Effect of Ni^{2+} doping on structural, morphological and optical properties of ZnS nanoparticles

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Abstract: *Nickel doped ZnSNpswere synthesizedby chemical precipitation technique using various concentrations of sodium hexametaphosphate (SHMP) as capping agent. Characterizations carry out to study different properties of the acquired particles crystalline size and shape analysis by X-ray diffraction, UV–Vis absorption spectroscopy show blue shift in absorption edge as compared to bulk ZnSand Nps size determined by using the mathematical model of effective mass approximation equation, surface morphology with particle size by Transmission Electron Microscope, photoluminescence (PL) spectrum of the ZnS:Ni^{2+}Nps exhibits strong emission centered at 468 nm, with increase in SHMP concentration upto 0.75 wt % and decrease in intensity for higher concentrations of SHMP.*

Keywords: *Zinc sulfide; Nanoparticles; UV Visible - Photoluminescence; XRD; TEM*

I.   Introduction

Zinc sulfide (ZnS) is one of the most important II–VI semiconductor compounds with wide bandgap of 3.68 eV that has a key material for some devices such as light emitting diodes, flat panel displays, biosensors, optoelectronic devices [1–2]. ZnS show considerable size dependent luminescence properties when an impurity is doped in a quantum confined structure. Divalent nickel ion Ni^{2+} with an ionic radius of 0.83 Å [3], which is close to that of divalent Zn^{2+} ion (0.88 Å), can be incorporated in ZnSNps by substituting at Zn site without destroying the structure.

Several techniques have been used to synthesize the ZnS NPs such as auto-combustion, sol–gel, solid–state reaction, laser–ablation, electrochemical fabrication, solvo-thermal methodsand chemical precipitation method etc [4]. During synthesis of Nps, II–VI semiconductor Nps are highly unstable, and in the absence of trapping media or some other form of encapsulation, they agglomerate or coalesce easily. To overcome this, bonding of capping agent to Nps is necessary to inhibit formation of larger particles and to improve the surface states that effectively influence the optoelectronic properties of the Nps [5–6]. Hence, SHMP has been chosen as a stabilizer in the present investigation. In this paper, the effect of Ni^{2+} doping on the structural, optical and magnetic properties of SHMP capped ZnSNps formed by chemical precipitation method and to explore, if there is any change in behavior with the change in concentration of Ni^{2+} ions in host ZnSNps.

II.   Experimental section

The SHMP capped ZnS:Ni^{2+}Nps were synthesized using chemical precipitation method. Zinc acetate Zn(CH$_3$COO)$_2$.2H$_2$O, Sodium sulfide flakes (Na$_2$S) and nickel acetate Ni(CH$_3$COO)$_2$.4H$_2$O were used as source of Zn, S and Ni respectively, in the aqueous mixture of ethanol. In a typical procedure, the separately prepared aqueous solution of 0.2 M of zinc acetate and 2mM of nickel acetate were mixed drop by drop with constant stirring until the solution become homogeneous. To this solution, 25 ml of aqueous SHMP with different concentrations (0.25, 0.5, 0.75, 1.0 and 1.25 wt %) were added and then 0.2 M of sodium sulfide was drop wise added. The resulting product Viz., Ni^{2+} doped ZnSNps capped with SHMP chains begin to precipitate when the solution stirring is stopped. The white precipitate indicates the formation of ZnS:Ni^{2+}Nps. precipitate was washed several times in the mixture of deionized water with ethanol to remove unreacted Zn, Na etc. Finally the products were dried in hot air oven at 90°C for12 hrs and crushed to powder form for further investigations.

The X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the Nps using X'PERT PRO diffractometer with Cu – Kα radiation (1.5406 Å) at 40 kv and 150 mA, 2θ range 20 - 80°. The particle size and structure were confirmed using a JEOL high resolution transmission electron microscope (HRTEM). The optical absorption spectra of all the samples in deionized water were analysised using SHIMADSU UV – Vis 117 double beam spectrophotometer.The photoluminescence measurements work was carried out on SHIMADZU RF 5301 PC spectroflurophotometer.

