Investigation of Structural, Optical and Electrical Performance of ZnS Sensitized PMMA Nanocomposite as an Emissive Layer for OLED Application

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Abstract. Pristine PMMA and PMMA-ZnS nanocomposites were synthesized via free radical polymerization process. The formation of the PMMA matrix and its nanocomposite were confirmed by X-ray diffraction technique (XRD) analysis. The FESEM and TEM image of PMMA-ZnS nanocomposites showed the mixture of pebbled and spherical ball-like structure. Increase rate of electron-hole recombination of PMMA-ZnS nanocomposites was studied from PL spectra. The PL spectra of nanocomposite showed four bands attribute to the blue-violet band, blue band, green band and yellow band. The color coordinate of PMMA-ZnS nanocomposite was found to be in the blue region. The electrical properties showed the good conductive response in PMMA-ZnS nanocomposite. These optical and electrical properties confirmed that the proposed PMMA-ZnS nanocomposite can be used for OLED application as emissive layer.

INTRODUCTION

Organic optoelectronic devices like organic light emitting diodes (OLEDs), organic phototransistors, organic photo detectors, organic solar cells etc. became the more prominent area of the current research [1]. OLEDs are attracted due to the promising application in compact cameras, laptop computers, monitors, TVs, car displays and public displays. OLEDs have attracted much more attention in research area due to the unique properties of lightweight, flexible, color tunable ability, transparent, a wide viewing angle display and cost-effective [2]. OLED is comprised of multilayer structure as an anode, electron transport layer (ETL), emissive layer (EL), hole transport layer (HTL) and cathode [3-4]. OLEDs works with the mechanism of electron-hole recombination which produces exciton in the form of light at the emissive layer [5,6]. Light emits mechanism in emissive layer is occurred due to the recombination of electron and hole, where electron transform from the cathode with the help of electron transport layer and hole transform from anode with the help of hole transport layer.

In the last few decades, to increase the efficiency, cost effectiveness and stability of OLEDs, researcher has introduced organic-inorganic composites materials. Polymers like polyethylene, polypyrrole, polymethyl methacrylate (PMMA), polyindole etc. is shown good characters in optoelectronics research area. PMMA has been extensively used in opto electronic application due to its transparency in nature, effective optical as well as electrical properties [7]. It also shows good thermal and chemical stability [8]. Semiconducting nanoparticles like ZnO, ZnS, CdS, and TiO\textsubscript{2} etc. can be impinged into the PMMA matrix to enhance the optical and electrical properties. Zinc sulfide (ZnS) nanoparticles are one of the most typical and important II–VI compound semiconductors with a wide direct band gap [9]. ZnS nanoparticles have been gaining extensive attention for their luminescence properties, high refractive index, and low absorption coefficient in the visible and near IR region, and good dielectric properties that can be applied for optical application [10]. PMMA and ZnS can be combined to access the optical properties of both
organic and inorganic materials. The present communication reports the structural, optical and electrical properties of PMMA-ZnS nanocomposite.

EXPERIMENTAL

Synthesis of PMMA-ZnS

PMMA-ZnS nanocomposite was synthesized via free radical polymerization method. Firstly, 0.10 gm. of polyvinyl alcohol (PVA) was dissolved in 40 ml of DI water. Then 4 ml of methyl methacrylate (MMA) monomer was added into the well-dispersed solution. After 1 h, 15% ZnS nanoparticle was added to the stock solution. Thereafter, 0.10 gm. of sodium phosphate and 0.30 gm. of benzyl peroxide (BPO) was added to the solution to initiate the reaction. To avoid evaporation of solvents, the entire setup was fitted with the condenser for a water bath and it was maintained at 80 °C for 28 hrs. The curdy white precipitate was obtained. Then the precipitate was washed with double distilled water and ethanol several times to avoided moisture and unreacted monomer. Further, the precipitate was dried at 60 °C in the vacuum oven for 24 hrs and was preserved.

RESULTS AND DISCUSSION

XRD and Surface Morphology

![Figure 1](image1)

**FIGURE 1:** (i) XRD pattern of (a) Pristine PMMA (b) ZnS (c) PMMA-(15%) ZnS nanocomposite, (ii) FESEM images of (a) pristine PMMA (b) ZnS and (c) PMMA-(15%) ZnS nanocomposite, and (d) TEM image of PMMA-(15%) ZnS nanocomposite.

XRD spectra for pristine PMMA, ZnS, and PMMA-(15%) ZnS nanocomposite showed in figure 1 (i). The XRD spectra of pristine PMMA represented three large humps located at 14.8°, 29.91°, 42.33°. The characteristic peaks of ZnS indexed to the hexagonal structure with a lattice constant a = 3.8210 Å and c = 6.2573 Å matched well with the JCPDS database (card no- 00-036-1450). The characteristic diffraction peaks confirmed the formation of PMMA-(15%) ZnS nanocomposites and it showed semi-crystalline behavior. Debye Scherrer’s formula \( D = \frac{N \lambda}{\beta \cos \theta} \) used for the calculation of crystallite size. Where D is the crystallite size, N is the Scherrer’s constant (0.9), \( \lambda \) is the wavelength of X-ray (1.5416Å), \( \beta \) is the line broadening at half the maxima intensity (FWHM) and \( \theta \) is the Bragg angle. The average crystallite size of PMMA-(15%) ZnS was around 43 nm.

