



Photoluminescence and photocatalytic studies of metal ions (Mn and Ni) doped ZnS nanoparticles



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ABSTRACT

The present study deals with the structural, optical and photocatalytic studies of thioglycerol capped doped ZnS nanoparticles (NPs). Effect of two dopant metal ions (Ni and Mn) on photoluminescence emission and photocatalytic properties have been studied in detail. $Zn_{1-x}M_xS$; $M = Ni$ or Mn ; $x = 0, 0.01, 0.02, 0.03$ and 0.04 NPs have been synthesized using simple chemical precipitation route. Structural and morphological studies have been done by using X-ray diffraction (XRD) technique and high resolution transmission electron microscopy (HRTEM). Capping of thioglycerol on the surface of doped ZnS has been confirmed by Fourier transform infrared (FTIR) studies. UV–Vis and photoluminescence studies have been carried out to study the effect of doping on optical properties of synthesized materials. Degradation of crystal violet has been carried out with the aim to investigate the effect of Ni or Mn doping on photocatalytic activity of ZnS. It has been observed that both the metal ions have decreased the photocatalytic activity of ZnS. The effect of photocatalytic reaction temperature on photocatalytic properties of one of the doped sample has also been investigated. It has been interpreted from the results that photocatalytic activity of doped semiconductor nanostructures is strongly dependant on their photoluminescence properties as well as on photocatalytic reaction temperature.

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1. Introduction

In recent years, semiconductor (SC) nanostructures (NSs), especially II–VI SCs have attracted great interest due to their unique structural, optical and electronic properties which arise due to their large surface to volume ratio (S/V) and quantum confinement effect [1]. Among the most extensively studied II–VI SCs, ZnS is a well known multifunctional material with a wide band gap of 3.54 eV (cubic zinc blende phase). This material has been proved as a better photocatalyst due to rapid generation of electron–hole pairs with photoexcitation as it is a direct wide band gap SC material [2]. Further, it possesses high negative reduction potential of excited electrons due to its higher conduction band position in aqueous solution as compared to other extensively studied photocatalysts [3]. Also, this material show good photocatalytic activity due to trapped holes arising from surface defects on the sulphides [4]. It has also been utilized in UV detectors due to its high resistivity at ambient conditions and fast switching time upon UV light illumination, thus exhibiting the highest potential for a UV-light detector [5]. An important subset of semiconductor NSs are those

doped with a small percentage of dopants to alter their structural, magnetic, electronic and optical properties for various desired applications. Owing to its large band gap, ZnS can easily host different transition metal ions acting as luminescent centres [6]. A number of transition metal ions such as Mn, Cu, Ag, and Eu have been successfully doped into ZnS to obtain desired structural and optical properties for their potential application in related areas [1]. Dopant ions offer a way to trap charge carriers which result in better photocatalytic activity of the material [7]. However, in some publications, it is reported that some dopant ions enhance charge carrier recombination resulting in decreased photoactivity of the host material [8,9]. Porambo et al. [10] have reported that doping of ZnS nanocrystals with Mn leads to an initial increase in the apparent rate constants in case of degradation of 2-chlorophenol and then decreased at higher dopant concentrations. Mohamed [7], in his work, investigated the effect of Cu content on photocatalytic activity of ZnS thin films. Photocatalytic degradation of methylene blue was recorded maximum in case of Cu content of 3%. Ullah and Dutta [8] have investigated the role of Mn on photocatalytic activity of doped ZnO NPs. Photocatalytic activity of Mn doped ZnO nanoparticles (NPs) has been observed to decrease as compared to that of undoped ZnO NPs under UV irradiation. Whereas, under visible irradiation, Mn doped ZnO NPs have shown

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enhanced photocatalytic activity as compared to that of undoped ZnO NPs. Recently, Ashkarran [9] has observed decrease in photocatalytic degradation of three dyes (Rhodamine B, Bromocresol Green and Bromochlorophenol Blue) using Mn doped ZnS NPs as compared to that of undoped ZnS.

From the above discussion, it is clear that dopant ions in SC NPs not always act as a trap for charge carriers (which ultimately enhances their photocatalytic activity), sometimes; these can enhance charge carrier recombination resulting in decreased photocatalytic activity. Although, photocatalytic studies of transition metal ion doped ZnS NPs have been carried out by various research groups, but, research related to investigate the effect of Mn and Ni doping on structural, optical and photocatalytic studies of ZnS NPs is still in its early stage and need more understanding. Also, it has been reported that there is a strong correlation between photoluminescence and photocatalytic properties of a material [11]. Hence, in the present work, thioglycerol capped ZnS NPs doped with Mn and Ni have been synthesized with the aim to study the effect of dopant ions on photoluminescence and photocatalytic properties of ZnS.

2. Experimental

2.1. Materials and reagents

Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2$], nickel acetate [$\text{Ni}(\text{CH}_3\text{COO})_2$], manganese acetate [$\text{Mn}(\text{CH}_3\text{COO})_2$], sodium sulphide nonahydrate [$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$], 1-thioglycerol [$\text{C}_3\text{H}_8\text{O}_2\text{S}$] and crystal violet [$\text{C}_{25}\text{N}_3\text{H}_{30}\text{Cl}$] were purchased from Sigma Aldrich and were of high purity (99.99%). All chemicals used in this work were of analytical grade and were used as such without further purification. Ultrapure water was used in the entire synthesis.

