Available Online at http://www.recentscientific.com

ISSN: 0976-3031

International Journal of Recent Scientific Research
Vol. 4, Issue, 4, pp. 405 - 409, April, 2013

International Journal of Recent Scientific Research

RESEARCH ARTICLE

OPTICAL, STRUCTURAL AND MORPHOLOGICAL STUDIES OF ZnS NANOPARTICLES BY CHEMICAL PRECIPITATION METHOD

[1]*Mohan, R., [2]Sankarrajan, S and [3]Santham, P

[1]Department of Physics, Surya college of Engineering and Technology, Vikiravandi – 605 652
[2]Department of Physics, Unnamalai Institute of Technology, Kovilpatti – 628 503
[3]Department of Chemistry, Annamalai University, Annamalai Nagar – 608 002

ARTICLE INFO

Article History:

Received 10th, February, 2013
Received in revised form 15th, March, 2013
Accepted 27th, March, 2013
Published online 30th April, 2013

Key words:

Zinc sulfide; Nanoparticles; UV-Visible; XRD; TEM; FTIR.

ABSTRACT

Zinc Sulfide (ZnS) nanoparticles of high level of photoluminescence have been successfully prepared using chemical precipitation method with Sodium HexaMeta Phosphate (SHMP) as capping agent. Particle sizes with band gap for undoped and doped nanoparticles are calculated using Ultraviolet / Visible (UV/Vis) absorbance spectra. The diameter of the particles is determined using X-ray diffraction (XRD) analysis. Transmission electron microscope (TEM) images imply that ZnS particles are evenly embedded in SHMP polymer. A good study of scanning electron microscope (SEM) images show that the particles have smooth surface passivated with polymer. Fourier transform infrared (FTIR) spectroscopy of ZnS/SHMP nanoparticles and SHMP shows strong chemical bond between ZnS nanoparticles and host SHMP polymer. An emission peak of the undoped and doped ZnS nanoparticles is recorded by Photoluminescence spectra which imply the existence of interesting optical properties.

INTRODUCTION

In recent days, the nanoparticles have been attracted many researchers in the various fields of science and technologies [1-4]. Particles in nanometric sizes have shown some unique physical properties. It is well known that the decrease of particle size results in high surface to volume ratio. The enhanced surface area has increased the surface states, which in turn changed the activities of electrons and holes affecting the chemical reactions. The transition from bulk to nanoparticles has been mainly due to the display of quantum mechanical properties [5]. The size quantization has revealed the increase the bandgap of photocatalysts to enhance the redox potential of conduction band electrons and valence band holes [6].

Among the family of semiconductors, from II to VI compound semiconductors have been immense technological importance in various applied fields of science and technology [7]. ZnO, ZnS, ZnSe, ZnTe [8-11], CdO, CdS, and CdTe [12-14] have been considered as important candidates because of their excellent electronic and optical properties for optoelectronic applications. ZnS is an important semiconductor material with a band gap of 3.68 eV at 300 K [15]. It has attracted considerable attention due to its applications such as flat panel display, electroluminescence devices, photonic devices, sensors, lasers, field emission devices [16-19] etc. In the present investigation, polymers have been chosen as good host material because of long term stability and flexible responsibility [20].

Many synthetic methods have been employed to prepare semiconductor nanoparticles including chemical vapor deposition, chemical precipitation method, sol-gel process, spray pyrolysis method, sonochemical precipitation etc [21].

Most of the physical or chemical properties exhibited by nanoparticles have been mainly attributed to crystallites agglomerating to form primary particles. It is clear that due to Oswald ripening and van der waals interaction between the particles, the growth of the particles is limited and hence agglomerate and settle down have happened [22]. These agglomerations have been arrested by either stabilitizing electrostically or inducing steric hindrances, to achieve size selective synthesis by employing SHMP as the stabilizing agent [23]. In the present investigation the efficient energy transfers occurring in the polymer functional group which are adsorbed at the surface with the dopant at the centre have been studied.

