J. Pure Appl. & Ind. Phys. Vol.1 (1), 101-106 (2010)

Synthesis of ZnS / Sodium Hexameta Phosphate Nanoparticles

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ABSTRACT

Zinc Sulfide (ZnS) nanoparticles with good photoluminescence have been successfully prepared using chemical precipitation method with Sodium HexaMeta Phosphate (SHMP) as capping agent. X-ray diffraction (XRD) analysis has determined the diameter of the particles as 3.6 nm , which is smaller than Bohr exciton diameter for ZnS. The study of scanning electron microscope (SEM) images has shown that the particles have smooth surface passivated with polymer and the average size of SHMP capped ZnS nanoparticle is less than 100 nm. Ultraviolet / Visible (UV/Vis) absorbance spectra for synthesized nanoparticles have shown an exitonic peak around 310 nm. Particle sizes with band gap for undoped and doped nanoparticles have been calculated respectively as 4.23 nm (3.74 eV) and 2.55 nm (4.01 eV). Photoluminescence (PL) spectra recorded for undoped and doped ZnS nanoparticles using an excitation wavelength of 310 nm, exhibit an emission peak centered around 447 nm.

INTRODUCTION

Nanocrystals have been described as materials of intermediate between individual molecules and bulk solids[1]. The transition from bulk to nanoparticles has been mainly due to the display of quantum mechanical properties[2]. Particles in nanometric sizes have shown the 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 charged the activities of electrons and holes affecting the chemical reactions. The size quantization has revealed the increase the bandgap of photocatalysts to enhance the redox potential of conduction band electrons and valence band holes[3].

Among the family of semiconductors, from II to VI compound semiconductors have been immense technological importance in various applied fields of science and technology[4]. ZnO[5], ZnS[6], ZnSe[7], ZnTe[8], CdO[9], CdS[10], and CdTe[11] 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[12]. It has attracted considerable attention due to its application in flat panel display[13], electroluminescence devices[14], photonic devices[15], sensors, lasers, field emission devices[16] etc. An important application of ZnS has been in the field of photocatalyst in environmental protection through the removal

of organic pollutants and toxic water pollutants such as dyes, p-nitrophenol, halogenated benzene derivatives in wastewater treatment. In the present investigation, polymers have been chosen as good host material because of longterm stability and possess flexible responsibility[17].

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[18]. Most of the physical or chemical properties exhibited by these nanoparticles have been mainly attributed to crystallites agglomerating to form primary particles. It is clear that if, due to Oswald ripening and van der waals interaction between the particles, the growth of the particles is limited agglomerate and settle down have happened[19]. 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[20]. In the present investigation the efficient energy transfer 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[21], which inturn 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[22].

EXPERIMENTAL

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.

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

The same procedure was carried out with different concentration of polymers. All steps of synthesis were performed at 80°C. 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 nanoparticle and then the powder was dried in the oven at 60°C for 12h.

INSTRUMENTATION DETAIL

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. The experiments were performed in the diffraction angle of 2θ = 10 to 70°. Samples were prepared by drying a drop of the sample solution in water on a copper grid and allowed to dry completely at room temperature. 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 carried out to identify the weight percentage of major elements present in the samples using the Oxford Inca energy dispersive X-ray spectrometer (EDX).

The UV–Vis spectra were measured in quartz cuvettes with spectrometer with equal amount of deionized water and

methanol as the reference The UV – Vis spectra of the samples have been studied with the help of Perkin-Elmer Lambda 20 UV–Vis. Photoluminescence spectra were recorded at room temperature using Elicosl–174 fluorescence spectrophotometer.

RESULT AND DISCUSSION

The structure of the obtained SHMP capped ZnS nanoparticles were characterized by X-ray powder diffraction. The XRD pattern of ZnS nanoparticle is shown in *fig.1*. 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[23]. 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 can be calculated using Debye-Scherrer's equation,

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

Where k is particle shape factor, λ is the X- ray wavelength used (1.542 A°), β is the angular line width of the half maximum intensity and θ is the Bragg angle in degree (half of the peak position angle). The grain size of ZnS and SHMP capped ZNS nanoparticle has 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 [30].

