Synthesis and Characterization of Mn Doped CdS Nanoparticles Prepared by Chemical Bath Deposition Method

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Abstract: In this paper, synthesis and characterization studies of nanocrystalline CdS semiconducting particles grown on the glass substrates by means of chemical bath deposition method has been reported. Mercaptoethanol ("capping agent") were added in different concentrations in order to limit the growth of the particles and control their sizes. UV-VIS optical absorption studies and Scanning electron microscopy images indicate that the volume of capping agent adjust the band gap of CdS to obtain stable and homogenous films. Band gaps are found to increase and article size is found to be in nano range from optical absorption studies. The present paper discuss the optical properties of semiconductors nanocrystal are strongly dependent on particles size.

Keywords: Optical properties; scanning electron microscope; mercaptoethanol; semiconductor nanocrystals;

1. Introduction

Nanotechnology is an emerging field of research and development dedicated to increasing control over material structures of nanoscale size in at least one dimension and nano-materials have indeed become a very active research field in the areas of solid state physics, solid state chemistry, solid state ionic, materials engineering, medical sciences and biotechnology. Nanotechnology is growing day by day because of its advantages in almost all fields like electronics, optoelectronics, single electron device, computers, biomedical and sciences etc. due to their size dependent properties, nanoparticles, nanomaterials, nanofibres plays a very important role in today’s technology.

Nanomaterials can be characterized using different techniques like X-ray diffraction (XRD) Scanning electron microscope (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM) and Ultraviolet spectroscopy (UVS) etc. Many features of nanoparticles differ from those of their bulk counterparts and are depending on their individual sizes. It has always been a prime goal since the beginning of research in the field to prepare samples of nanocrystals as identical as possible. CdS is known to be direct band gap II-VI semiconductor having band gap of 2.4 eV several workers prompted the small Bohr exciton radius to synthesize doped or undoped CdS quantum dots in the past [1-3] and such synthesis with narrow size distribution is relevant even today. These quantum particles have demonstrated high luminescence efficiencies and remarkably short luminescence decay. Additionally, without affecting the absorption spectrum, the nature of the chemical treatment can dramatically effect the emission and its kinetics. Nanoparticles or quantum dots have drawn considerable interest and are currently being investigated by scientist in various laboratories all over the world. These nanoparticles may find application in nonlinear optical devices, photo catalysis etc. [4-6]. Synthesis, characterization, and the actual use of nanoparticles in device fabrication are carried out to understand the physicochemical properties of the nanoparticles.[7-10]. Quantum dots exhibit the property of the quantum size effect, which occurs when the cluster size is smaller than the Bohr exciton radius. Nanoparticles prepared in inverse micelle [7] Zeolites. [12]. etc., result in a very low yield of the clusters thereby making their characterization difficult. Here, we have used a chemical route for synthesis of CdS nanoparticles. In this method, organic and inorganic reagents can be used to control the size of the clusters [6, 9]. Free standing clusters of semiconductors can be easily formed in large quantities by relatively inexpensive means. Additionally, doping of the nanoparticles is easily possible at room temperature. The present paper reports the synthesis of Mn doped CdS nanocrystals, Scanning electron microscope (SEM), X-ray diffraction patterns (XRD) and also the analysis of their optical absorption spectra.

2. Experimental Method

Chemical synthesis of CdS quantum dots has been carried out by an aqueous chemical method similar to that used by Nosaka et al. [7] and reported elsewhere [13] for CdS quantum dots. Here aqueous solutions of cadmium chloride (CdCl₂), mercaptoethanol (C₂H₅OSH) and sodium sulfide (Na₂S), each with 1×10⁻⁵M are prepared and equal volume of each solution is used for the reaction. First, mercaptoethanol (C₂H₅OSH) solution was added drop wise to the CdCl₂ (+MnCl₂ in case if doping ) solution were mixed at a rate of 1 ml per minute, stirring it continuous so that solutions are mixed properly then sodium sulphide is added drop wise in the same reaction vessel. The experiments have been carried out at room temperature. The end product is washed thoroughly in double distilled water to remove any excess sodium sulphide which may be present is air-dried. It is expected for the samples prepared by the chemical route to have the size distribution, which ultimately will influence the experimental results.