The advantage of the present study has been mainly due to high surface area to volume ratio with effective prevention of further aggregation of the nanoparticles, so as to retain high catalytic activities. In addition, nanometer sized semiconductor particles with higher redox potentials has resulted in the increase in band gap energy [24], which in-turn enhanced the charge transfer rates in the system and drastically reduced the volume recombination i.e. radiationless recombination of the electron-hole pair within the semiconductor particle [25]. In the present investigation, an attempt has been made to characterize the SHMP capped ZnS nanoparticles in order to explore various interesting properties.

---

* Corresponding author**:** Tel: +91 9488471588.
E-mail address: rrrmohan9@gmail.com

EXPERIMENTAL AND TECHNIQUES

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 stabilizied with SHMP.

$Zn\ (C_2H_3O_2)_2 + Na_2S + SHMP \rightarrow SHMP - ZnS + 2NaC_2H_3O_2$ -------- (1)

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.

Instrumentation detail

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 Jso – 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 JEOL SEM 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 Elico sl– 174 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

It is seen that the strongest absorption peak of the prepared sample appears around 310 nm (Fig.1) which is fairly blue shifted from the absorption edge of the bulk ZnS (345 nm). With the help of UV-Vis studies, the energy bandgap of ZnS/SHMP nanoparticles has been calculated. Manifacier model has been used to determine the absorption coefficient (α) from the transmittance data [26]. The fundamental absorption, which corresponds to the transmission from valence band to conduction band, has been employed to determine the bandgap of the material.

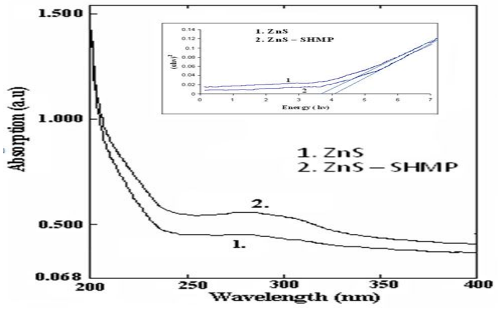


Fig.1. UV-Vis Spectra Band gap for Pure and capped ZnS nanoparticle

$\alpha = A\ (h\gamma - E_g)^n / h\gamma$ ----------- (3)

Where, A is a constant and E_g is the bandgap of the material [27]. The exact value of the bandgap has been determined and it is quiet interesting to observe that the bandgap value is higher than the bulk value of ZnS. The bandgap energy (E_g) of nearly 2.55 nm size capped ZnS nanoparticle of zinc blende structure with the effective mass of electron $0.19m_e$ and hole $0.8m_e$ is nearly 4.01 eV, calculated by using equation (3), given by the effective mass approximation model of Brus [28]. This suggests that the excitation at 4.01 eV (310 nm) is due to the band to band transition of electrons in ZnS nanoparticles. The grain sizes of ZnS and SHMP-ZnS nanoparticle has been calculated as 4.23 nm and 2.55 nm respectively which are nearly same as in ZnS nanoparticles [29].

The structure of the obtained SHMP capped ZnS nanoparticles have been characterized by X-ray powder diffraction. The XRD pattern of ZnS nanoparticles has shown in Fig.2. The obtained diffraction peaks at 2θ values of 28.52°, 47.9° and 56.7° have been matching perfectly with the (111), (220) and (311) crystalline planes of cubic ZnS JCPDS NO. 77-2100, which have indicated the formation of ZnS [30]. The peak broadening in the XRD patterns clearly has indicated the nature of the very small nanocrystals. From the width of the XRD peak, the mean crystalline size have been calculated using Debye-Scherrer's equation,

$D = k\lambda/\beta\cos\theta$ ----------- (2)

Where, k is particle shape factor, λ - the X- ray wavelength used (1.542 A°), β - the angular line width of the half maximum intensity and θ - the Bragg angle in degree (half of the peak position angle).