The surface morphology of pristine PMMA, ZnS and PMMA-(15%) ZnS nanocomposites showed in fig (ii). Figure ii(a) showed FESEM image of pristine PMMA and it showed spherical in nature. The surface topology of ZnS showed the mixture of pebbled like structure in figure ii(b). Figure ii(c) showed the surface morphology of
PMMA-(15%) ZnS nanocomposite. Addition of ZnS nanoparticles into PMMA matrix exhibited the mixture of pebbled and spherical ball like structure that caused aggregation in the polymer chain.

An in-depth nanostructured topology of the as-synthesized PMMA-(15%) ZnS nanocomposite was characterized by transmission electron microscopy (TEM). Figure ii(d) showed the TEM image of PMMA-(15%) ZnS nanocomposite. The TEM image of composites was in good agreement with the FESEM image. The TEM image of composite showed that low dense PMMA capping over the dense ZnS nanoparticles.

**Optical properties**

The PL spectra of as-synthesized pristine ZnS and PMMA-(15%) ZnS nanocomposite that duly excited by 280 nm have been shown in figure 2(a). The emission spectra of nanocomposite was similar to the pristine ZnS. The PL spectra of nanocomposite was observed at ~ 452 nm, ~ 475 nm, ~ 496 nm, ~ 520 nm, and ~ 535 nm. The PL peaks were observed under the blue-violet band, blue band, green band and yellow band due to the recombination between the sulfur vacancy related donor and the valence band, surface stacking defects and self-trapped excitons respectively. The emission intensity was increased in the nanocomposite due to the increased rate of electron-hole recombination.

![FIGURE 2](a) Photoluminescence spectra of pristine ZnS and PMMA-(15%) ZnS nanocomposite, (b) CIE diagram for pristine ZnS and PMMA-(15%) ZnS nanocomposite.

Commission International de l’Eclairage (CIE) system was used to evaluate the color coordinates (x-y) and color purity (CP). The color coordinate for pristine ZnS nanoparticles and PMMA-(15%) ZnS nanocomposite were calculated by using GoCIE software and it has been shown in figure 2(b). The color purity was calculated using the following relation:

$$C_p = \frac{\sqrt{(a_x-a_i)^2 + (b_x-b_i)^2}}{\sqrt{(a_y-a_i)^2 + (b_y-b_i)^2}} \times 100\%$$

(1)

Where \((a_x, b_x)\) coordinates of the substrate, \((a_i, b_i)\) coordinates of reference white illuminate point and \((a_y, b_y)\) coordinates of the dominant wavelength. For the PMMA–ZnS nanocomposite, \((a_x, b_x) = (0.200, 0.210), (a_i, b_i) = (0.310, 0.316)\) (CIE-C), \((a_y, b_y) = (0.09, 0.137)\) for the dominant wavelength at 475 nm. Color purity for the PMMA–ZnS nanocomposite was calculated ~ 60%.

**Electrical properties**

The current-voltage (I-V) characteristic of pristine ZnS and PMMA-(15%) ZnS were measured at room temperature in the potential range -10.0 to +10.0 V as shown in Figure 3. The results were showed the ohmic behavior. The incorporation of ZnS nanoparticles into the PMMA matrix enhanced the current density. The increase in
conductance with the addition of ZnS nanoparticles was attributed to the enhancement in the mobility of electrons due to the extension of the polymer chain. The higher conductivity and increased rate of electron-hole recombination confirmed that PMMA-ZnS nanocomposite could be used as an emissive layer in OLED devices.

**FIGURE 3.** J-V characteristics for ZnS and PMMA-(15%) ZnS nanocomposite.

**CONCLUSION**

PMMA–ZnS nanocomposite was synthesized via free radical polymerization process. Their structural, optical and electrical properties were investigated. The FESEM and TEM images showed the mixture of pebble and spherical ball like structure. The XRD spectra confirmed the formation of PMMA-ZnS nanocomposite. The PL spectrum showed the increased rate of electron-hole recombination. The dominant peak of nanocomposite showed at ~475 nm which was attributed to the blue band. The color coordinate of PMMA-ZnS nanocomposite was calculated by the CIE diagram and observed to be in the blue region with color purity ~60%. The electrical properties showed better enhanced current density as compared to pristine ZnS. These optical and electrical properties led to justify that the PMMA-ZnS nanocomposite could be used as emissive layer material in OLED application.

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**REFERENCES**