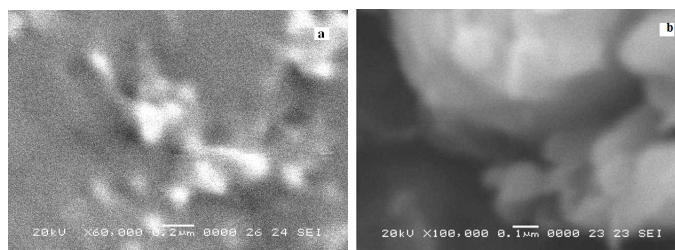


Fig.5. Scanning Electron Microscopy images (a&b) of low and high magnification of PVP capped ZnS nanoparticles

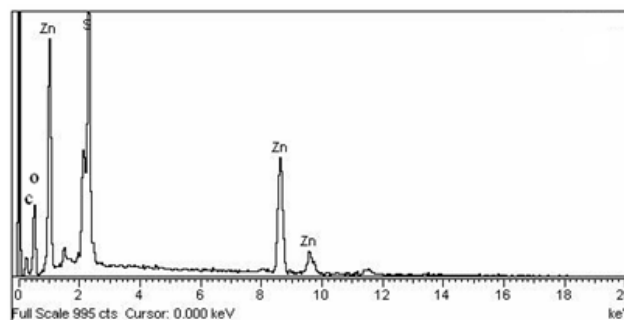


Fig.6: EDX spectrum of the PVP capped ZnS nanoparticle
FT-IR study

In FT-IR spectrum, the shift was observed for bands of C-H at 2956 and 2882 cm^{-1} due to asymmetrical and symmetrical stretching for pure PVP. After the formation of PVP capped ZnS nanoparticles, the peaks were observed at 2929 and 2861 cm^{-1} .

In FT-IR spectrum of pure PVP, the band at 1659 cm^{-1} due to C=O stretching mode and after formation of PVP capped ZnS nanoparticles this C=O stretching would be shifted to lower frequency about 64 cm^{-1} indicating red shift of strong interaction between ZnS nanoparticles and C=O of PVP host matrix.

PVP has fairly strong absorption in the region 1500-1370 cm^{-1} and the bands in this region have contributions mainly from the plane C-H bending of different CH_2 and CH moieties. The C-H bending modes are coupled with C-N stretching mode.

In FT-IR spectrum of pure PVP peaks were observed at 1465, 1437, 1420 and 1374 cm^{-1} but after the synthesis of PVP capped ZnS nanoparticles, the peak position were changed at 1457, 1400 and 1339 cm^{-1} respectively.

The FT-IR spectrum of polymer after being embedded with ZnS nanoparticles shows the significant change with respect to intensity shape and absorption in this region which suggests the existence of interaction between N and ZnS. This is further supported by the fact that the absorption bands of the PVP at 1319, 1229 and 1169 cm^{-1} but in PVP capped ZnS nanoparticle peaks were obtained at 1291 and 1127 cm^{-1} these are due to C-N stretching, the frequency shift due to after formation of nanoparticles (Rema *et al.*, 2007).

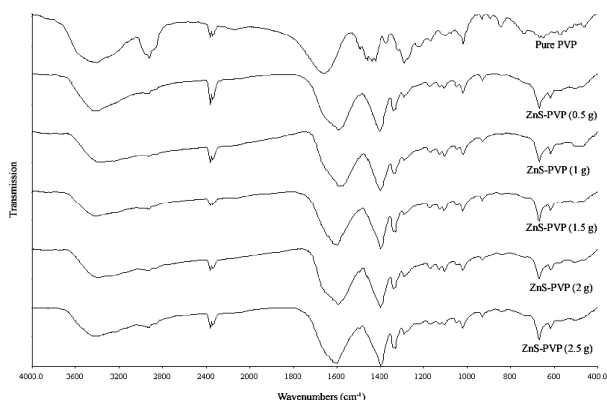


Fig.7: FT-IR spectra of PVP capped ZnS nanoparticles

In pure PVP, the peaks were obtained at 1100, 934 and 895 cm^{-1} but in our sample (PVP capped ZnS nanoparticle), the peaks were positioned at 1050, 931 and 841 cm^{-1} respectively. The functional group at 619 cm^{-1} was obtained that was proved in the presence of ZnS nanoparticle (Manoj *et al.*, 2010).

