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Structural and optical characterization of ZnS nanoparticles

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Abstract

The present paper reports the structural and optical characterization of the ZnS nanoparticles, where as mercaptoethanol (ME) was used as the capping agent. Nanoparticles of zinc sulphide were prepared by chemical route technique. The particle size of such nanocrystals was measured using XRD pattern and it is found to be in between 3nm - 5nm. The blue-shift in the absorption spectra was found with reducing size of the nanoparticles. It was also found that the change in Mn concentrations does not influence the particle size and blue-shift in the absorption spectra. The optical absorption edge was found at 280 nm for all the doped samples for fixed concentration of capping agent. The particle size of nanoparticle has been calculated both theoretically and experimentally, which is nearly the same. The FTIR spectra inferred that the stabilizing agent passivates the surface of the particles.

Keywords: Nanoparticles; XRD, luminescence, optical absorption spectra, ZnS:Mn, FTIR.

INTRODUCTION

Semiconductor nanocrystals are described as a state of matter that is intermediate between individual molecule and bulk [1]. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include tunable bandgap [2] and catalytic behavior [3]. The small size and high optical activity of certain semiconductors make them interesting for applications in disciplines ranging from optoelectronics [4], catalysis [5] to fluorescence microscopy [6]. Semiconductor nanocrystals are potentially useful for technological applications like indicators, analysis of water pollution, environmental studies, pathological investigations etc. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects. Particles in nanometric sizes show unique physical properties, for example with the decrease of particle size, extremely high surface area to volume ratio is obtained leading to an increase in surface specific active sites for chemical reactions and photon absorption to enhance the reaction and absorption efficiency. The enhanced surface area increases surface states, which changes the activity of electrons and holes, affecting the chemical reaction dynamics

The conventional approach for synthesis of nanoparticles involves chemical or physical attrition from bulk into objects of desired sizes and shapes (e.g. mechanical milling, ion implantation, etc.), and is referred as the 'top-down' approach. Inverse to the 'top-down' approach is a process universal in nature, involving the assembly of materials from molecular levels to form micro or macro-sized shapes and structures, often referred as 'bottom-up' approach or 'self-assembly' [7].

It has been reported that Mn doping in ZnS nanoparticles enhances the optical transition efficiencies of carriers, and increases the number of optically active sites. Nanoparticles can induce the possibility of indirect electron transitions at the boundary of the crystals and realize the essential enhancement of light absorption. Novel luminescence characteristics, such as stable and visible light emission with different colours has been observed from doped ZnS nanoparticles

In this work zinc sulfide nanocrystals are prepared by chemical precipitation technique and mercaptoethanol has been used for capping, which modifies surface of nanoparticles and prevents the growth of the particles to larger size. The effect of Mn concentrations on optical absorption spectra has been investigated. XRD, SEM and FTIR studies of the samples were also made.

EXPERIMENTAL

The most important step in the studies of nanoparticles is their synthesis. There are various methods supported for synthesis of nanoparticles. Chemical route is used in the present investigation. The powder of ZnS nanoparticles were prepared by using chemical deposition technique described by Khosravi [8]. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethenol (C_2H_5OSH) solution. $MnCl_2$ was also mixed in the solution in various ratio, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times in double distilled water and then separated by centrifuge at 3500 rpm, and finally air dried. Special care has to be taken to maintain the same physical condition during the synthesis of the sample.

All the samples were characterized at Inter University Consortium (IUC) Indore. For Scanning Electron Microscope (SEM), JSM – 5600 LV was used. The morphologies and sizes of the mercaptoethanol capped ZnS:Mn were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were

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collected over the range 20^0-70^0 at room temperature. X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer. The particle size was calculated using the Debye-Scherrer formula.

Absorption spectra of the samples prepared with various concentrations of Mn was recorded with the help of UV-Visible spectrometer (SHIMADZU).

The FTIR spectra were recorded by the help of FTIR spectrometer (SHIMADZU) in the range of 500 cm^{-1} to 4000 cm^{-1}.
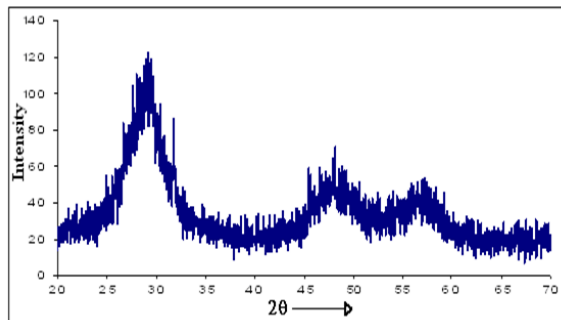
RESULTS AND DISCUSSION

