SYNTHESIS AND PHOTOOLUMINESCENCE STUDIES OF ZnS/PVK NANOCOMPOSITES

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Abstract

ZnS/PVK nanocomposites have been successfully prepared by chemical method. The optical and electrical properties of nanomaterials can be controlled by their particle size and therefore attracted much interest for their fundamental and applied aspects. The size of the particle was varied with different ZnS loading. The XRD pattern showed that the ZnS nanoparticles has zinc blend structure and line broadening suggests the formation of amorphous compound. The broadening of peaks tends to increase with decreasing ZnS loading showing decrease in particle size. The crystalline size is found to be in range of 04 to 11 nm. Absorption measurements reveals blue shifting of absorption edge from bulk ZnS. The photoluminescence properties of ZnS/PVK show the PL intensity is increase with increasing ZnS loading with PVK.

Keywords: - XRD, absorption spectra, photoluminescence, ZnS, PVK.

1. INTRODUCTION: Poly N-vinyl carbazole (PVK) is a hole transport organic semiconducting polymer. It has been widely used as an electronic and optical material. ZnS is a well known inorganic and wide band semiconductor that has been a subject of considerable research due to its potential application in the areas of spin-electronics, optoelectronics, sensors, photocatalyst etc [1-4].

Previously, the nano composite ZnS/PVK was prepared simply by mixing PVK and ZnS nano cluster or their precursors were prepared by simply mixing the synthesized nanoparticles with polymer. The effect of the inevitably introduced precursor molecules or the synthesized semiconductor nanoparticles is not clear to date, further more the conventionally synthesized semiconductor nanoparticles have a tendency to aggregate into larger clusters and their fine dispersion in the polymer is not very easy. Wang et al [5-7] has made a new approach for the preparation of truly two components ZnS/PVK nanocomposite. Khanna et al [8] have reported that the careful preparation of ZnS/CdS nanoparticles in DMF with metal rich surface can be considered responsible for stable light emission. This desire has promoted us to extend the synthetic methodology to functionalized and non- functionalized polymers. Polymers are considered a good choice as matrix materials for such purpose due to their long time stability and because they possess flexible reprocessibility.

Present studies have been undertaken to synthesize ZnS/PVK nanocomposite with various loading of ZnS, characterize them by XRD, absorption spectra and investigate their photoluminescence.

2. EXPERIMENTAL: For the synthesis of nanocomposite ZnS/PVK films, 400 mg. of poly N-vinyl carbazole (PVK) was dissolved in dimethylformaldehyde (DMF) by constant stirring and heating at 80°C temperature. Zinc acetate was added to the solution as 10, 20, 30 40 and 50% weight of PVK, so that ZnS loading in polymer equivalent weight. The resulting solution was stirred for 30 minutes. The solution was refluxed by applying nitrogen and then H₂S gased for a 30 second. The solution immediately turned milky white. Now again the solution was stirred for a few seconds. The chemical reaction as follows:

PVK + Zn(CH₃COO)₂ + H₂S → ZnS/PVK + 2CH₃ COOH
Then the solutions were cast over glass slides and dried in an oven for several hours to obtain uniform film of ZnS/PVK nanocomposite. The samples were characterized by using Bruker D8 advance X-Ray diffractometer at IUC Indore. Optical absorption studies were performed by Perkin Elemer spectrometer. In the photoluminescence study, the excitation wavelength of ZnS/PVK was observed at 370 nm and 425 nm by the photospectrometer (at MANIT Bhopal).

3. RESULTS AND DISCUSSION: Fig 1 shows that the XRD peaks at 20 values of 28.91°, 48.11° & 57.10° matching the (111), (220) and (311) crystalline planes of cubic or zinc blende structure, indicated the formation of ZnS. The broad nature of the XRD peaks could be attributed to the nanocrystalline nature of the ZnS particle. The Debye–Scherrer formula is used to approximately estimate the size of the nanoparticles [5-7]. According to the calculation the ZnS nanoparticle size for 10, 20, 30, 40, & 50% loading of Zinc acetate are found to be in range of 04 to 11 nm.

Fig-2 shows absorption spectra of ZnS/PVK thin film. The absorption peaks are found at 236, 296, 311, 327, 330 and 342 nm corresponding to 0, 10, 20, 30, 40 & 50% loading of Zinc acetate. Therefore there is an increased energy gap as compared to bulk material. Absorption spectra shows the shifting of edge towards shorter wavelength with decreased ZnS loading. This indicates increased effective band gap and reduced particle size. The increase in the effective band gap of nanoparticles calculated by using effective mass approximation model. The band- gap are obtaining 4.1, 3.9, 3.79, 3.75, 3.62, eV for 10, 20, 30, 40, & 50% loadings of Zinc acetate.

Fig 2 Absorption spectra of ZnS/PVK

Fig 3 shows the photoluminescence studies of ZnS/PVK nanocomposites for 10, 20, 30, 40 and 50% loading of ZnS in PVK, by exciting the sample with 370 nm wavelength the emission peak observed at 435, 439, 446, 448 and 450 nm. The sample was also excited by the wavelength 425 nm then the emission wavelength peak observed at 470, 472, 472.5, 473 and 474 nm. It is quite evident that PL intensity and PL peak are found to increase by increasing the loading concentration of ZnS in PVK. Single state shifted PL peak indicates sulphur ion (S²⁻) energy shifted in the band-gap and PL emission occurs due to transition from sulphur ion state to valence band. For smaller particles, valence band shift down word which causes shifting of PL peak towards lower wavelength.

Fig 3: Photo- luminescence spectra of ZnS/PVK
4. CONCLUSION: The ZnS/PVK composite has been prepared by chemical method. The XRD studies have indicated that in the ZnS/PVK composites, ZnS particles are of nanometer size. The size of nanoparticle is found to increase by increasing the concentration of ZnS in the composites. The absorption spectra show blue shift and increase the energy band-gap by increasing the loading concentration of ZnS. In the photoluminescence study, the excitation wavelength of synthesized ZnS/PVK composite was observed at 370 nm and 425 nm, in different concentration of the samples with different emission wavelengths.

5. ACKNOWLEDGMENT: We would like to acknowledge prof. A. Gupta, Director and Prof. V. Ganeshan, Scientist from UGC-DAE, INDORE and MANIT, Bhopal for providing facilities for XRD and PL characterization.

6. REFERENCES:


<table>
<thead>
<tr>
<th>Different loading of ZnS in PVK</th>
<th>Particle size (nm)</th>
<th>Band gap (eV)</th>
<th>PL Emission peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>4.8 nm</td>
<td>4.1eV</td>
<td>470nm</td>
</tr>
<tr>
<td>20%</td>
<td>5.2 nm</td>
<td>3.9eV</td>
<td>472nm</td>
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<tr>
<td>30%</td>
<td>7.8 nm</td>
<td>3.79eV</td>
<td>472.5nm</td>
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<tr>
<td>40%</td>
<td>8.6 nm</td>
<td>3.75eV</td>
<td>473nm</td>
</tr>
<tr>
<td>50%</td>
<td>10.6nm</td>
<td>3.62eV</td>
<td>474nm</td>
</tr>
</tbody>
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Table 1- Show the result from XRD, Absorption and PL spectra