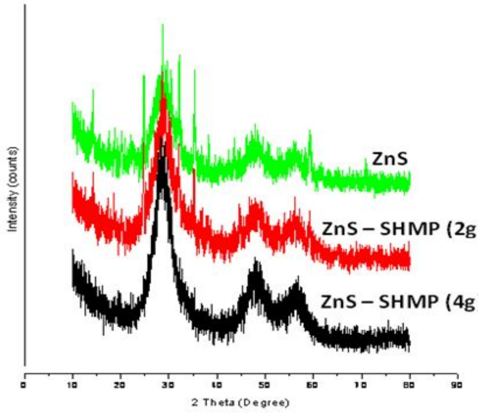
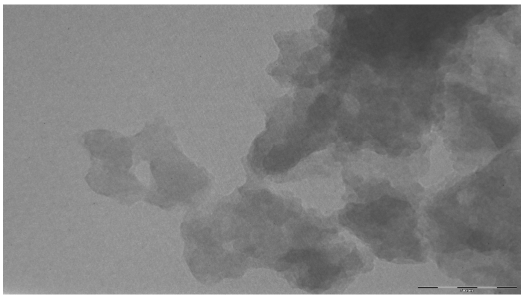
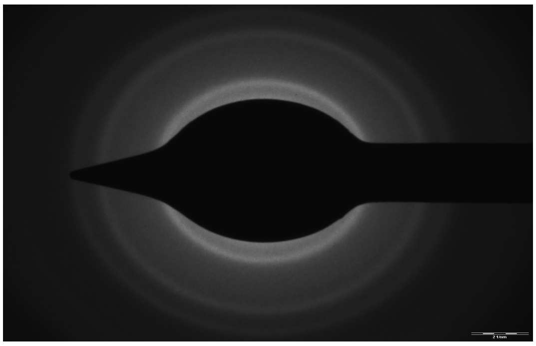


Fig. 2 XRD spectra for capped ZnS nanoparticles



(a)



(b)

Fig.3 (a & b) TEM and Selected area energy dispersive image for SHMP capped ZnS nanoparticle.

The grain size of ZnS and SHMP capped ZNS nanoparticles have been calculated as 4.54 nm and 3.61 nm 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 [31]. Fig.3. shows the TEM image of ZnS-SHMP nanoparticles along with selected area energy dispersion (SAED) of ZNS-SHMP and Fig. (3a) indicates that nanoparticles are high homogeneously dispersed in the host polymer matrix. The particle size is in the range of 5 nm. The SAED pattern of a typical nanoparticle is shown in Fig. (3b) which consists of concentric rings which revealed the purity and grain size of the SHMP capped ZnS nanoparticles [32].

A typical SEM picture ZnS nanoparticles shows that particles have smooth surfaces due to the surface passivation with polymer and the average agglomerate size of the order below 100 nm. Fig. 4a. shown SHMP capped ZnS nanoparticle at high magnification. Fig.4b has shown the EDX spectrum of SHMP capped ZnS nanoparticles. It is interesting to observe the existence of polymer molecules on the ZnS nanoparticles [33].

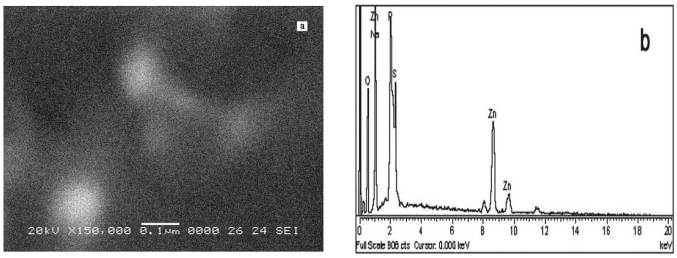


Fig. 4 (a & b) SEM spectra for high magnification of SHMP capped ZnS nanoparticles and EDX spectra of SHMP capped ZnS nanoparticles

FTIR spectra implied (Fig.5) the nitrogen-oxygen interaction at 1636 cm^{-1}. The distinct peaks at 1262 and 1086 cm^{-1} are due to phosphorus-oxygen interaction, establishing the presence of covalently bonded phosphates on ZnS nanoparticle [34]. From FTIR spectroscopy, it can be inferred that the stabling agent that passivates the surface of the particle. The presence of covalent bonded phosphate group even after rigorous washing of the colloidal nanoparticles suggests that SHMP inhibits the growth of particle by steric stabilization. The peak at 882 cm^{-1} is mainly due to nitrogen-oxygen interaction, whereas the presence of the peak at 537 cm^{-1} represents sulfur-oxygen interaction [35]. Passivation with polymers reduces the unsaturated bond density, thereby reducing the surface trapsites for non-radioactive recombination process. Thus, capping agents play an important role in the luminosity of the nanophosphors [36].