Fig. 1 XRD pattern of ZnS:Mn   nanoparticles

Figure 1 shows the XRD spectra of the ZnS:Mn nanoparticles. Three different peaks are obtained at 2Θ values of 29.50^o, 48.80^o and 57.80^o. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively [9]. The lattice parameter has been computed as 5.31 Å, which is very close to the standard value (5.42 Å). The broad peak indicates nanocrystalline behavior of the particles. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [10]. It was also found that peaks get broadened for higher concentration of capping agent. The particle size of the samples of Zns:Mn are measured and are found in the range 3- 5 nm.
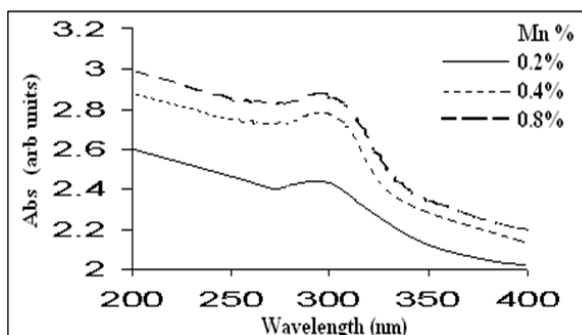

Fig. 2 Absorption spectra of ZnS:Mn nanoparticles with different Mn concentration

Figure 2 shows the optical absorption spectra of ZnS nanoparticles with different concentration of Mn where as the concentration of capping agent remains same. The optical absorption spectra were measured in the range of 400 nm-200 nm. It was found that the spectra are featureless and no absorption occurs in the visible region (800 nm-390 nm). It was found that the peak position for all the samples, with and without Mn is same with different intensity of absorption. Absorption edge was obtained at shorter wavelength. The optical absorption edge is at 280 nm which is nearly same for all the samples. Hence the change in the concentration of Mn does not make change in the absorption edge of the optical absorption spectra i.e. no change in the particle size.

A typical SEM image of ZnS nanoparticle is shown in Fig. 3. SEM image shows clearly that the particles are not spherical. Figure shows that particles are highly agglomerated. The particle sizes obtained from SEM images are found to be in the range of 10nm to 20nm.
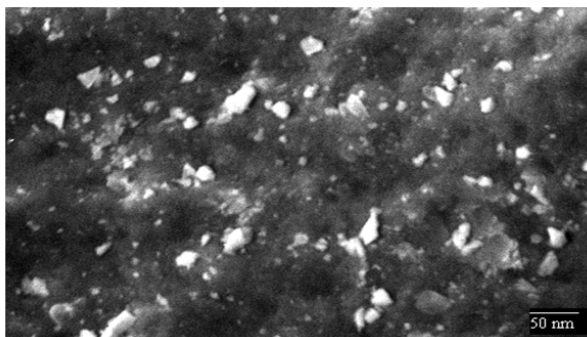
Fig. 3 SEM photograph of ZnS:Mn nanoparticles

Figure 4 shows the FTIR spectra of ZnS:Mn nanoparticles. Bands around 3000-3600 cm^{-1} are due to the hydrogen stretching frequency (OH stretching). The band at 3450 cm^{-1} corresponds to characteristic vibration band of hydroxyl groups of ME molecules. Our measurement of the spectrum of powdered sample yields the bands, which are in good agreement with the reported values [11-13]. The changes in the observed values are due to the formation of nano phase. Table 1 shows the position of different peaks assigned for ZnS:Mn nanoparticles.

Table 1: FTIR Peak assignments for the ME-capped ZnS:Mn nanoparticles

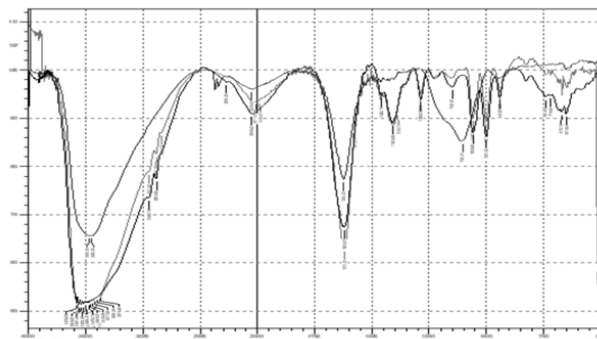|	
513 cm^{-1}	Asymmetric bending
612 cm^{-1}	Symmetric bending
690–740 cm^{-1}	C–H out-of-plane bending
1000–1282 cm^{-1}	C–O stretching of ME
1407–1475 cm^{-1}	C–H bending of methylene in ME
1575 cm^{-1}	C–C stretching of phenyl ring
2875, 2925 cm^{-1}	C–H stretching of methylene in ME
3051 cm^{-1}	C–H stretching
3450 cm^{-1}	O–H stretching

Fig. 4 The FTIR spectra of ZnS:Mn

CONCLUSIONS

The ZnS nanoparticles of manganese doped zinc sulfide have been successfully synthesized by a simple precipitation reaction using aqueous in which mercaptoethanol was used as a capping agent. It is found that the change in the concentration of Mn does not change significantly the particle size. The XRD pattern indicated the growth of the nanoparticles. It is found that SEM sees the agglomeration of nanocrystals and therefore larger size is observed whereas XRD give the extent to which regular arrangement of atoms exists and hence gives the average crystal size. XRD analysis shows the sample prepared is in a cubical phase. The absorption peak appears at around 280 nm, which is fairly blue-shifted from the absorption edge of the bulk (345 nm). The solid-state theory based on the delocalized electron and hole within the confined volume can explain the blue-shifted optical absorption spectra. The measurement of optical absorption spectra indicates that no blue-shift occurs for the samples with different concentration of Mn for the same concentration of ME. Prominent IR peaks are analyzed and assigned.

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