III. Results and Discussion

Typical XRD patterns exhibits cubic zinc blende structure with a comparison to the standard card (JCPDS No. 05-0566; Fig. 1). The appearance of three diffraction peaks at 2θ values 28.5°, 48.28°, 57.15°are due to reflection from the (111), (220) and (311) planes [7]. No impurity peaks are detected, such as Ni(CH$_3$COO)$_2$.4H$_2$O and Zn(CH$_3$COO)$_2$.2H$_2$O.This confirms that Ni^{2+} dopant does not alter the crystal structure. Scherrer formula is used for particle size determination[8].

$$D = \frac{k\lambda}{\beta Cos\theta} - - - - - - - - - (1)$$

Where λ=X-Ray wavelength, β=FWHM, θ=diffraction angle and D=particle size. The calculated lattice parameter value 'a' was found to vary with SHMP concentration. Small lattice contraction was detected along (111), which may be due to lattice strain induced due to large surface to volume ratio. It is already discussed that decreasing size is responsible for lattice contraction [9]. The other calculated parameter viz., dislocation density (δ),specific surface area (SSA) and strain are tabulated in Table 1. For SHMP concentration of 0.75%, 'a' value is minimum (5.367 Å) and strain is maximum indicating that the particle size is very small, when compared to other concentrations of 0.2 % and 1.0 %. For the same concentration, SA/V value is quite high which indicate the possible size reduction of ZnS:Ni^{2+} at 0.75% .

Fig.2.shows the high-resolution transmission electron micrograph (HRTEM) of Zn$_{0.96}$Ni$_{0.04}$S/SHMP Nps. The diameters of most of these particles lie in the range 5−10 nm. These results are nearly in accordance with those of the X-ray diffraction analysis. The SAEDpattern illustratespolycrystallanity of the fabricated Nps. The dominant diffraction patterns in the micrograph are well indexed as (1 1 1), (2 2 0) and (3 1 1) planes of the cubicle zinc blende structure, which are in the good agreement with the XRD pattern [10].

The UV-Vis absorption spectra of synthesized uncapped and capped ZnSNps with Ni^{2+} dopant are shown in Fig.3a, to measure their bandgap. The spectra show absorption edge of the Nps in the range 298 – 319 nm, showing these Nps being blue-shifted as compared to bulk ZnS for which the peak is at 345 nm. The blue shift in the absorption edge is due to the quantum confinement of the excitons, resulting in a more discrete energy spectrum of the individual Nps. The effect of the quantum confinement on impurity depends upon the size of the host crystal. As the size of the host crystal decreases, the degree of confinement and its effect increases [11]. Tauc's relation was applied to determine the bandgap of the synthesized samples (Fig.3b) [12].i.e. the energy gap increases with increasing capping concentration of SHMP. This change in bandgap suggests that there is direct energy transfer between the host semiconductor excited states. The radius of the particles can be calculated by using the mathematical model of effective mass approximation presented in table 1 [13].

PL study is a powerful tool to investigate the optical properties of SHMP capped and uncapped ZnS:Ni^{2+}Nps. The PL emission spectra for SHMP capped and uncapped ZnS:Ni^{2+}Nps are shown in Fig.3a. It consists of sharp peak centered at 445 nm in blue region (due to sulfur vacancies). This is close to value reported by Li et al [14] and a small hump is observed around 468 nm (due to donor acceptor D-A type transition). The uncapped sample consists of a strong peak centered at 433 nm and a weak broad peak centered at 450 nm, which is considered to be associated with defects [15].It seems that there is a complex interaction between the capping agent and dopant ion with the host the ZnS giving the raise to different luminescence centers. Fig.3b.reveals the optimum capping concentration of SHMP(0.75wt %), the PL intensity is enhanced and with increase in capping concentration, surface quenching is observed. Therefore we conclude that SHMP is good stabilizing agent to prevent agglomeration of ZnS:Ni^{2+}Nps, Moreover the ZnS:Ni^{2+}Nps are remarkably small in size due to SHMP are finely adsorbed on ZnS:Ni^{2+} host lattice.

