Asian Journal of Chemistry Vol. 21, No. 10 (2009), S039-042

High Temperature Synthesis and Characterization of Mn^{2+} Doped Zns Nanoparticles

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Undoped and Mn^{2+} doped ZnS nanoparticles of sizes 1-3 nm have been synthesized at 95°C by chemical precipitation method. X-ray diffraction (XRD), high-resolution TEM, SEM, UV-vis spectroscopy, and photoluminescence (PL) spectroscopy have been used for the characterization of the samples. UV-vis spectra shows appearance of an absorption peak ~ 325 nm, which confirms the blue shift as compared to that of bulk ZnS. Photoluminescence spectra of all the samples have been recorded at room temperature and observed yellow emission from the doped ZnS samples.

Key Words: Mn^{2+} doped ZnS nanoparticles, Band gap shift, Photoluminescence.

INTRODUCTION

Colloidal II-VI ZnS and CdS NCs are wide band gap semiconductor, known for their novel optical properties and attracted much attention over the past few years.[1-9] Due to Quantum confinement effect, band gap of these nanomaterials can be tuned by changing the particle size that leads to tunable band edge light emission and hence exhibit novel optical properties.[2-4] Doped semiconductor nanomaterials have potential application as luminescent materials for cathode ray tube, flat panel displays, sensors and for many other opto-electronic devices.[1-4] Several approaches have been made in the past to improve the optical properties of ZnS, by gradually reducing the particle size[1-9]. The synthesis has mainly been done by inverse micelle and zeolite techniques[5,6]. These techniques have poor efficiency with complexity in sample processing. On the other hand the solution route synthesis technique used in the present study has removed many difficulties. Also, in order to improve the photoluminescence (PL) properties in visible region, doped semiconductor nanocrystals are synthesized. There are several attempts in this regard by using Mn^{+2}, Cu^{2+}, Pb^{2+} doping[6-9] at room temperature. But recently it has been found that temperature plays an important role in this kind of modification of properties[8,9] for optical semiconducting nanomaterials.

However, here we have reported the high temperature synthesis of undoped and Mn^{2+} doped ZnS nanoparticles of sizes 1-3 nm via chemical precipitation

method and obtained enhanced yellow light PL emission from the doped samples.

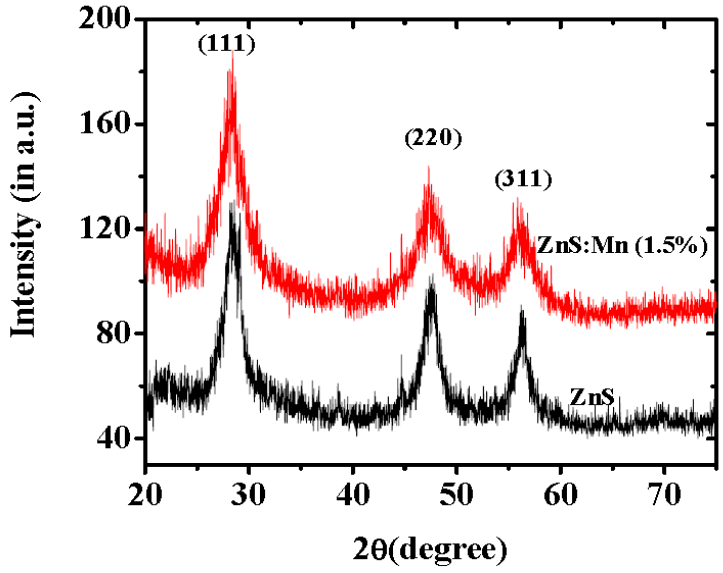

Fig. 1 XRD pattern of undoped and Mn^{2+} doped ZnS nanoparticles.

EXPERIMENTAL

Undoped and 1.5% Mn^{2+} doped ZnS samples have been prepared by chemical co- precipitation method.[2] All the chemicals used are of AR grade (Merck & SD fine chemicals) and they are used without further purification. Freshly prepared aqueous solutions of the chemicals are used for the synthesis of nanoparticles. The procedure of synthesis is the same as described in detailed in Ref. 2, except the temperature of synthesis, which is 95°C in the present work.

RESULTS AND DISCUSSIONS

The XRD patterns of the prepared samples were recorded by an X-ray diffractometer (PANalytical) are shown in Fig 1. There are three diffraction peaks appeared at ~28.30°, 47.20° and 56.20° due to the reflections from (111), (220) and (311) planes of cubic ZnS, respectively.[2] The average particle size is calculated by using Debye-Scherer formula[2] and found to be in range of 1-3 nm. The nanostructures of the samples are confirmed by using SEM (HITACHI S-3000N) and HRTEM (JEOL JEM 2100) micrographs as shown in Figs. 2(a) and 2(b), respectively. The average particle size obtained from the analysis of HRTEM micrograph (Fig. 2b) is ~ 3 nm. The optical absorption spectra have been recorded by UV-visible spectrophotometer (Hitachi U-3010) that shows the

absorption peak around 325 nm for ZnS nanoparticles as shown in Fig. 3a. The absorption onset wavelength of bulk ZnS is at 345 nm. This confirms the blue shift in the bandgap of the synthesized sample in comparison to that of bulk ZnS due to the quantum confinement effect.

