Synthesis of Highly Luminescent Manganese Doped ZnS Nanophosphor

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Abstract: *Nanophosphor material such as ZnS has potential applications in high brightness light emitting diode applications. Here we are reporting the synthesis of luminescent nanoparticles of manganese doped zinc sulfide with an emission peak at around 590 nm. Nanoparticles of Zinc sulphide are prepared by a co-precipitation reaction from homogenous solutions of zinc and manganese salts. These nanoparticles are capped with biocompatible histidine molecule. XRD pattern shows the particle size of ZnS Nanophosphor around 15-20 nm.*

Keywords: Nanophosphor; Biocompatible; Histidine.

Introduction

Materials with nanoscopic dimensions such as quantum dots, nanowires, nanorods and nanotubes, have attracted a great deal of attention recently due to their intriguing properties that cannot be obtained from the conventional macroscopic materials.Various technological applications require materials that are ordered on all length scales,from the molecular to nano. These novel Nanoscale materials are expected to have potential applications in areas such as optoelectronic devices technology, photo catalyst fabrication and drug delivery systems [1-2]. Nanophosphors material are of potential interest in non-linear optics and in fast optical switching [3-4].Quantum dots of II-VI semiconductors have attracted particular attention, because they are easy to synthesize in the size range required for quantum confinement. A reduction in the particle size strongly influences the crystallinity, melting point and structural stability. The unique characteristics of the Nanomaterials are believed to have originated from the quantum confinement effects due to the reduction of band structure into discrete quantum levels as a result of the limited size of the nanoparticles.

ZnS is semi-conducting materials, which has a wide band gap material of 3.70eV [5, 6]. Among these, luminescent semi-conducting nanocrystal, also termed as nanophosphors, were paid much attention particularly for their life time shortening and enhanced emission efficiencies [7,8].There have been extensive reports in the past few years demonstrating the systematic exploration of growing ZnS nanoparticles in the surfactant system to control the particle size. Tang et al. [9] for example studied the luminescence and photo physical properties of ZnS nanoparticles prepared by reverse micelle method. There is increasing interest in the synthesis and characterization of nanometer sized semiconductors.

Many approaches has been explored for the preparation of small clusters [10], including the use of colloids [11], polymers [12-14]. Currently, we have synthesized these materials chemically by co- precipitation process with a precise control over the size of ~ 4- 6nm. ZnS:Mn is a favourable phosphor which exhibits better optical properties such as high luminescent intensity,narrow emission band.here we report that ZnS:Mn nanocrystals were synthesized by utilizing histidine as the capping material. There is still challenge in order to stabilize the nanoparticles, often steric hindrance by capping with various polymers occurs. Depending on the capping molecules present on the Zns:Mn particles passivate surfaces.

One of the foremost challenges in device technology is in distributing nanoparticles uniformly of precise control on particle density. The room temperature photoluminescence (PL) and photoluminescence excitation (PLE) shows a broad and intense peak but the annealing of the same degraded the PL and PLE intensities by several orders.

Experimental Section

Synthesis of nanoparticles in a solution occurs by chemical reactions resulting in the formation of nuclei and subsequent particle growth. In the precipitation of multicomponent material, special attention is needed to control co-precipitation conditions in order to achieve chemical homogeneity of the final product. This is due to the fact that different ions often precipitate under different conditions of pH and temperature having different solubility product constant.The possibility of co-precipitation of ZnS and MnS is greatly improved during the precipitation which makes it possible to obtain well doped ZnS:Mn nanocrystals. Moreover on titration of sulfide, due to the formation of histidine capped ZnS:Mn, agglomeration is prevented by the Steric barrier introduced by the capping group. All steps of the synthesis were performed at room temperature and under ambient conditions [15]. The chemicals used for these experiments were Zn $(CH_3COO)_2.2H_2O$, Mn $(CH_3COO)_2.4H_2O$, $Na_2S.9H_2O$, Histidine. In a typical experiment 0.1M Zinc acetate and 0.1M Manganese acetate was mixed in 50 ml of ethanol to 0.1% histidine solution to which 0.1M Sodium sulphide was added dropwise to form histidine capped ZnS nanoparticles and finally washed and dried in oven at 40^0C. Here we introduce a novel biocompatible passivation layer "histidine" on the nanophosphors, which shows interesting enhancement in the luminescence efficiency. These histidine coated ZnS: Mn nanoparticles can have

