ZnS nanocomposite nanorods prepared by simple method of chemical bath deposition

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ABSTRACT

ZnS nanocomposite nanorods have been prepared by chemical bath deposition technique taking Zinc acetate and Sodium sulphide as the source of Zinc and Sulphur respectively. The composite thin film is characterized by XRD, TEM, UV-Visible, PL and FTIR. Nanocrystalline thin film prepared under optimum growth condition shows band gap of 3.7eV as observed from optical absorption data. XRD shows peaks at 2θ values of 28.50°, 47.58° and 56.39° for (111), (220), and (311) planes respectively. TEM micrograph of the film reveals the formation of ZnS nanorods of diameter ranging from 15nm to 20nm and length from 20nm to 220nm. Along with the rods there are some quasispherical small clusters also. Photoluminescence (PL) measurement showed blue emission centered at 413.5nm and green emission at 561nm.
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INTRODUCTION

During the recent decade, much attention has been focused on the preparation of one- dimensional (1D) nanostructures, such as nanorods[1], nanowires[2], nanobelts[3] and nanotubes[4] because they exhibit physical and chemical properties different from their bulk counterparts and also from those of two-dimensional (2D) and three-dimensional (3D) structures. The growth of special shaped nanostructures in a controllable manner is a critical issue in nanoscience. Zinc Sulphide (ZnS) is an important II-VI semiconductor. It has a wide band gap of 3.6eV at 300K in its bulk form[5]. It is one of the most important semiconductor material used in electronics industry. Also, it has other variety of applica-

tions covering electroluminescence, nonlinear optical devices, light emitting diodes, flat panel displays, IR windows, sensors and lasers etc[6]. ZnS forms two structural polymorphs, hexagonal wurtzite and cubic sphalerite. Controlled and reproducible growth of one-dimensional nanostructures has been achieved by various synthetic methods[7-9]. The methods utilized are mostly sol-gel, sonochemical, using surfactant/micelle etc. To the best of our knowledge, chemical bath deposition (CBD) method is not used for the fabrication of ZnS nanorod. In this communication, we report the success of synthesizing ZnS nanorods by this simple and inexpensive technique of CBD and alongwith we report its properties as revealed by various studies, viz, XRD, TEM, UV-Visible absorption, PL and FTIR.

EXPERIMENTAL SECTION

Materials used for the present study are Zinc acetate[$Zn(CH_3COO)_2$] as Zinc source, Sodium Sulphide (Na_2S) as Sulphur Source, Polyvinyl alcohol (PVA) as capping agent and dispersing agent, NH_3 as reducing agent and deionized water as medium. All the reagents and solvents are purchased from E. Merck, Ranbaxy Fine Chemicals Ltd., LOBA Chemie and Merck respectively and used as received. To prepare nanocomposite ZnS films, $1.33x10^{-5}$ mol (0.9985gm) PVA is stirred in 75ml distilled water at 70°c for one and half an hour with temperature controlled magnetic stirrer. Then the solution is left to itself for 2hrs. After ageing this solution for 2hrs, as prepared Zinc acetate solution (0.005mol or 1.0974 gm in 5ml NH_3) is mixed to it. Next a solution prepared by taking 0.01mol (0.7804gm) Na_2S in 25ml distilled water is added to the above solution. The resulting mixture is heated at 100°c under continuous stirring for 20 minutes. NH_3 is used as complexing agent. The pH of the resultant solution is maintained at 10.5. After 20 minutes clean glass substrates are used for the deposition of the films.

Crystallinity of the ZnS-PVA nanocomposite film is confirmed using X-ray Diffractrometer (Philips X-pert prodiffraction, PW 1830 with Cukα 1.54A°). The morphology of the products is observed using Transmission electron microscope (JEM 100 CXII, JEOL. JAPAN) (Accelerating voltage 100KV), Optical absorption spectra at 300K are obtained using UV visible spectrometer (Hitachi U-3210 spectrometer). Photoluminescence spectra are recorded on (Hitachi, F-2500, and Fluorescence spectrophotometer). An IR spectrum is recorded on Perkin Elmer Spectrum RXI FTIR system.