4. Conclusion

We have successfully synthesized ZnS:Ni^{2+} with different SHMP concentrations through chemical precipitation method. XRD pattern showed the ZnS:Ni^{2+} Nps have cubic structure.It confirms with slight variation in lattice parameter due to the influence of SHMP. From the HRTEM, the grown particles are spherical in shape within a diameter of ~5 – 10 nm. SAED pattern confirm the crystalline nature of the sample. Absorption edge shifted towards the shorter wavelength side and it reflects corresponding bandgap values increase as compared to uncapped ZnS:Ni^{2+}Nps. However, photoluminescence spectra show the emission peak at higher intensity compared to the uncapped sample. It illustrates two emission peaks at 445 and 468 nm. It was clear that emission intensity of the ZnS:Ni^{2+}Nps increased significantly with increasing SHMP concentration.

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Figure captions:

Fig. 1 XRD patterns of SHMP capped and uncapped ZnS:Ni²⁺ nanoparticles

Fig. 2 (a) HR-TEM image and (b) SAED pattern of SHMP encapsulated ZnS:Ni²⁺ nanoparticles

Fig. 3 (a) UV-Vis spectra and PL spectra of SHMP capped and uncapped ZnS:Ni²⁺ nanoparticles

Fig. 3 (b) $(\alpha h\nu)^2$ vs. photon energy for SHMP capped and uncapped ZnS:Ni²⁺ nanoparticles

Table captions:

