



Research Article

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## Optical and photoluminescence properties of HMTA capped transition metals (Cu, Co and Mn) doped ZnS nanoparticles

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### ABSTRACT

Transition metals (Cu, Co and Mn) doped ZnS nanoparticles have been prepared by surfactant-assisted controlled synthesis route using Hexamethylenetetramine (HMTA) as surfactant in aqueous solution. X-ray diffraction (XRD) studies show that the average grain size of the prepared ZnS nanoparticles is about 2 nm with cubic zinc blende structure and doping of transition metals has no effect on the structure. The ultraviolet-visible (UV-Vis) absorption spectra of the synthesized nanoparticles exhibit a blue shift in the absorption onset compared to the bulk ZnS, which is due to the quantum confinement of charge carriers in the nanoparticles. From the photoluminescence (PL) spectra, except for the HMTA stabilized ZnS nanoparticles doped with copper ( $\text{Cu}^{2+}$ ) ion, the relative emission intensity of the ZnS samples doped with cobalt ( $\text{Co}^{2+}$ ) and manganese ( $\text{Mn}^{2+}$ ) ions are higher than that of pure ZnS. The PL spectra exhibit two emission peaks at around 420 and 442 nm attributed to deep-trap emission of ZnS and presence of various surface states.

**Keywords:** HMTA; ZnS nanoparticles; Doping; Hydrothermal synthesis; Optical properties

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### INTRODUCTION

Doped metal chalcogenide nanostructured materials have attracted much attention due to their wide range of applications in light emitting displays, optical sensors, electroluminescence devices etc. This kind of nanomaterials exhibit unusual physical and chemical properties in comparison with their bulk materials, such as size dependent variation of the band gap energy. Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities [1]. The doped semiconductor nanoparticles have also attracted great interest due to their characteristics such as short luminescence life-time, size independent emission color tunability, low-voltage cathodoluminescence and alternate-current electroluminescence [2]. As an important II-VI semiconductor material, ZnS is chemically more stable and technologically important than other chalcogenides, it is considered to be a promising host material. Transition metal ions ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ ) have been incorporated into ZnS nanostructures by various routes such as hydrothermal, thermal evaporation, co-precipitation, micro emulsion etc. [3-7]. In our previous work, pure ZnS nanoparticles have been synthesized using Hexamethylenetetramine (HMTA) as surfactant in aqueous solution by hydrothermal method and wet chemical method [8-11].

In this present investigation, the optical and photoluminescence properties of transition metals (Cu, Co and Mn) doped ZnS nanoparticles has been investigated. The tunable emission characteristics of HMTA stabilized ZnS samples with change in excitation wavelength have also been studied.

## EXPERIMENTAL SECTION

### *Synthesis of HMTA stabilized pure and transition metals doped ZnS nanoparticles*

HMTA stabilized pure ZnS nanoparticles were synthesized as per the procedure reported earlier [8]. In the case of HMTA stabilized transition metals (Cu, Co and Mn) doped ZnS nanoparticles, dihydrates of zinc, copper, cobalt and manganese

acetate were mixed with Hexamethylenetetramine (HMTA) ( $C_6H_{12}N_4$ ) and thiosemicarbazide ( $CH_5N_3S$ ) along with sodium hydroxide (NaOH). The synthesis was carried out by adding zinc acetate dihydrate/ thiosemicarbazide/ HMTA/sodium hydroxide=0.95/1/0.5/0.5 (mole ratio) along with 0.05 M of copper acetate dihydrate ( $(CH_3COO)_2 Cu \cdot 2H_2O$ ) for Cu doped ZnS, 0.05 M of cobalt acetate dihydrate ( $(CH_3COO)_2 Co \cdot 2H_2O$ ) for Co doped ZnS and 0.05 M of manganese acetate dihydrate ( $(CH_3COO)_2 Mn \cdot 2H_2O$ ) for Mn doped ZnS in the Teflon-lined chamber, which was then filled with deionized water up to 80% of its volume. The closed chamber was placed inside a resistive heating furnace and heated at 180 °C for 8 h and then cooled down to room temperature. The resulting precipitate were filtered off and washed several times in distilled water and ethanol. The final products were dried in vacuum at 90 °C for 4 h.

### *Characterization of nanoparticles*

The XRD patterns of the prepared samples were recorded with Siemens D-5005 X-ray powder diffractometer, using  $CuK_{\alpha}$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). Optical absorption was studied using Perkin Elmer UV-Visible spectrophotometer. Emission spectra (PL) were recorded at room temperature using Perkin Elmer LS 5B Fluorescence spectrophotometer over the range of 400 to 600 nm.

## RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD) patterns for pure and transition metals (Cu, Co and Mn) doped ZnS nanoparticles are shown in Fig. 1. The patterns indicate that all the samples possess cubic zinc blende structure of ZnS (JCPDS file No. 05-0566) [12]. Diffraction peaks from (111), (220) and (311) planes alone appeared in the XRD pattern and all other high-angle peaks have submerged in the back ground due to the large line broadening, which is attributed to nanosize of the particles. No additional peaks were observed, indicating that within the resolution of XRD measurement, there were no structural changes and formation of additional phases due to the incorporation of transition metal dopants in ZnS. This confirms that the cubic phase of ZnS structure is not disturbed by the transition metals (Cu, Co and Mn) substitution. The XRD peaks of all the samples are quite similar, except a small shift in the peak positions, which may be due to the difference in the ion radii of the transition metal ( $Cu^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$ ) compared to Zn. The average size of the nanoparticles was estimated from the full width at half-maximum (FWHM) of the most intense peak using the Scherrer's equation [13] and the size distribution was found to be 2 nm.

The UV-Vis absorption spectra for HMTA stabilized pure and transition metals (Cu, Co and Mn) doped ZnS nanoparticles are shown in Fig. 2. The absorption edges of the ZnS samples exhibit a blue shift in comparison to bulk ZnS [14]. This shift of the absorption edges to shorter wavelengths is explained due to the quantum confinement of ZnS nanoparticles [12]. The absorption edges of the nanocrystallites are also sharp, indicating that the synthesized particles have relatively narrow size distribution. Compared to pure ZnS nanoparticles, the doped ZnS absorbs at a higher wavelength. Hence, pure ZnS nanoparticles exhibits a strong quantum confinement effect as the optical band gap energy is increased significantly compared to the doped ZnS [15, 8]. For Cu doped ZnS nanoparticles, the decrease in the optical energy band gap may be due to the slight increase in particle size [16]. The decrease in the optical energy band gap of Co doped ZnS nanoparticles is mainly due to the sp-d exchange interactions between the band electrons and the localized d electrons of the  $Co^{2+}$  ions substituting host ions and is consistent with the reported results [17, 18]. In the case of Mn doped ZnS nanoparticles, the decrease in the optical energy band gap is due to the Mn related levels introduced in the host lattice [19].

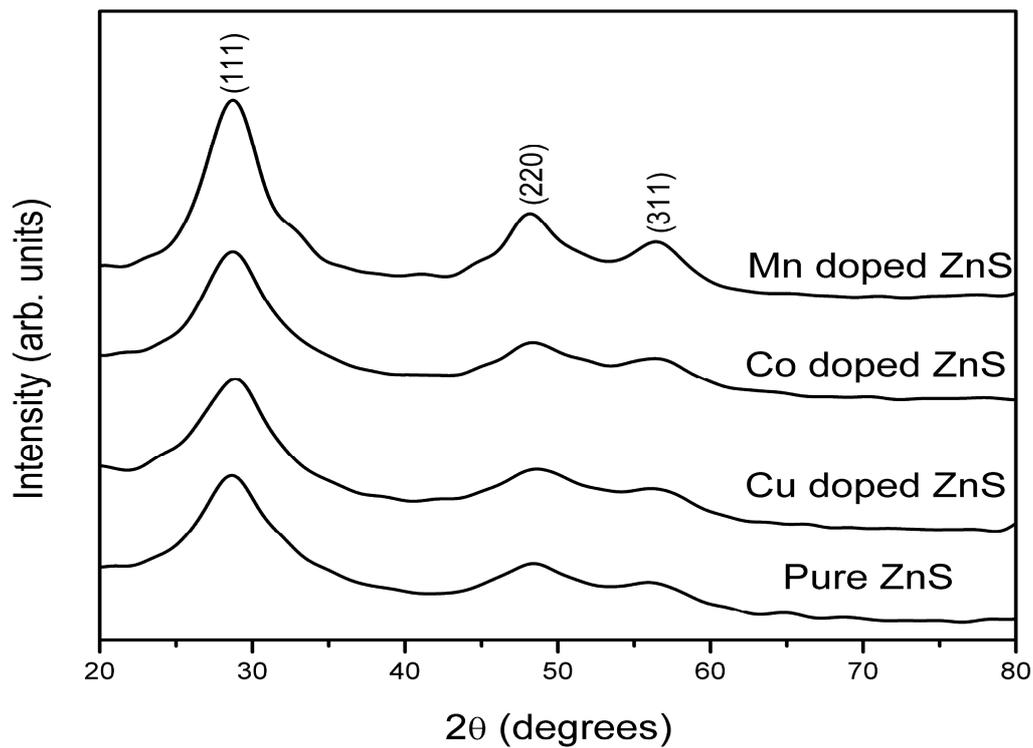


Fig. 1. XRD patterns of HMTA stabilized pure and transition metals doped ZnS nanoparticles