RESULTS AND DISCUSSION

XRD study

In figure 1 we show the XRD pattern of the composite film on glass subtract. This clearly shows the peaks at 2θ value of 28.50°, 47.58° and 56.39° corresponding to the planes of (111), (220) and (311) respectively[10].
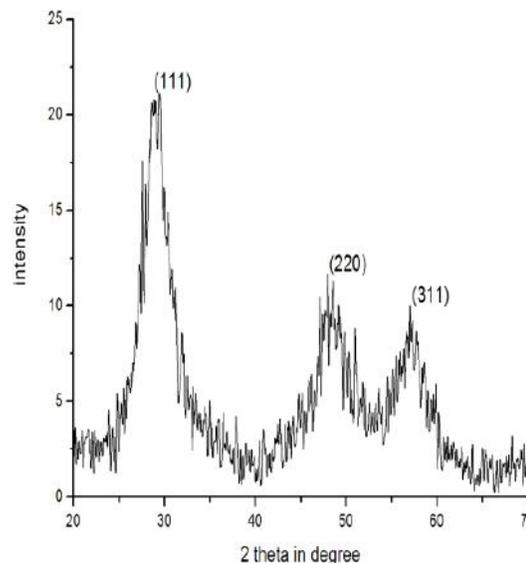
Figure 1 : XRD pattern of ZnS nanocomposite thin film

TEM study

In figure 2 we show the HRTEM micrographs of the composite film coated on borax grid. This shows straight but non uniform and randomly distributed rods. Their diameter lying in the range of 15-20 nm and the length 20-220nm. Also alongwith these prominent rods there are some stray quasispherical clusters of much small dimension around. Nevertheless in the few rods present the aspect ratio is substantially high (nearing a maximum value of ~20) compared to that obtained by some earlier groups by different processes[11,12].

Figure 2 : HRTEM micrograph of ZnS nanocomposite nanorods.

UV-Visible study

The optical property of the composite film is determined from the UV-Visible absorbance measurement. Figure 3 (a) shows the absorption spectra of the composite thin film. This shows appreciable absorption of the composite film in the wavelength range of 230-

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350nm[13]. Transmittance plot is shown in figure 3 (b). From this we determine the bandgap for direct transition using the relation[14]

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \qquad (1)$$

Where A is a constant, E_g is the band gap of the material and the exponent n depends on the type of the transition.
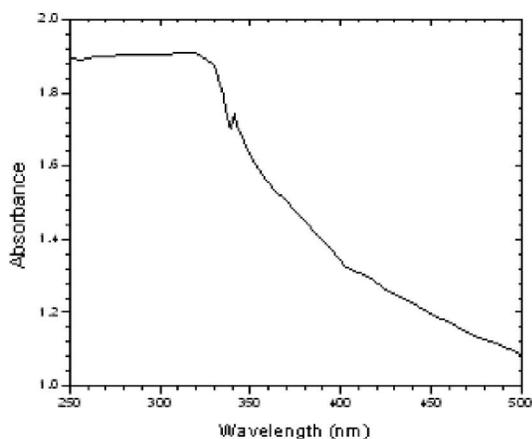
Figure 3(a) : Absorption vs. wavelength plot of ZnS nanocomposite film
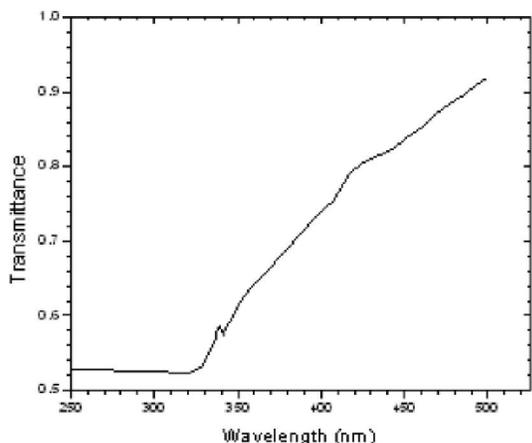
Figure 3(b) : Transmittance vs. wavelength plot of ZnS nanocomposite film