2.2. Synthesis

ZnS NPs doped with 0, 1, 2, 3 and 4 wt.% of Mn and Ni ($\text{Zn}_{1-x}\text{M}_x\text{S}$; M = Mn or Ni; $x = 0, 0.01, 0.02, 0.03$ and 0.04) were synthesized by simple chemical precipitation method as reported earlier with some modifications [12,13]. Solution of $\text{Zn}(\text{ac})_2$ and $\text{M}(\text{ac})_2$ was prepared in ultrapure water and were stirred for 30 min separately. After 30 min., solution of $\text{M}(\text{ac})_2$ was poured dropwise into the stirred solution of $\text{Zn}(\text{ac})_2$. Solution of Na_2S was also prepared separately and was stirred for 30 min. To this solution, stirred solution of thioglycerol was added dropwise. After 30 min. of stirring, solution of Na_2S was added into the above stirred solution. The reaction mixture was allowed to stir for 3 h at 80°C followed by overnight ageing. The resulting solution was centrifuged to remove the unreacted species and excess capping agent. The washed precipitates were then dried at 80°C for 24 h. and were crushed to obtain fine powder. For comparative study, undoped ZnS was also prepared using the above mentioned procedure. For the purpose of simplification, $\text{Zn}_{1-x}\text{Ni}_x\text{S}$; $x = 0.01, 0.02, 0.03$ and 0.04 have been coded as N1, N2, N3 and N4 respectively. Similarly, $\text{Zn}_{1-x}\text{Mn}_x\text{S}$; $x = 0.01, 0.02, 0.03$ and 0.04 have been coded as M1, M2, M3 and M4 respectively unless otherwise specified. Undoped ZnS has been coded as NMO.

2.3. Characterization techniques

The as prepared samples were characterized by X-ray diffraction (XRD) technique using Panalytical's X'Pert Pro diffractometer with $\text{Cu K}\alpha$ radiation. Elemental analysis of as prepared samples was done using scanning electron microscope (SEM; JEOL, JSM-6510LV) equipped with energy dispersive X-ray spectrometer (EDS; Oxford INCA) having Si(Li) detector. For measurement,

operating voltage was kept at 20 kV and tungsten filament is the source. Morphological study of the samples was done by high resolution transmission electron microscope (HRTEM) JEOL 2100F having operating voltage of 200 kV. FTIR spectrum was recorded using Bruker Alpha-T. Optical absorption spectra of the samples were recorded with a double beam UV-Visible spectrophotometer (Hitachi, Model-U-3900H). Photoluminescence (PL) emission spectra of samples has been recorded with Edinburgh Instruments FS920 spectrometer equipped with 450 W Xenon Arc Lamp and a cooled single photon counting photomultiplier (Hamamatsu R2658P). Photocatalytic experiments were carried out in dark using self designed photoreactor at room temperature [13].

2.4. Apparatus for photocatalytic study

The photocatalytic degradation experiment was conducted in dark at room temperature using self designed photochemical reactor. Details of the photochemical reactor are given in our previous publication [13]. A known amount of catalyst (0.5 g/L) was mixed in 50 mL of dye solution (1 mg/L) for photocatalytic experiments.

3. Results and discussion

3.1. XRD studies

Fig. 1(a) and (b) shows the XRD patterns of ZnS doped with Ni and Mn ions respectively. As can be seen in the figure, all samples exhibit cubic zinc blende phase with no impurity phase indicating that Ni and Mn ions are successfully doped in the host lattice. However, the presence of Ni and Mn in prepared samples has been confirmed through Energy Dispersive X-ray (EDS) spectroscopy analysis. For instance, EDS patterns for one of the Ni and Mn doped ZnS are shown in Fig. 2(a) and (b) respectively. Diffraction peaks from (111), (220) and (311) planes match well with those of the β -ZnS (cubic) reported in the ICDD Powder Diffraction File No. 80-0020. In all the samples, broadening of diffraction peaks indicate nanosize formation of ZnS. It is to be noted that in Fig. 1(a) and (b), the XRD peaks of doped ZnS NPs became weaker and broader as compared to that of undoped ZnS. This suggests that the crystallinity of doped ZnS NPs is deteriorated with the increase in doping content in the source material. Decreased crystallinity of doped samples as compared to that of undoped ZnS indicates the increase in disorder due to incorporation of impurity ions.

To investigate the effect of doping on ZnS host lattice, the most intense diffraction peak corresponding to (111) plane was selected (Fig. 3(a) and (b)). Larger line broadening in case of doped samples indicates their smaller particle size as compared to the undoped ZnS sample. A careful comparison of diffraction peak in the range $2\theta = 22\text{--}38^\circ$ for all samples indicates that this peak is slightly shifted towards higher angle which indicates that Ni is successfully substituted for Zn in the host lattice. In case of Mn doped ZnS, no appreciable peak shift has been observed in any sample which may be attributed to the very small difference in ionic radius of Mn^{2+} (0.66) and Zn^{2+} (0.6). Crystallite size of NPs was calculated by following Scherrer's equation

$$t = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where $k = 0.9$, t is the crystallite size (\AA), λ (\AA), the wavelength of $\text{Cu K}\alpha$ radiation and β is the corrected half width of the diffraction peak [14]. Crystallite size for Ni and Mn doped ZnS came out in the range of 1.98–2.19 nm and 1.9–2.0 nm respectively.

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