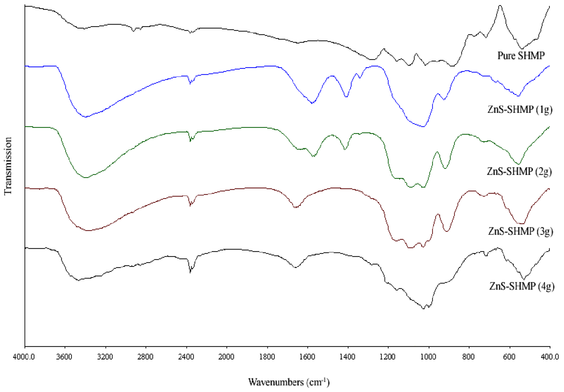


Fig.5. FTIR spectrum of SHMP capped ZnS nanocrystals**.**

The excitation peaks with capped and without capped ZnS nanoparticles at different concentration have been observed. The absorption edge of capped ZnS is 310 nm (4.01 eV) and uncapped is 325 nm (3.74 eV). From Fig.6 a, it is clearly understood that there is considerable increase in intensity of emission peaks of SHMP capped ZnS nanoparticles when compared to uncapped ZnS nanoparticles. This has been mainly due to absence of capping agent which leads to uncontrolled nucleation and growth of the particles occurred resulting in the formation of defect states [37].

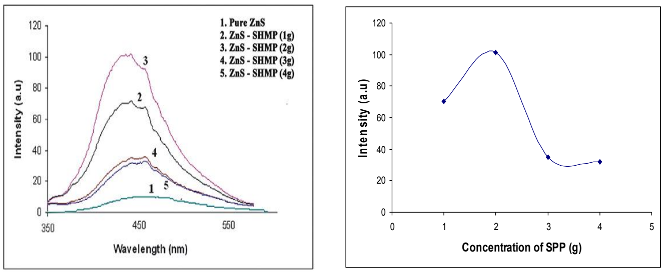


Fig.6 (a & b) PL Spectra for uncapped & capped ZnS nanoparticle and Concentration of SHMP.

This is mainly attributed to transfer of energy from chemisorbed SHMP molecules to intestinal sites and vacancy centers [38]. This study brings out a sensitizer (energy donor) – activator (energy acceptor) type relation between the polymeric capping agent and luminescent semiconducting nanoparticles as reported elsewhere [39]. The emission peaks has been centered at 447 nm. The broadening width of the spectrum indicates the growth of highly homogeneous solution with well dispersed particles. The variation of the intensity with different concentration of SHMP is shown in Fig.6 b. It indicates, the intensity of PL is increasing with increase of capping concentration up to 1.5g

CONCLUSION

The exact value of band gap has been determined with the help of UV/Vis spectra and it is quiet interesting to observe that the band gap value of SHMP capped ZnS is higher than the bulk value of ZnS. The peak broadening in the XRD patterns has clearly indicated the nature of the very small nanocrystals. It is realized from the TEM image that nanoparticles are homogeneously dispersed in the host polymer matrix. The approximate size of the nanoparticles with a good surface morphology and the elements that exist in the sample are pointed out from SEM with EDX analysis. From the FTIR spectra, function groups line nitrogen-oxygen interaction, phosphorus-oxygen interaction and sulfur-oxygen interaction are identified. It is shown that the capping agents play an important role in the luminising of the nanophosphors. Further, it is noticed that the band gap value is higher than the bulk value of ZnS. From the PL spectra, it is clear that the intensity of SHMP capped ZnS nanoparticle changed with respect to the SHMP concentration. The present study indicates that SHMP is a suitable capping agent for semiconductor nanoparticles targeted for applications such as photo catalysis in aqueous system.