The samples were characterized by scanning electron microscope (SEM), optical absorption spectra and Photoluminescence (PL) spectra. The scanning electron micrographs were obtain by SEM of stereoscan 430 made by...
Leica company at TFRI at Jabalpur. For photo physical characterization the optical absorption spectra of the sample were recorded with the help of Perkin Elemer Lamda 12 Spectrometer.

3. Results and Discussion

The absorption spectra of sample were recorded with the help of the Perkin Elmer Lamda 12 spectrometer. It was observed that with systematic variation of morality of the additive mercaptoethanol concentration, the optical band gap could be varied from a bulk value of 2.4 eV to 3.98 eV for clusters figure 1 illustrates this observation. As the mercaptoethanol concentration increases the excitonic peak shifts to a shorter wavelength as it becomes sharper. This indicates the narrow size distribution, increase in energy gap, and creation of sharp excitonic level with increasing additive concentration. As expected, doping did not have any measurable effect on the absorption spectra.

X-ray diffraction patterns of CdS nanoparticles are shown in fig.2. We have used an x-ray diffractometer with Cu kα (λ = 1.5405 Å) as the source of incident radiation. It was observed that as the concentration of the additive mercaptoethanol increased from 10⁻⁴ M, 10⁻² M to 0.5 M particle diameter reduced from 40±2Å, 30 ±2Å, and 18±2Å, respectively. Particles with intermediate sizes were also obtained for intermediate concentration of mercaptoethanol. Particles sizes were calculated using the Debye Scherer equation [6]. X-ray diffraction (XRD) patterns of CdS: Mn nanoparticles are shown in fig.2. This figure shows three peaks are observed for concentration of mercaptoethanol is 10⁻⁴ M. with increasing the concentration of mercaptoethanol, third peak merges in second peak due to more capping agent. The broad XRD lines are indicative of small sized CdS nanoparticles. The average sizes of the nanoparticles widths of these lines were calculated using the Debye-Scherer equation [8].It was observed that as the concentration of the additive mercaptoethanol increased from 10⁻⁴ M, 10⁻² M to 0.5 M, and particle size reduced from 2.8 nm, 2.1 nm to 1.8 nm respectively. This XRD pattern confirms the CdS: Mn²⁺ prepared in nanocrystalline form and the size of particle is dependent on the concentration of mercaptoethanol use in synthesis of CdS: Mn. Therefore, the higher the concentration of mercaptoethanol the smaller will be the cluster size. It can also be seen clearly from fig.2.

Fig.3. shows the optical micrographs of Mn doped CdS nanocrystals by scanning electron microscope of stereoscan 430 made by Leica company, fractal feature a re observable in sample whose thickness range in between 20 nm to 359 nm by the micrograph under optical microscope the fratacls appear but when sample are zoomed to higher magnification they are formed to consists of several crystallites.

4. Conclusion

The study have revealed that chemical method used for synthesis of nanoparticles of manganese doped CdS nanoparticles can be adopted for obtaining nanocrystals with narrow size distribution. The size of the particle of CdS: Mn decreased with increasing the mercaptoethanol concentration. The crystal field strength of synthesis materials is dependent on the synthesis of CdS: Mn nanoparticles. SEM shows the size of the particles about 20 nm where as XRD indicates crystallites size of the order of ~2 nm. Lower value of crystallite size by XRD indicates that the crystallites are very small and they are capped and joined together to give larger size.

References


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Figure 1: Optical absorption spectra of CdS nanoparticles capped with mercaptoethanol.

(1) Mercaptoethanol $10^{-3} \text{ M}$, $E_g=3.48 \text{ eV}$.
(2) Mercaptoethanol $10^{-2} \text{ M}$, $E_g=3.97 \text{ eV}$.
(3) Mercaptoethanol $0.5 \text{ M}$, $E_g=3.98 \text{ eV}$.
Figure 2: XRD patterns of the CdS nanoparticles capped with mercaptoethanol

Figure 3: Micrograph of CdS nanoparticles (SEM)