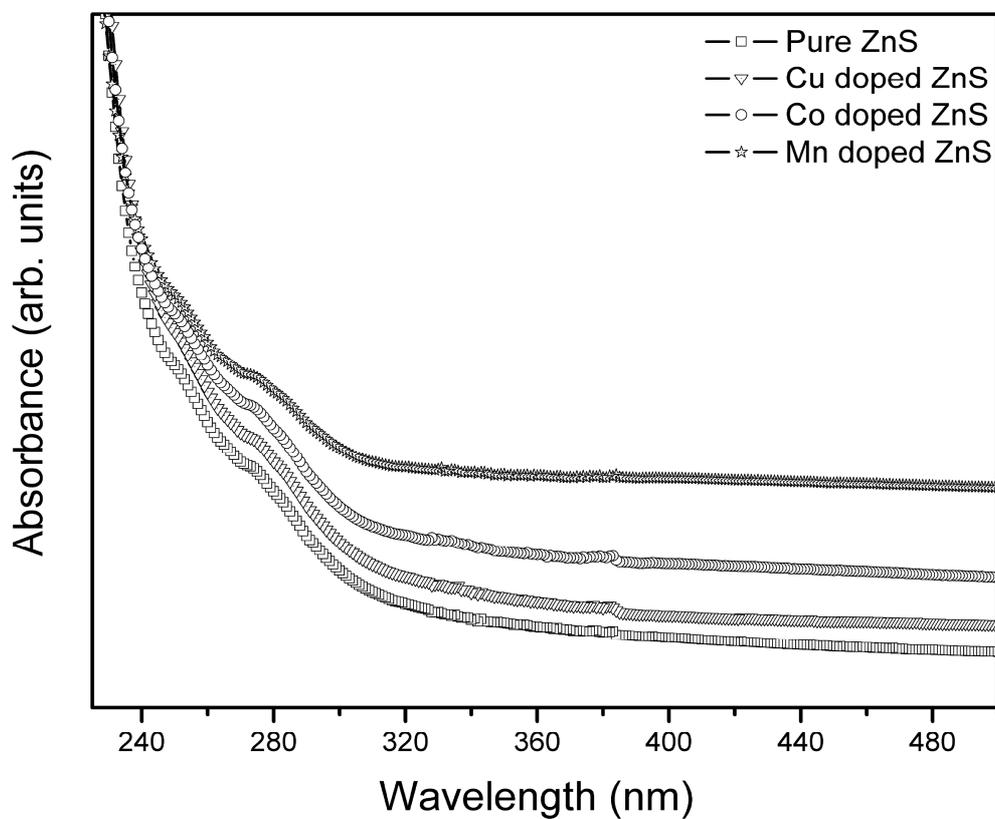


Fig. 2. UV-Vis absorption spectra of HMTA stabilized pure and transition metals doped ZnS nanoparticles

Photoluminescence (PL) spectra of HMTA stabilized pure and transition metals (Cu, Co and Mn) doped ZnS nanoparticles recorded at room temperature with an excitation wavelength ( $\lambda_{exc}$ ) of 380 nm is shown in Fig.3. Broadening of the emission peak is attributed to both size distribution and increase in the surface states owing to the increase in surface to volume ratio for nanoparticles [20]. The high luminescent intensity of HMTA stabilized cobalt and manganese doped ZnS nanoparticles compared to pure ZnS are mainly due to the enhancement of radiative recombination in the luminescence process. The emission intensity of ZnS samples doped with copper ions is lower than the pure ZnS, which may be due to the enhancement of non-radiative recombination. Since the ionic radius of  $Zn^{2+}$  and  $Cu^{2+}$  are 0.74 and 0.62 Å respectively,  $Cu^{2+}$  ions may occupy the Zn sites or as interstitial sites of ZnS nanoparticles. When these ions are doped into the ZnS nanoparticles, their deep centers are formed, which can inhibit more electrons to be excited and can lead to the enhancement of non-radiative recombination processes. As a result, their emission intensity becomes weaker than that of pure ZnS nanoparticles. However, since the ionic radius of  $Co^{2+}$  and  $Mn^{2+}$  (0.82 and 0.80 Å) are larger than that of  $Zn^{2+}$  (0.74 Å), it is difficult for the  $Co^{2+}$  and  $Mn^{2+}$  ions to substitute the  $Zn^{2+}$  sites in ZnS lattice [21]. It is also observed that the emission peak of all the samples are at 420 and 442 nm, indicating that the luminescent centers of the various transition metal ions are not formed within the doped ZnS nanoparticles. The emission at 420 nm is assigned to deep-trap emissions or defect-related emission of ZnS. The peak at 442 nm may be attributed to the presence of various surface states [22, 23].