A typical SEM of ZnS nanoparticles shows that particles have smooth surfaces due to the surface passivation with polymer and the average agglomerate size of the order of below 100 nm. *Fig 2* a shown SHMP capped ZnS nanoparticle at high magnification. *Fig.2* b shown the EDX spectrum of SHMP capped ZnS nanoparticles. It is interesting to observe the existence of polymer molecules on the ZnS nanoparticles.

From *fig.3,* it is seen that the strongest absorption peak of the prepared sample appears around 310 nm, which is fairly blue shifted from the absorption edge of the bulk ZnS (345 nm). Semiconductor crystallites in the diameter range of a few nanometers show a three dimensional quantum size effect in their electronic structure. In the UV-Vis study, the energy bandgap has been calculated. Manifacier model has been used to determine the absorption coefficient (α) from the transmittance data[25]. The fundamental absorption, which corresponds to the transmission from valence band to conduction band, is employed to determine the bandgap of the material.

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

where A is a constant and E_g is the bandgap of the material[26]. 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 ~ 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[27]. 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.

The excitation peaks of without capped and with 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),

which clearly show the emission intensity of capped ZnS nanoparticles are comparatively higher than the 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. From *fig.4* a, it is clearly shown that there is considerable increase in intensity of emission peaks of SHMP capped ZnS nanoparticles when compared to uncapped ZnS nanoparticles. This is mainly attributed to transfer of energy from chemisorbed SHMP molecules to interstial sites and vacancy centers. This study brings out a sensitizer (energy donor) – activator (energy acceptor) type relation between the polymeric capping agent and luminescent semiconducting nanoparticles as reported else where[28]. 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.4 b*. It indicates, the intensity of PL is increasing with increase of capping concentration upto 1.5g.

