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Synthesis of $Cd_{1-x}Mn_xS$ nanoclusters by surfactant-assisted method: Structural, optical and magnetic properties

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Abstract

$Cd_{1-x}Mn_xS$ nanoclusters were synthesized by surfactant-assisted chemical method for different Manganese (Mn) concentration ($0.40 \leq x \geq 0.10$) at 60 °C in argon atmosphere. Incorporation of magnetic ions (Mn) results a decrease in band gap of $Cd_{1-x}Mn_xS$ nanoclusters. The room temperature ferromagnetic behaviour is demonstrated first time in $Cd_{0.60}Mn_{0.40}S$ nanoclusters by vibrating sample magneto (VSM) measurements and the origin of magnetization has been discussed.

Keywords: Nanomaterials; Magnetic materials; Optical properties

1. Introduction

The introduction of magnetic ions in semiconductors results in a fascinating class of semiconducting alloys — known as diluted magnetic semiconductors (DMS'). In recent years Mn-based II–VI DMS' have attracted considerable attention as a result of the large exchange interaction between the band electrons and Mn^{2+}, the so-called "sp–d exchange interaction." Also, Mn^{2+} is electrically neutral in a semiconductor host, thus avoiding the formation of any acceptor or donor impurities in the crystal. According to the solubility limit, the Mn-based DMS can be grown over a wider composition range than Fe- and Co-based DMS [1]. In the last few decades, DMS of $A^{II}_{(1-x)}$ Mn_xB^{VI} type alloys (where A^{II}=Zn, Cd, Hg and B^{VI}=S, Se, Te) have been studied extensively [2]. Incorporation of magnetic ions in quantum confined systems opens new possibilities for the spin-dependent electronics due to the combination of the exchange interaction and quantum confinement [3]. Among the various Mn^{2+}doped II–VI semiconductor DMS alloys, $Cd_{1-x}Mn_xS$ finds much attention because of its considerably large p–d exchange integral value that causes various abnormal phenomena [4].

Synthesis procedure for the preparation of $Cd_{1-x}Mn_xS$ QDs based on the reverse micelles as templates has been reported [5] and detailed colloidal chemistry has been described by A.I. Savchuk et al. [6]. Several reports were devoted to both semiconducting or magnetic properties of $Cd_{1-x}Mn_xS$ alloys in a bulk [7], quantum dots [8,9] and thin films form [10]. But, there is no report available in the form of nanoclusters. This paper reports the structure, optical and magnetic properties of $Cd_{1-x}Mn_xS$ nanoclusters for different Mn concentration synthesized by surfactant-assisted method.

2. Experimental techniques

$Cd_{1-x}Mn_xS$ nanoclusters were prepared by surfactant-assisted technique using Triton 100 X as templates similar to that of the procedure reported earlier [11]. Typical synthesis of $Cd_{1-x}Mn_xS$ alloys are as follows: a suspension consisting of cadmium dichloride ($CdCl_2$, 50 mmol) in 20 ml of Triton 100-X (~24 mmol) was prepared. Aqueous solution of thioacetamide in basic medium was added drop by drop to the above suspension under constant stirring at 60 °C in argon atmosphere. The desired amount of aqueous solution of manganese acetate (0.10 M to

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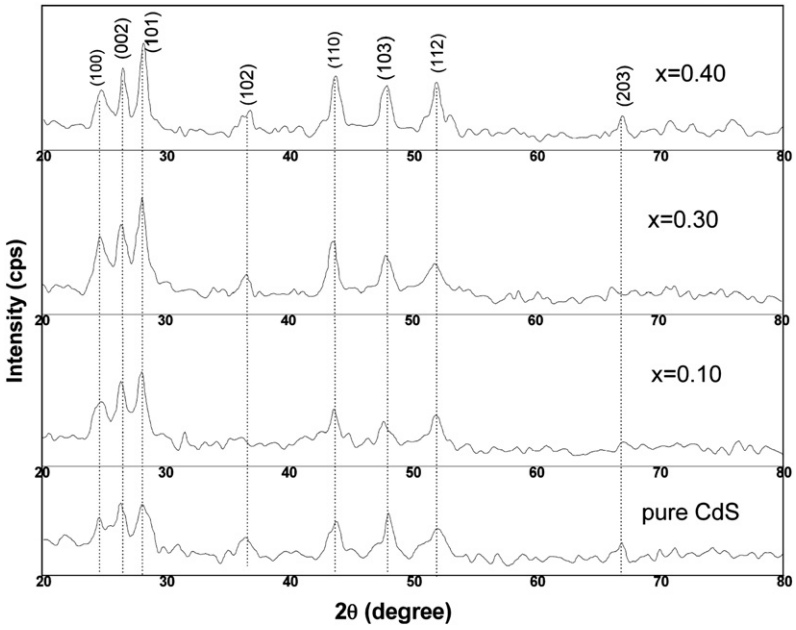

Fig. 1. X-ray diffraction spectra of pure and Mn doped CdS nanoclusters for different doping concentrations (x=0.10, 0.30 and 0.40).

