

Photoluminescence of ZnS:Cu nanoparticles in PVA matrix Sakshi Sahare and Meera Ramrakhiani

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Abstract

The ZnS:Cu nanocomposites were prepared by using chemical deposition technique and characterized by XRD and absorption spectra. The estimated size of ZnS:Cu/PVA nanocomposites are 3 to 7nm by absorption spectra and XRD. No effect of doping has been observed on the absorption spectra. Photoluminescence spectra are reported in this paper.

Keywords:- Copper doped zinc sulphide, polyvinyl alcohol (PVA), absorption spectra, Photoluminescence.

1.0 Introduction

Quantum dots or nanostructures having sizes comparable that of the bulk Bohr exciton radius [1-2] exhibit discrete electron energy levels with large oscillator strength and strong luminescence. These systems have a very high surface to volume ratio and hence surface defects play an important role in their characteristics. A poorly passivated surface of a quantum dot characterized by the presence of electron or hole traps, play a significant role in the luminescence properties. It is therefore essential to carefully control the surface defects along with the size of a quantum dot in order to obtain the desired radiative properties.

Doped ZnS semiconductor material also has a wide range of applications in electroluminescence devices; TV phosphors and optical sensors. Type and concentration of dopants play key roles in luminescence efficiency and the position of emission bands of semiconductor nanoparticles [3]. Recently quantum dots are being explored as alternative emissive materials in view of their efficient, stable, and tunable emission from the doped transition-metal ions [4-8]. Among this category, doping of Mn in ZnS is widely studied and reported. Many groups have synthesized Mn doped ZnS by different approaches and used them as candidates for many applications such as electroluminescence devices [9], field emission displays [10], and sensors [11, 12]. Thus considering their practical applications, it is very important to investigate how the dopant concentration affects optical property of semiconductor nanoparticles from the viewpoints of understanding trapping and recombination process and applications. ZnS:Cu was the first formulation successfully displaying electroluminescence, tested in 1936 by Georges Destriau in Madame Marie Curie laboratories in Paris. The band gap of the nanoparticles increases with increasing

copper concentrations. Green, blue and violet emission band located at 420 - 510 nm was observed by UV excitation of the ZnS host. Cu²⁺ ions in the lattice act as luminescent center [13].

Luminescence of II-VI materials has been, and still is, an extremely active area of research. ZnS is promising host material for development of phosphors in different visible emission bands. Transition metal or rare earth doped zinc sulfide (ZnS) crystals have been used as phosphors for a long time. Photoluminescence (PL) of bulk and nanocrystalline ZnS is given special attention due to its potential technological applications. Photoluminescence can also be very effectively used to determine the size dependent electronic structure.

The main objective of the present work is to investigate the photoluminescence properties of ZnS:Cu/PVA composite by varying size of nanocrystals. The experimental work consists of preparation of five different ZnS:Cu/PVA nanocomposites by chemical route. The samples are characterized by X-Ray diffraction (XRD) and UV-Vis optical absorption and study their photoluminescence.

2.0 Experimental Technique

Nanostuctures of copper doped zinc sulfide have been synthesized and characterized by XRD, absorption and luminescence investigations. All the samples were prepared by chemical route. In all the samples, the Cu doping was kept at the level of 0.01% because it is found to show maximum luminescence [14]. For the synthesis of composite films, 400 mg poly vinyl alcohol (PVA) was dissolved in dimethylformamide (DMF) by constant stirring and heating at 70°C. Zinc acetate was added to it in appropriate quantity. For doping 0.01% copper acetate was mixed in the initial solution. The resulting solution was



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stirred for 30 minutes. The solution was refluxed by applying nitrogen and then H₂S gas was passed for 30 second. The solution immediately turned milky white. Now again the solution was stirred for a few seconds, then caste over glass slides and dried to obtain uniform film of ZnS:Cu/PVA nanocomposite [15-16]. Five different samples ZnS:Cu-1, ZnS:Cu-2, ZnS:Cu-3, ZnS:Cu-4, and ZnS:Cu-5 were prepared by varying loading percentage of ZnS:Cu as 5, 10, 20, 30 and 40 % by weight, respectively. structures and regularity The crystal of atomic arrangements in all the samples were studied by X-ray diffraction technique using Rigaku Rorating Anode (H-3R) diffractometer at UGC-DAE Consortium for Scientific Research Indore. The UV-Vis absorption studies were carried out by Perkin Elimer, Lambda-12 spectrometer in the range 200-600 nm. The photoluminescence spectra of ZnS:Cu were recorded with F-7000 fluorophotometer. The PL was excited with 212 nm from a UV lamp and the PL spectra ZnS:Cu nanocomposites in PVA matrix have been studied in the range of 300 nm - 600 nm.