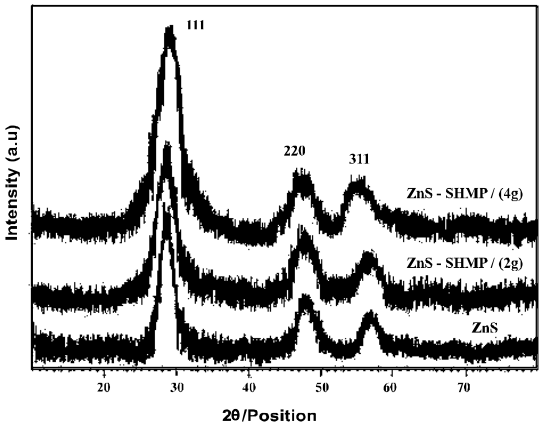

Fig. 1.XRD spectra for capped ZnS nanoparticles

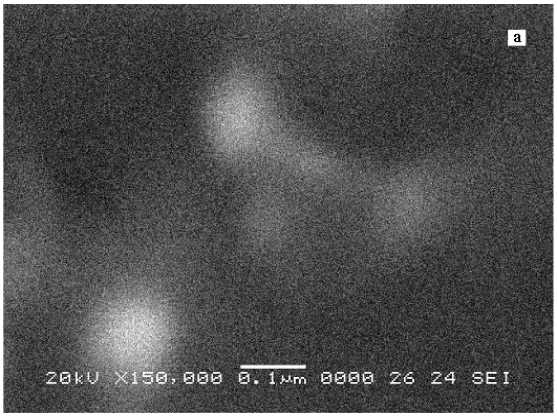

Fig. 2 a. SEM spectra for high magnification of SHMP capped ZnS nanoparticles

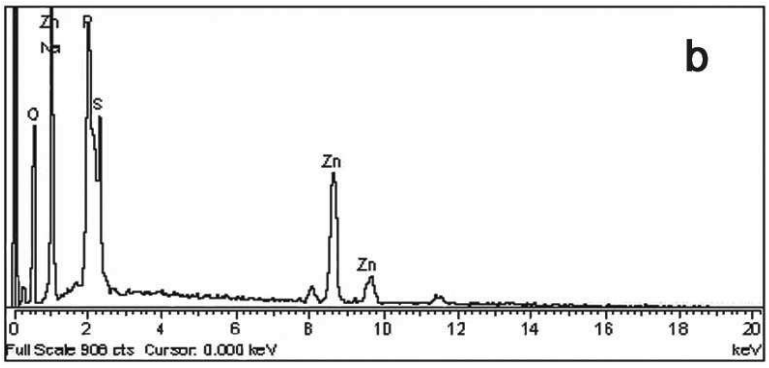

Fig. 2 b. EDX spectra of SHMP capped ZnS nanoparticles

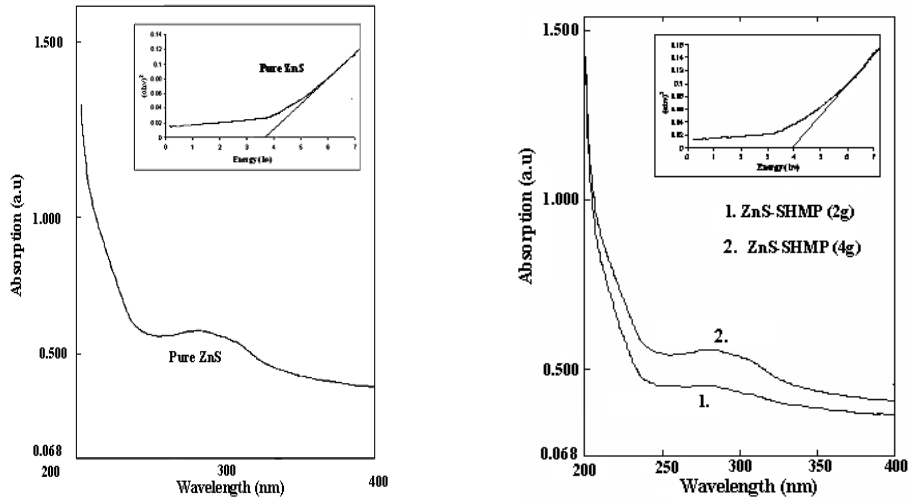

Fig.3. UV-Vis Spectra Band gap for Pure and capped ZnS nanoparticles

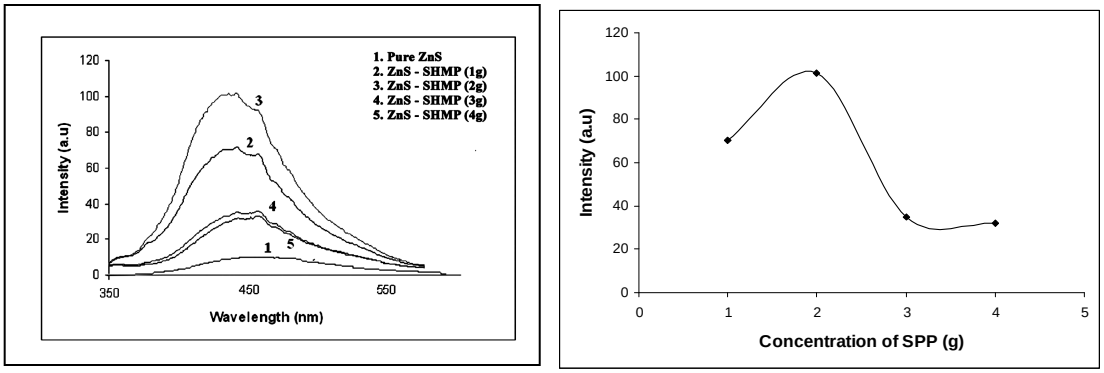

Fig.4 a. PL Spectra for uncapped & capped ZnS nanoparticle and Concentration of SHMP

CONCLUSION

From the XRD analysis zinc blended (cubic) structure and the average particle size of SHMP capped ZnS nanoparticle (3.6 nm) is less than the without capped ZnS nanoparticle (4.54 nm). From the SEM with EDX analysis, the morphology images show the approximate size of the nanoparticles. In addition, the EDX analysis indicates the elements existing the sample. It is shown that the capping agents play an important role in the luminosing of the nanophosphors. Further, it is noticed that the band gap value is higher than the bulk value of ZnS. From the UV spectra, the strongest absorption peaks are obtained at 310 nm for SHMP capped ZNS and 325 nm for uncapped ZnS nanoparticles. The calculated average particle size (2.55 nm – 4.01 eV) is less than that of uncapped ZnS (4.23 nm – 3.74 eV). From the PL spectra, 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 those targeted for applications such as photocatalysis in aqueous system.

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