0.40 M) has injected in the above mixture. The resulting mixture is refluxed for 12 h and left overnight. By taking in to account the reaction mechanism proposed for synthesize of CdS nanoparticles by Zhu et al. [12], we propose a similar mechanism for the growth of $Cd_{1-x}Mn_xS$ nanoclusters as follows:

$$CH_3CSNH_2 + H_2O \rightarrow CH_3(NH_2)C(OH) - SH \quad (1)$$

$$CH_3(NH_2)C(OH) - SH + H_2O \rightarrow CH_3(NH_2)C(OH)_2 - H_2O \rightarrow CH_3(NH_2)C(OH)_2 + H_2S \quad (2)$$

$$CH_3(NH_2)C(OH)_2 \rightarrow CH_3(NH_2)C = O + H_2O \quad (3)$$

$$H_2S + CdCl_2 \xrightarrow[\text{injection-of-}Mn^{2+}\text{-refluxed-at-60 °C}]{\text{Triton-X-100}} Cd_{1-x}Mn_xS + 2HCl \quad (4)$$

3. Results and discussion

3.1. Structure and surface analysis

Fig. 1 represents the XRD (Shimadzu XRD 6000) spectra of pure CdS and $Cd_{1-x}Mn_xS$ for different Mn doping concentration. The observed diffraction peaks for pure and Mn doped CdS samples are indexed in Fig. 1. The absence of MnS peaks in the spectra reveals that a single compound or alloy ($Cd_{1-x}Mn_xS$) is formed as resultant DMS materials. The mean crystallite size, D, of the nanoclusters has been calculated using the Scherrer formula [11].

The calculated crystallite size of the pure and Mn doped CdS nanoclusters are given in Table 1 and clearly evident that the crystallite growth in $Cd_{1-x}Mn_xS$ has enhanced with the increase of Mn doping and particularly for x=0.40 larger cluster size has been achieved.

Fig. 2 shows the SEM images of $Cd_{1-x}Mn_xS$ alloys for various Mn concentrations. It clearly shows that the constituent particles of $Cd_{1-x}Mn_xS$ are agglomerated and leads to the formation of cluster like patterns. The size of $Cd_{1-x}Mn_xS$ nanoclusters increases with increase in Mn concentration which is in good agreement with the estimated particle size from XRD analysis. In the case of $Cd_{0.6}Mn_{0.4}S$, the clusters are almost amalgamated (Fig. 2d) and it may form bigger particles. Therefore in the present work, we have concluded that above certain doping concentration (x>0.4), $Cd_{1-x}Mn_xS$ nano clusters may get enhanced in its particle size and consequently attains the bulk properties.

3.2. Optical properties

Diffused reflectance spectra of $Cd_{1-x}Mn_xS$ nanoclusters for different Mn doping concentration were recorded using Varian 5000 spectrophotometer and the resulting spectrum is shown in Fig. 3 (i). A blue shift of the absorption onset of about 0.26 eV compared to the bulk CdS material [2.4 eV] can be noticed in undoped CdS nanoclusters. This result is a direct consequence of the quantum confinement effect associated with the small particle size. The absorption onset of $Cd_{0.90}Mn_{0.10}S$ could turn to red shift with increase in x value. The value of the band gap energy for different Mn concentrations in $Cd_{1-x}Mn_xS$ nanoclusters obtained from the diffused reflectance spectra at room temperature are given in Table 1. The observed band gap bowing effect may be due to the exchange interactions of the conduction and valence band electrons with the Mn^{2+} d electrons [13]. Precisely, presence of localized magnetic ions in semiconductor alloys leads to exchange interactions between s–p band electrons and the Mn^{2+} electrons. It plays a double role in determining optical properties. (i) The band gap

Table 1
Summary of particle size, band gap energy, and magnetic parameters of $Cd_{1-x}Mn_xS$ for various Mn doping concentration (x)

	(hkl)	Doping concentration			
		x=0	x=0.10	x=0.30	x=0.40
Particle size (nm)	101	9.7	20.3	23.3	26.4
(from XRD)	002	20.7	22.9	31.6	28.1
	103	29	18.6	18.7	30.8
	110	13	22.3	22.7	31.9
Particle size (nm) (Diffused Reflectance Spectra)		6.93	7.21	9.94	11.8
Band gap (eV)		2.68	2.66	2.54	2.50
M_s (emu/g)		–	0.203	0.252	0.614
H_Φ (O_e)		–	4956	7815	83