3.0 Result and Discussion

The samples of ZnS:Cu/PVA nanocomposites were prepared as films on glass slides. Figures 1 show the XRD patterns of ZnS:Cu/PVA nanocomposites. In case of nanocompsites the peaks due to ZnS are superimposed over the pattern due to PVA with major peak at ~ 28° (2 θ).



Fig. 1: X-Ray Diffraction Patterns of ZnS:Cu/PVA nanocomposites

The particle size of ZnS:Cu in nanocomposites are obtained in the range of 5 nm to 3 nm. It can be seen that the crystalline size decreases with increasing capping agent or loading percentage.

3.1 Absorption spectra:

The optical absorption spectra of samples are shown in figure 2. It can be seen from the spectra that there is

practically uniform absorption in the visible range (800 nm-390 nm). Absorption increases suddenly in the UV region. No absorption peaks are found. The gradual shift in absorption edge to the shorter wavelength side (blue shift) indicates increased band gap with reducing particle size because of quantum confinement effects.



Fig 2 Optical absorption spectraofZnS:Cu/PVAnanocomposite

It is observed that in the ZnS:Cu nanocomposites the particle size is reduced by increasing loading percentage of zinc sulfide.

3.2 Photouminescence:

ZnS:Cu is well known luminescent materials having a band gap of 3.68 eV at 300K. This correspond to ultraviolet (UV) radiation for optical interband transition with a wavelength of 335 nm.

Luminescence studies provide information regarding defect states, which take part in radiative de-excitation of samples. In nanocrystals the defect states may shift or their density may change which is revealed in luminescence studies.



Fig 3 Photoluminescence spectra of ZnS:Cu/PVA nanocomposites



In present studies the PL was excited by 212 nm. Photoluminescence spectra ranging from 400 nm to about 500 nm were measured at room temperature (300 K) for the nanocrystalline samples are shown in figures 3. In all samples single peak was obtained. The ZnS:Cu/PVA nanocomposites show broad emission peaked at 415 nm. It is seen that with an optimum Cu doping of 0.01%, the PL intensity increases with increasing capping agent concentration or loading % of ZnS:Cu, indicating that the dangling bonds are better passivated with higher loading of ZnS:Cu, which also reduces the size of ZnS:Cu nanoparticles.

Peng et al [17] have also reported PL of undoped ZnS nanoparticles with a peak at about 415 nm which, after deconvolution, indicates two peaks at 411 and 455 nm. The PL peak at 410 nm has been known due to the recombination between the sulfur-vacancy-related donor and the valance band [18] and the peak position of this blue emission does not change with the increase of the low concentration of Cu⁺⁺ but for higher concentration above 0.5% the peak shifts towards longer wavelength. Jayanthi et al [19] have also reported the same thing when lower concentration of Cu in ZnS is increased. The intensity of PL peak at particular concentration of Cu (0.01%) is maximum and further, the overall PL, intensity decreased at the higher Cu^{++} concentration of 0.1%. The concentration quenching of the luminescence may be caused by the formation of CuS compound. Similar results are obtained in our earlier work for electroluminescence [14]. It can be explained by the effect of doping. As explained above, these two peaks are related with native defects (e.g. sulfur vacancy). When Cu⁺⁺ ions are doped into ZnS nanoparticles, more defect states will be introduced. Therefore, it is reasonable that these two defect-related peak intensities are enhanced for the doped samples compared with the undoped samples.

4.0 Conclusions

The studies have shown that smaller size ZnS:Cu nanocomposites with PVA matrix can be prepared by increasing loading percentage of ZnS:Cu. X-ray diffraction (XRD) has revealed cubic zinc blend structure of ZnS:Cu nanocrystals of size below 20 nm. Optical absorption spectra show blue shift in the absorption edge indicating increase in effective band

gap due to quantum size effect. The PL spectra of ZnS:Cu/ PVA nanocomposite films show quite broad emission peak at 415 nm

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