Table 1 Estimated structural parameters and band gap values with particle sizeof SHMP capped and uncapped ZnS:Ni²⁺ nanoparticles
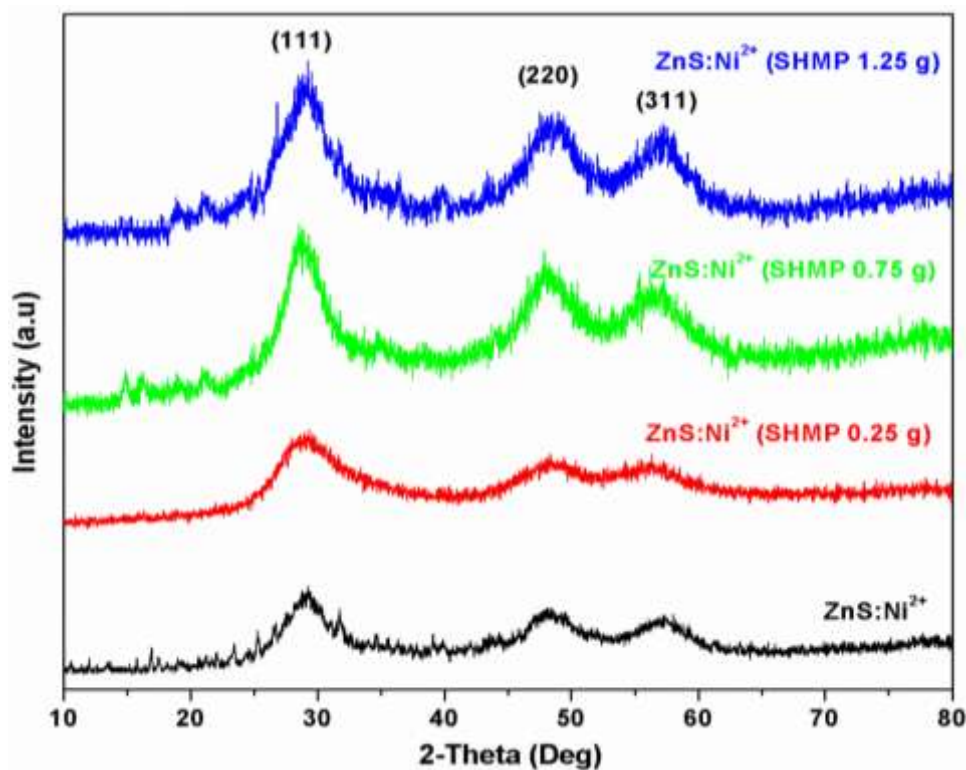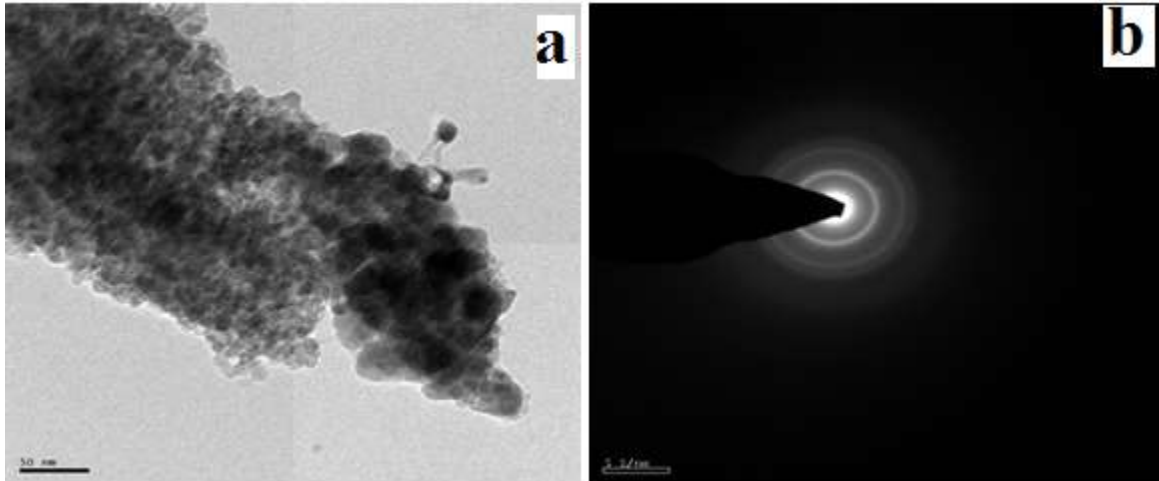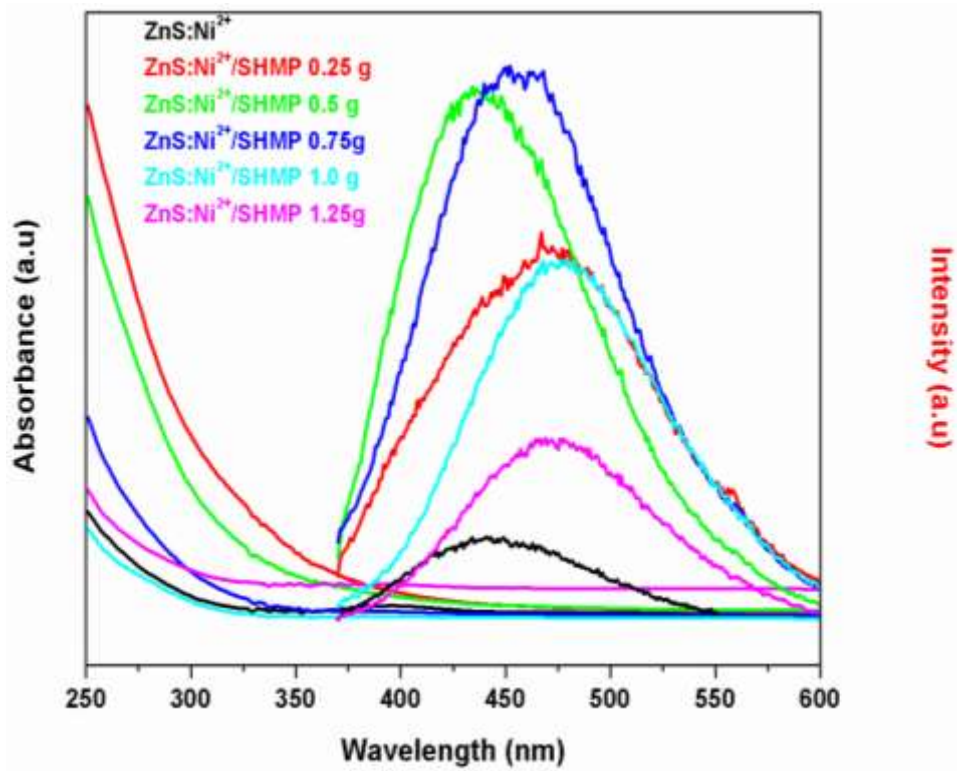