References

1. Wang Y., Zhang C., Siwei B., and Guangsheng L., 2010, Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro structured reactor. *Powder Technology,* 202: 130-136.
2. He H., and Zhang W., 2006, Synthesis and properties of transition metals and rare earth metals doped ZnS nanoparticles. *Optical materials,* 28: 536-556.
3. Dhawale D.S., More A.M., Lathe S.S., Rajpure K.Y., and Lokhande C.D., 2008, Room temperature Synthesis and Characterization of CdO nanowires by Chemical bath deposition method. *Applied Surface Science,* 254: 3269-3273.
4. Leatherdale C.A., Kagan C.R., Morgan N.Y., Empedocles S.A., Kastner M.A., and Bawendi M.G., 2000, Photoconductivity in CdSe quantum dot solids. *Physics Review B*, 62: 2669-80.
5. Yang J., Dabin Y., Zirong W., Kun T., and Xiaoquan S., 2007, Synthesis, nonlinear optical properties and photoluminescence of ZnSe quantum dots in stable solutions. *Materials Letters*, 61: 1541-1543.
6. Yu J.H., Joo J., Park H.M., Baik S., Kim Y.W., and Kim S.C., 2005, Synthesis of quantum sized cubic ZnS nanorods by the oriented attachment mechanism. *Journal of American Chemical Society*, 127: 5662-70.
7. Yuan G.D., Zhang W.J., Jie J.S., Fan X., Zapien J.A., and Leung Y.H., 2008, P – Type ZnO nanowire arrays. *Nano Letters,* 8: 2591-9.
8. Ruoyu H., Tingting P., Jianzhong Q., and Hongzhong L., 2006, Synthesis and surface modification of ZnO nanoparticles. *Chemical Engineering Journal*, 119: 71-81.
9. Somayeh N., Esmaiel SI., Zahra D., and Mehdi M., 2011, Synthesis and photoluminescent and nonlinear optical properties of manganese doped ZnS nanoparticles. *Physica B*, 406: 108-111.
10. Aparna CD., Shashi BS., Majid KA., Renu P., and Kulkarni S.K., 2008, Low temperature Synthesis of ZnSe nanoparticles. *Materials Letters,* 62: 3803-3805.
11. Dwivedi D.K., Dayashankar., and Maheshwar D., 2009, Synthesis, Characterization and electrical properties of ZnTe nanoparticles. *Journal of Ovonic Research,* 5: 35-41.
12. Singh G., Kapoor I.P.S., Reena D., and Pratibha S., 2011, Synthesis, Characterization and Catalytic activity of CdO nanocrystals. *Materials Science and Engineering B*, 176: 121-126.
13. Murray C.B., Norris. D.J., and Bawendi M.G., 1993, Synthesis and characterization of nearly monodisperse CdE (E=S, Se, Te) semiconductor Nanocrystallites. *Journal of American Chemical Society,* 115: 8706-15.
14. Xavier M., Pantoja JE., Alessandro R., and Ayodhya NT., 2004, CdTe/CdS solar cells on flexible substrates. *Solar Energy,* 77: 831-88.
15. Qadri S.B., Skelton E.F., Su D.H., Dinsmore A.D., Yang J., and Gray H.F., 1999, Size – induced transition temperature reduction in nanoparticles of ZnS. *Physics Review B*, 60: 9191-3.
16. King C.N., 1996, Electroluminescent display. *J. vaccum surfaces and films*, 14: 1729-35.
17. Breen M.L., Dinsmore A.D., Pink R.H., Qadri S.B., and Ratna B.R., Sonochemically produced ZnS coated Polystyrene core – shell particles for use in photonic crystals. *Longmuir,* 17: 903-7.
18. Yu QC., and Chia J., 2009, Surface modification on Silver nanoparticles for enhancing vapor selectivity of localized surface plasmon resonance sensors. *Sensors and Actuators B*, 135: 492- 498.
19. Fang X.S., Bando Y., Gautam U.K., Ye C., and Golberg D., 2008, Inorganic semiconductor nanostructures and their field emission applicatopns. *Journal of Material Chemistry*, 18: 509-22.
20. Jie B., Yaoxian L., Chaoqun Z., Xiaofei L., and Qingbiao Y., 2008, Preparing AgBr nanoparticles in Poly(Vinyl Prrolidone) PVP nanofibers. *Colloids and Surfaces A: Physico Chem. Eng. Aspects,* 329: 165-168.
21. Xiaosheng F., Tianyou Z., Ujjal K., Gautam., Liang Li., Limin Wu., Yoshio B., and Dmitri Golberg., 2011, ZnS nanostructures : From synthesis to applications. *Progress in Materials Science*, 56: 175-287.
22. Prinsa V., and Avinash CP., 2011, Capped Semiconductor nanocrystals for device applications. *Optics communication*, 284: 881-884.
23. Subir CG., Chanchana T., and Joydeep D., 2004, Studies on ZnS nanoparticles for field emission devices. The I ECTI Annual Conference (ECTI-CON) Thailand, 145-148.
24. Hamid RP., Abbas N., Mohammad HK., and Abolfazl S., 2009, Nanoparticles of Zinc Sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes. *Journal of Hazardous materials*, 162: 674-681.
25. Subhendu KP., Anuja D., and Subhadra C., 2007, Nearly monodispersed ZnS nanospheres: synthesis and optical properties. *Chemical Physics Letters*, 440: 235-238.
26. Jianfeng C., Yaling L., Yuhong W., Jimmy Y., and Dapeng C., 2004, Preparation and characterization of Zinc Sulfide nanoparticles under high gravity environment. *Material Research Bulletin*, 39: 185-194.
27. Maity R., Kundoo S., Ghosh P.K., and Chattopadhayay K.K., 2004, Synthesis and characterization of