applications as phosphors for display applications. Morphologies and sizes of the final products were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 30^0-80^0 with a step interval of 0.02^0 at room temperature. The photoluminescence and photoluminescence excitations were studied by 225nm radiation from He-Cd laser at room temperature. Particle size distribution is carried out by Small angle X-ray scattering studies in the range of (0.02-5 degree using Cu-Kα radiation). All measurements were done at room temperature.

Results and Discussion

Characterization of ZnS doped with Mn nanoparticles were done by XRD based on Debye Scherrer's formulae, the average particle size are in the order of 4-6nm. (Fig.1)

Average crystallite size calculated by Debye Scherrer formula are of the order of 5-6nm for the sample as prepared by wet chemical route. Small angle X-ray (SAXS) studies on the prepared material shows the maximum uniform particle size distribution of 3.5nm [16]. Quantum size effects are mainly determined by the cluster size, and the cluster size depending on the cluster growth conditions such as the distribution of groups in the polymer molecule, the reaction time between Zinc-acetate and sodium sulphide, the concentration of Zinc-acetate and sodium sulphide solution and the reaction temperature.

Optical properties like photoluminescence (PL) and photoluminescence excitation (PLE) for ZnS: Mn is compared with capping agent. Subsequent transfer of electron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn^{2+} in ZnS [17]. Fig (2) shows the room temperature photoluminescence studies, the broad and intense peak at ~593nm and the emission at ~ 421 nm is typical luminescence of undoped ZnS resulting from the transition of electrons from shallow states near the conduction band to sulfur vacancies present near the valence band.

In PL spectra there is no different in intensity while there is a shift in heated ZnS:Mn capped with histidine.

Conclusion

One of the foremost challenges in device technology is in distributing nanoparticles uniformly of precise control can be processed by using histidine as one of the capping agent and might be a good capping agent for band gap engineering. The room temperature photoluminescence (PL) and photoluminescence excitation (PLE) shows a broad and intense peak, but the annealing of the same degraded the PL and PLE intensities by several orders. Size determined from structural and the optical studies

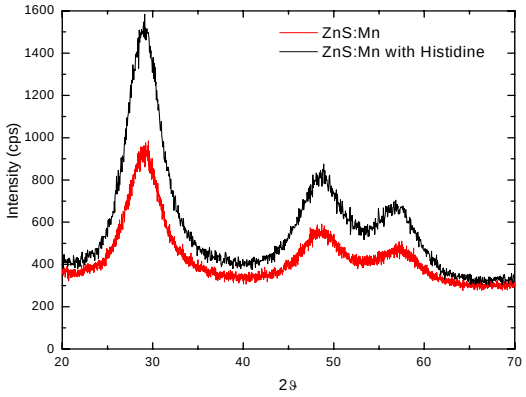

Figure 1. XRD scan of Histidine capped ZnS:Mn.The crystallite size is estimated to be 5-10 nm from Debye-Scherrer formula

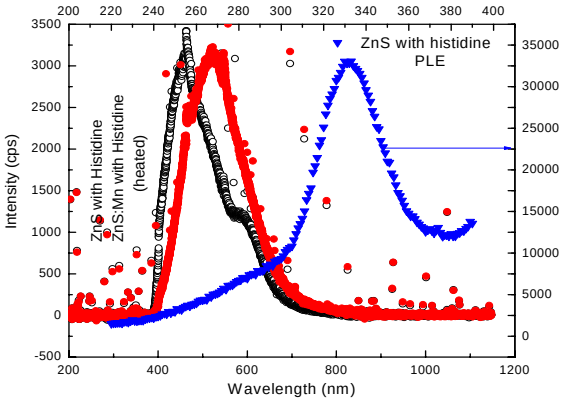

Figure 2. PL spectra of ZnS,ZnS:Mn capped with Histidine

matches' well with in agreement. There is a further need to study in order to stabilize the nanoparticles.

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