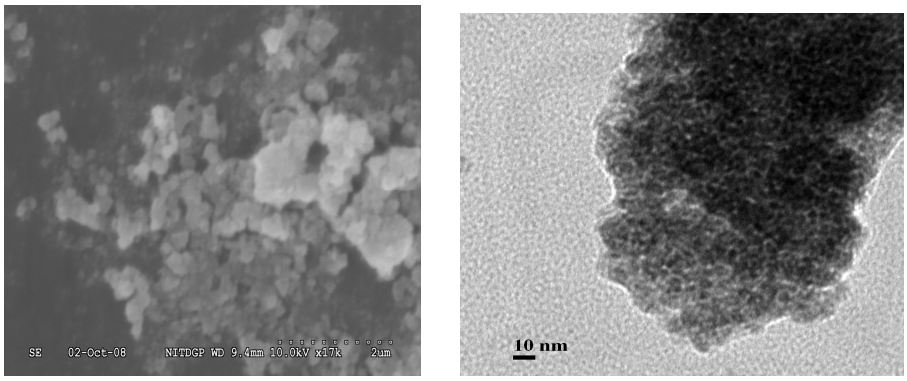

Fig. 2 (a) SEM micrograph of Mn^{2+} doped ZnS nanoclusters. (b) HRTEM image of Mn^{2+} doped ZnS nanoparticles.

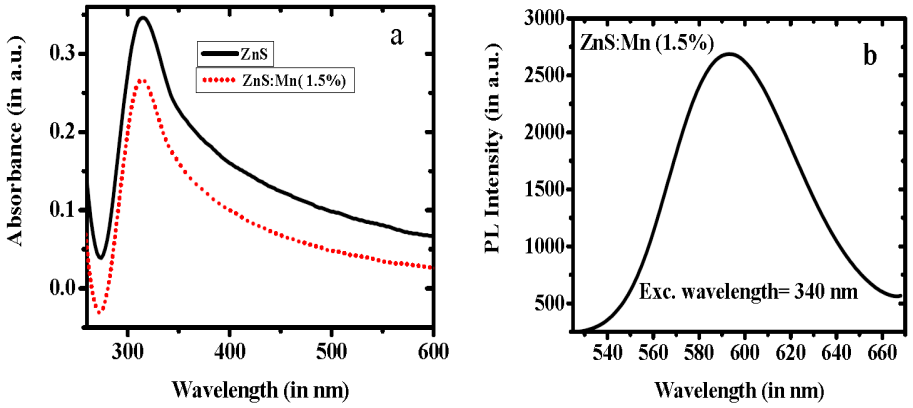

Fig. 3 (a)UV-vis absorption spectra and (b) PL emission from ZnS:Mn nanoparticles.

TABLE 1
PARTICLE SIZE CALCULATED FROM XRD AND UV-VIS ABSORPTION ANALYSES

Sample	E_g (in eV) (calculated from UV-Vis Abs. curve)	Particle size d (in nm)	
		From XRD pattern	Using Brus Eq^n
Undoped ZnS	5.24	2.66	2.26
ZnS-1.5% Mn	5.32	1.28	2.10

Direct band gap of the sample is evaluated by plotting $(\alpha h\nu)^2$ against $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis, at $\alpha = 0$. The obtained band gap of the samples is blue shifted in compared to the band gap of bulk ZnS. Particle size has been calculated by putting the bandgap shift in Brus equation.[1] The photoluminescence (PL) spectra of ZnS and ZnS:Mn nanoparticles have been recorded by a spectroflourimeter (F 2500 FL, Hitachi). For undoped ZnS, emission peak occur around 350 nm that is because of recombination of electrons at the sulphur vacancy donor level. The PL spectrum of ZnS:Mn nanoparticles is shown in Fig. 3b which shows that efficient emission of yellow color light with appearance of peak at ~ 591 nm is taken place from this sample. The doping of Mn^{2+} in host ZnS produces energy levels between the valence band and conduction band of the ZnS and leads to the emission of yellow colour light from Mn^{2+} doped ZnS nanoparticles[1,2].

In conclusions, broad photoluminescence emissions are obtained from 1-3 nm sizes undoped and Mn^{2+} doped ZnS nanoparticles synthesized at 95^0C temperature through low cost chemical precipitation method. The blue shift in the band gap of the synthesized nanoparticles is observed from the bulk band gap value of ZnS, due to the quantum confinement effect. Undoped ZnS nanoparticles show violet photoluminescence emission and the Mn^{2+} doped samples show visible emission with the peak at ~591 nm wavelength due to from the Mn^{2+} $^4T_1$–$^6A_1$ transition[2].

ACKNOWLEDGEMENTS

Authors are grateful to MHRD, GOI for the financial support and one of the authors (CR) is grateful to MHRD for his maintenance scholarship.

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