From transmission data absorption co-efficient (α) can be calculated by the relation

$$\alpha = \frac{1}{d}\ln(1/T) \qquad (2)$$

Where d is the thickness of the films which is 1800A^O for the present case. The value of the optical band gap is found by extrapolating the straight line portion of ($\alpha h\upsilon$)^2 vs. hυ graph to hυ axis as shown in Figure 3(c). The direct band gap is found to be 3.7eV, which is

higher than the bulk value of ZnS (3.6eV), which is conventionally ascribed to quantum confinement in the ZnS nanocrystallites[15].
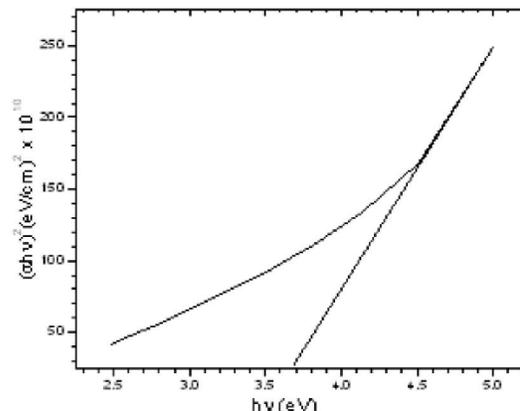
Figure 3(c) : Plot to determine the direct bandgap of ZnS the nanocomposite thin film.

Photolumilescence study

In figure 4 we show the PL spectra of the composite film taken at 300K for excitation wavelength of 280nm. This shows a broad peak centered at 413.5 nm with hump at 344 nm and a very sharp peak centered at 561 nm. The hump at 344 nm is believed to be due to the small sized quasispherical cluster (<10nm) formed in ZnS[1]. The presence of such cluster is evident from TEM picture. The broad peak at 413.5 nm is due to small sized particles in association with trap, defect or vacancy related emission[16]. The sharp peak at 561 nm may be assigned to be due to emission from the rod shaped clusters for excitation beam falling in the direction of length of rod[7].
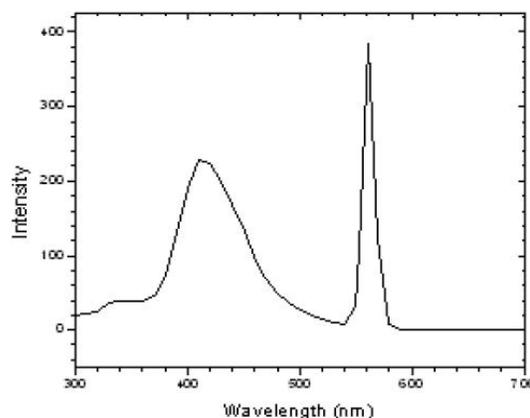
Figure 4 : PL spectrum of ZnS nanorod.

FTIR study

FTIR spectrum of the composite thin film is shown

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in figure 5. This shows peaks at 1655.8 cm⁻¹ for N-O interaction. Bands around 900-1500 cm⁻¹ are due to O-H stretching and bending frequency. Weak additional bands are observed at 925.9 and 846.4 cm⁻¹. These modes indicate the presence of resonance interaction between vibrational modes of sulphide ions in the crystal[17]. The peak at 625.7 cm⁻¹ is assigned to ZnS band (i.e. corresponding to sulphides).
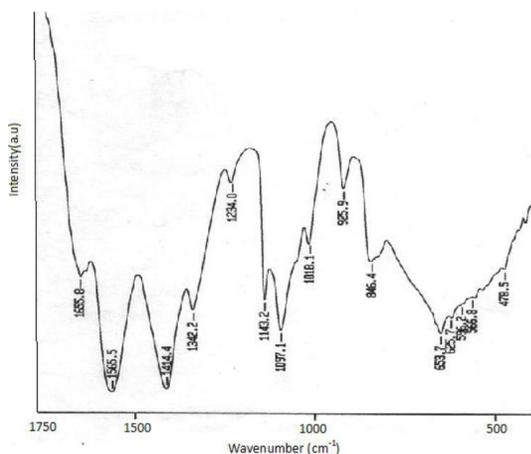
Figure 5 : FTIR spectrum of ZnS nanocomposite nanorod.

CONCLUSION

ZnS nanorods have been prepared successfully by simple method of chemical bath deposition . Bandgap for direct optical transition is found to be 3.7 eV. These nanorods show very sharp green emission along with a broad blue emission. IR spectra give the indication of presence of sulphide species and interlinking with PVA.

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