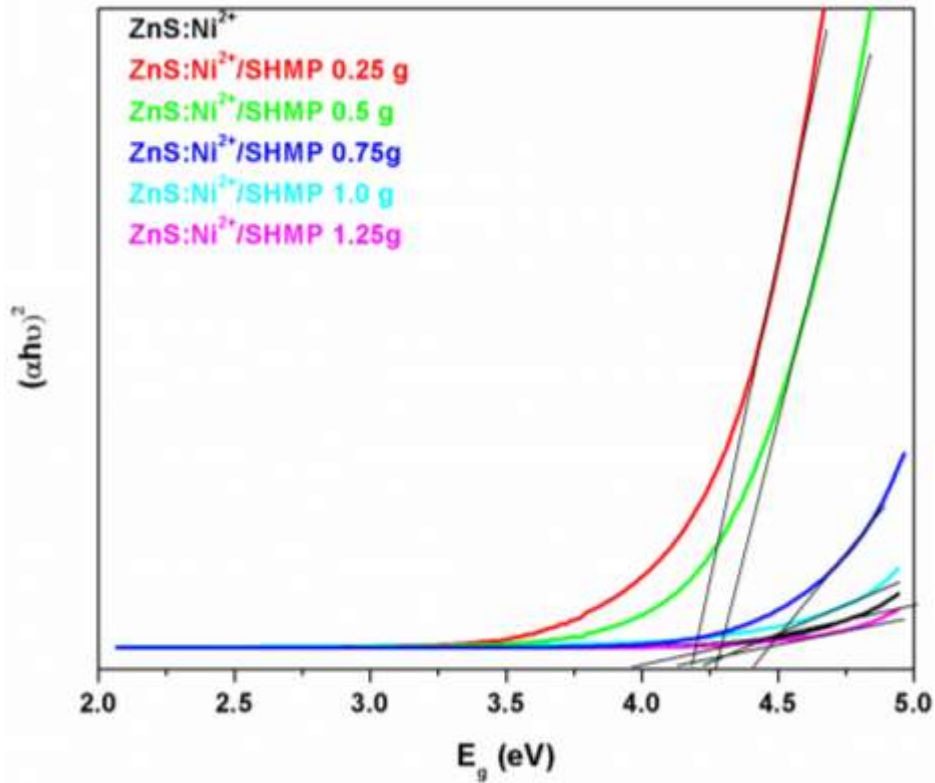**Fig. 1**

Fig. 2

Fig. 3a

Fig. 3b

Table: 1

Estimatedstructural parameters and band gap values with particle sizeofSHMP capped and uncapped ZnS:Ni²⁺ nanoparticles

Sl.No	NAME	d–Space Å	a Å	D (nm)	Sa (nm)²	SSA 10*10⁶ cm²/g	V (nm)³	SA/V	ϵ	δ 10*10¹⁶lin/m²	Bandgap (eV)	Grain Size (nm)
1	ZnS:Ni	3.0924	5.35	5.34	89.58	279.29	79.73	1.1235	0.02606	3.5068	3.94	3.57
2	ZnS:Ni/SHMP 0.25 g	3.0672	5.31	5.328	89.18	279.92	79.19	1.1261	0.0259	3.5226	4.18	2.57
3	ZnS:Ni/SHMP 0.5 g										4.27	2.37
4	ZnS:Ni/SHMP 0.75 g	3.0936	5.35	3.235	32.89	461.03	17.74	1.8541	0.04303	9.5554	4.43	2.1
5	ZnS:Ni/SHMP 1.0 g										4.23	2.45
6	ZnS:Ni/SHMP 1.25 g	3.0672	5.31	4.29	57.81	347.65	41.34	1.3985	0.03217	5.4335	4.13	2.71