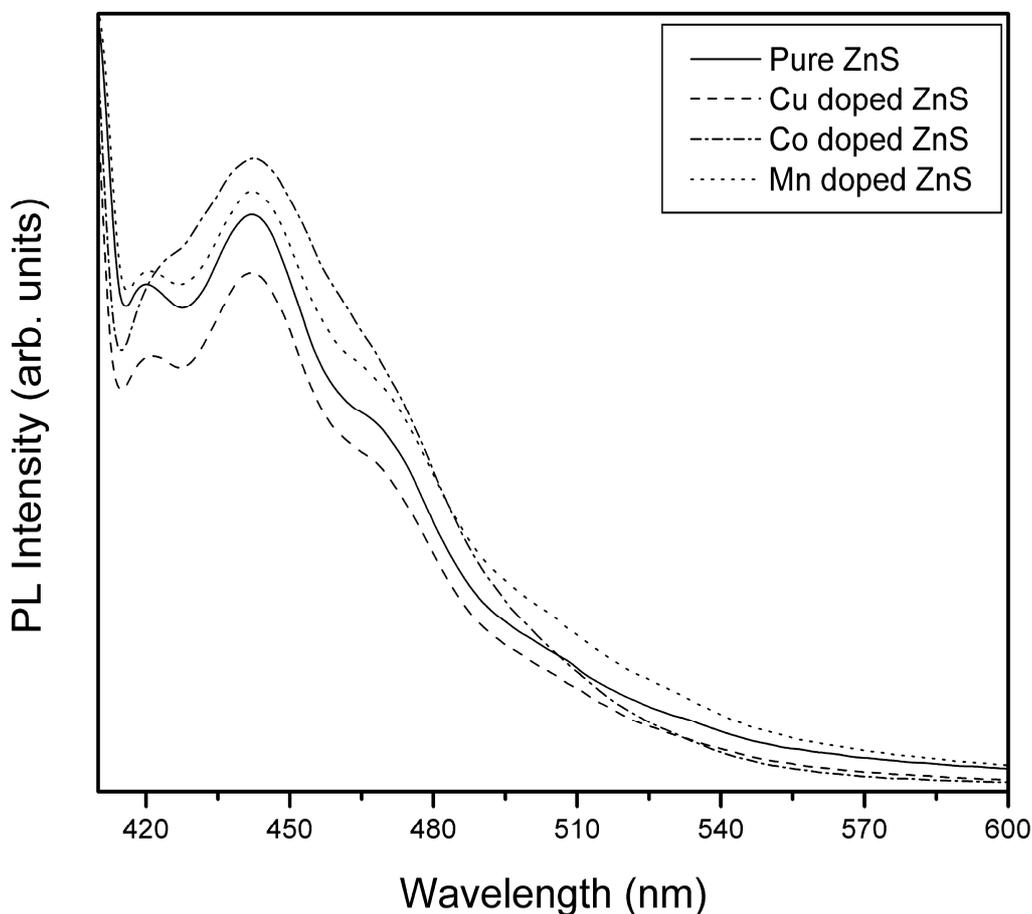


Fig. 3. Photoluminescence spectra of HMTA stabilized pure and transitions metals doped ZnS nanoparticles

#### CONCLUSION

A facile surfactant-assisted controlled method has been adopted for the synthesis of transition metals (Cu, Co and Mn) doped ZnS nanoparticles using hexamethylenetetramine (HMTA) as a surfactant in aqueous solution. The crystal structure and average grain size of the HMTA stabilized ZnS samples were determined by XRD analysis. The absorption edges of the prepared HMTA stabilized ZnS samples exhibit a blue shift in comparison to bulk ZnS

due to strong quantum confinement effect. From the photoluminescence (PL) spectra, the high luminescent intensity of HMTA stabilized cobalt and manganese doped ZnS nanoparticles compared to pure ZnS are mainly due to the enhancement of radiative recombination in the luminescence process. The emission intensity of ZnS samples doped with copper ions is lower than pure ZnS, which may be due to the enhancement of non-radiative recombination. The PL studies demonstrate two emission peaks at around 420 and 442 nm for all the samples, which are attributed to the deep-trap emission or defect-related emission of ZnS and presence of various surface states.

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