nanocrystalline zinc sulphide by wet chemical route. *Indian Journal of Physics A*, 78: 121-124.

28. Brus L.E., 1986, Electronic wave functions in semiconductor cluster: experiment and theory. *Journal of Physical Chemistry,* 90: 2555-2560.
29. Kirti V., and Vishwaharma O.P., 2010, Nanoparticle size effect on photoluminescent. *International journal of nanotechnology and applications,* 4: 13-19.
30. Rong H., Xue FQ., Jie Y., Hong X., Juan B., and Kang Z., 2003, Formation of monodispersed PVP capped ZnS and CdS nanocrystals under microwave irradiation. *Colloids and Surfaces A: Physicochem. Eng. Aspects,* 220: 151-157.
31. Yung TN., and Kuang HH., 2008, In – Gann Chen and Kui Yu. Photoluminescence enhancement of ZnS:Mn nanoparticles by SiO_2 coating. *Journal of Alloys and Compounds,* 455: 519- 523.
32. Karar N., Singh F., Mehta B.R., 2004, Structure and photoluminescence. *Journal of Applied Physics,* 95: 656-660.
33. Manoj S., Sunil K., and Pandey O.P., 2010, Study of energy transfer from capping agents to intrinsic vacancies / defects in passivated ZnS nanoparticles. *Journal of Nanoparticle Research,* 12: 2655-2666.
34. Warad H., Suhane A., Boontongkong Y., Thanachayanont C., and Dutta J., 2004, Colloidal synthesis of semiconductor nanoparticles. The Third Thailand materials science and technology conference (MSAT III), Bangkok, 16-18.
35. Rema B.S.D., Raveendran R., and Vaidyan A.V., 2007, Synthesis and chacterization of Mn^{2+} doped ZnS nanoparticles. *Pramana journal of Physics*, 68: 679-687.
36. Underwood D.F., Kippeny T., and Rosenthal S.J., 2011, Ultrafast carrier dynamics in CdSe nanocrystals determined by spectroscopy. *Journal of Physical Chemistry B*, 105: 436-443.
37. Debolina M., Indranil C., and Satya P.M., 2005, Studies on ZnS nanoparticles prepared in Aqueous Sodium Dodecylsulphate (SDS) miceller medium. *Colloid Journal,* 67: 445-450.
38. Navendu G., and Sen P., 2007, Photoluminescent properties of ZnS nanoparticles prepared by Electro – Explosion of Zn wires. *Journal of Nanoparticle Research,* 9: 513-517.
39. Manam J., Chatterjee V., Das S., Choubey A., Sharma S.K., 2010, Preparation, Characterization and Study of optical properties of ZnS nanophosphor. *Journal of Luminescence*, 130: 292-297.

****