Photoluminescence studies

The excitation peaks of without and with capped ZnS nanoparticles at different concentration were absorbed. The absorption edge of capped ZnS is 310 nm (3.8eV) and uncapped is 320 nm (3.7eV), which clearly show the quantum size effects. The emission spectra show the emission intensity of capped ZnS nanoparticles are comparatively higher than the uncapped ZnS nanoparticles. This is expected because in the absence of capping agent uncontrolled nucleation and growth of the particles occurred, resulting in the formation of defect states. From figure 24 it is clearly show that there is considerable increase in intensity of emission peaks of PVP capped ZnS nanoparticles as compared to uncapped ZnS nanoparticles. This is attributed due to transfer of energy from chemisorbed PVP molecules to interstitial sites and vacancy centers. So enhanced photoluminescence has been observed from the ZnSnanocrystals due to efficient energy transfer from the surface adsorbed PVP molecules to interstitial and vacancy centers in nanocrystals. This study brings out a sensitizer (energy donor)-activator (energy acceptor) type relation between the polymeric capping agent and luminescent semiconducting nanoparticles (Karar, 2004).

Fig.8 shows, intensity versus concentration of PVP. It indicates, the intensity of PL is increasing with increase of capping concentration up to 1.5 g. After that, the PL intensity has been decreased. It may be due to the disturbance of growth rate by increasing organic material in prepared solution.

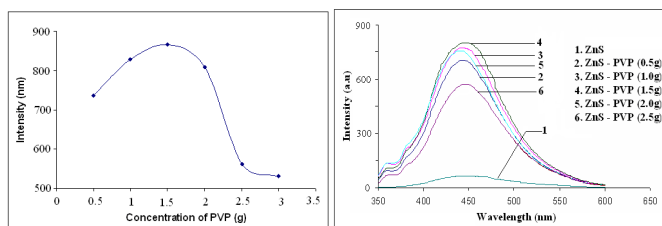


Fig.8: Photoluminescence spectra of PVP capped (0.5, 1.0, 1.5, 2 and 2.5g) ZnS with the optimum concentration of PVP on ZnS

CONCLUSION

From the UV spectra, the strongly absorption peaks were obtained at 310 nm (3.82 eV-PVP capped ZnS). The average particle size of PVP capped ZnSnanoparticles were determined by Brus equation. The XRD analysis show the sample have zinc blended (cubic) structure. This XRD patterns are also used to calculate the size of the nanoparticle. From this analysis the appropriate size of ZnS is ~ 4.54 nm, PVP capped with ZnS nanoparticle. It is realized from the TEM image that nanoparticles are homogeneously dispersed in the host polymer matrix. The morphology images show the approximate size of the nanoparticles. In addition to that the EDX analysis indicates what are the elements contain in this sample and then the functional group line of C–H, C=O and C–N stretching mode are identified in PVP capped ZnS nanoparticles. The frequency shift also identified as compared with the capped and uncapped ZnS nanoparticles. From the emission peaks of PVP capped ZnS nanoparticles were centered at 440 nm. The intensity of PVP capped ZnS nanoparticle changed with respect to the PVP concentration. We conclude that PL intensity was higher than the without capped ZnS nanoparticles.

Reference

Patolsky F, Gill R, Weizmann Y, Mokari T, Banin and U and Villner I. 2003. Lighting up the dynamics of telomerization and DNA replication by CdSe – ZnS quantum dots. *J. Am. Chem. Soc.*, 125: 3918-13919.

Kim Y.D, Sonezaki K, Maeda H and Kato A. 1997. Sintering behavior of monodispersed ZnS powders. *J. Mat. Sci.*, 32: 5101-5106.

Kim M.R, Ahn S. J and Jang D.J. 2006. Preparation and characterization of Titania / ZnS core – shell nanotubes. *J. Nanosci. Nanotechnol.*, 6: 180-184.

Pavel F.M and Mackay R.A. 2006. Reverse Micellar Synthesis of a Nanoparticle / Polymer composite. *Langmuir*, 16: 8586-8574.

Hongjin J, Kyoung S.M, Yangyang S, Wong C.P, Fay H, Tarasankar P and Anjali P. 2008. Tin/Indium nanobundle formation from aggregation or growth of nanoparticles. *J. Nanoparticle Res.*, 10: 41-46.

Maity R, Maiti U.N, Mitra M.K and Chattopadhyay K.K. 2006. Synthesis and optical characterization of polymer capped nanocrystalline Zn S thinfilms by chemical process. *Physica E*, 33: 104-109.

Shiquan W, Chunliang L, Ping Y, Masanori A and Norio M. 2012. Silica encapsulation of highly luminescent hydrophobic quantum dots by two-step microemulsion method. *Colloids and Surfaces A: Physicochem. Engineering Aspects* 395: 24-31.

Xiaochuan C and Yongxing L. 2005. Photochromism of peroxotungstic acid / PVP nanocomposite obtained by Sol – Gel method. *Journal of Sol – Gel Science and Technology*, 36: 197-201.

Calandra P, Goffredi M and Liveri. V.T. 1999. Study of the growth of ZnS nanoparticles in water/AOT/n-heptane microemulsions by UV – absorption spectroscopy. *Colloidal Surface A*, 160: 9–13.

- Yanbin T, Zijiang J, Cheng W, Yi X, Zonghao H, Sidong L and Chunbo L. 2008. Effect of annealing on the morphology and properties of ZnS:Mn nanoparticles PVP nanofibers. *Mat. Lett.*, 62: 3385-3387.
- Yinyan G, Tamar A, Gertrude F, Neumark, Stephen O'Brien and Igor L. 2007. Origin of defect – related green emission from ZnO nanoparticles: Effect of surface modification. *Nanoscale Res. Lett.*, 2: 292-302.
- Rast L and Stanishevsky A. 2005. Aggregated nanoparticle structures prepared by thermal decomposition of Poly (vinyl) – N – Pyrrolidone / Ag nanoparticle composite films. *App. Phy. Lett.*, 87: 223118-223120.
- Yanan L, Chuanbao C and Zhuo C. 2011. Magnetic and optical properties of Fe doped ZnS nanoparticles synthesized by microemulsion method. *Chem. Phy. Lett.*, 517: 55-58.
- Ujjal K, Gautam, Kripasindhu S, Deepak F. L and Rao C.N.R. 2005. Soft chemical routes to semiconductor nanostructures. *Pramana-J. Phy.*, 65: 549-564.
- Byrappa K and Adshiri T. 2007. Hydrothermal technology for Nanotechnology. *Prog. Cryst. growth and character. Mat.*, 53: 117-166.
- Kanemaru M, Shiraishi Y, Koga Y and Toshima N. Calorimetric study on self – assembling of two kinds of monometallic nanoparticles in solution. *J. Therm. Anal. Calorim.*, 81: 523-527.
- Seung S.L. Ki-T.B., Jong P.P. Sin K.K., Jong C.L., Suk-K.C., Young K and Wun S. 2008. Homogeneous ZnS coating onto TiO₂ nanoparticles by a simple one pot sonochemical method. *Chem. Engine. J.*, 139: 194-197.
- Manzoor K, Vadera S.R, Kumar N and Kutty T.R.N. 2003. Synthesis and photoluminescent properties of ZnSnanocrystals doped with copper and halogen. *Mat. Chem. Phy.*, 82: 718-725.
- Jianfeng C, Yaling L, Yuhong W, Jimmy Y and Dapeng C. 2004. Preparation and characterization of ZnS nanoparticles under high gravity environment. *Mat. Res. Bulletin*, 39: 185-194.
- Brus L.E. 1986. Electronic wavefunctions in semiconductor cluster: Experiment and theory. *J. Phy. Chem.*, 90: 2555-2560.
- Hamid R.S. 2011. A detailed study of Physical properties of ZnS quantum dots synthesized by reverse micelle method. *Physica E*, 44: 641-646.
- Ranjani V, Sameer S, Subhra S.G, Satpati B, Satyam P.V, Dev B. N. and Sarma D. D. 2004. Synthesis and characterization of Mn doped ZnOnanocrystals. *J. Phy. Chem. B*, 108: 6303-6310.
- Gopa G, Milan K.N, Amitavapatra and Minati C. 2006. Synthesis and characterization of PVP encapsulated ZnS nanoparticles. *Optical Mat.*, 28: 1047-1053.
- Gayou V. L, Salazar B, Delgado R.M, Zavala G, Santiago P and Oliva A.I. 2008. Structural studies of ZnS Nanoparticles by High Resolution Transmission Electron Microscopy. *J. Nano Res.*, 10: 41-46.
- Xinjun W, Fuquan W, Kun H, Chunxia C and Kai J. 2008. Large – scale synthesis well – dispersed ZnS microspheres and their photoluminescence, photocatalysis properties. *Mat. Characterization*, 59: 1765-1770.
- Rema B. S. D., Raveendran R and Vaidyan A.V. 2007. Synthesis and chacterization of Mn²⁺ doped ZnS nanoparticles. *Pramana J. Phy.*, 68: 679-687.
- Manoj S, Sunil K and Pandey O.P. 2010. Study of energy transfer from capping agents to intrinsic vacancies / defects in passivated ZnS nanoparticles. *J. Nanoparticle Res.*, 12: 2655-2666.
- Karar N. 2004. Structure and photoluminescence studies on ZnS:Mn nanoparticles. *J. Appl. Phy.*, 95: 656-660.
