

Research Article

Investigation on the Optical and Surface Morphology of Conjugated Polymer MEH-PPV:ZnO Nanocomposite Thin Films

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Thin films of red color poly(2-methoxy-5(2'-ethylhexyloxy)-phenylene vinylene) (MEH-PPV) containing different weight percent of ZnO nanoparticles were obtained by spin-coating techniques. The MEH-PPV:ZnO solutions were spin coated onto silicon and glass substrates. The spun MEH-PPV:ZnO thin films were then used to investigate optical properties by using ultraviolet-visible spectrometer (UV-Vis) and photoluminescence spectrophotometer (PL). The morphologies were investigated by using field emission scanning electron microscopy (FESEM), while the identification of ZnO in the final product was determined by using energy-dispersive X-ray spectroscopy (EDS). The UV-Vis absorption band increases, while the optical bandgap decreases when the amount of ZnO nanoparticles increases. ZnO nanoparticles apparently have no effect on the conjugation segments of MEH-PPV. PL spectra show that the emission peak increases and slightly red shift as ZnO concentration increases. Based on SEM images of MEH-PPV:ZnO nanocomposite thin films, ZnO nanoparticles form agglomerated regions.

1. Introduction

Recently, the preparation of polymer-inorganic composite has been increasingly studied due to the novel synergy effects as well as enhanced optical and electronic properties. Previous studies have reported on polymer-inorganic solar cells using CdSe [1], TiO₂ [2], SiO₂ [3], and ZnO nanoparticles [4]. The composites have good effects on optical, electronic properties [5] and also improve the stability [6] which is important in organic devices. The effects of the nanoparticles on the structure and optical properties of the polymer are still a subject of research. Baraton et al. reported that blends using TiO₂ nanoparticles do not break the PPV, conjugation lengths [7]. Yang et al. observed that SiO₂ nanoparticles would reduce the conjugation lengths of PPV and this reduction becomes significantly important as the content of SiO₂ increases [8].

Conducting unsaturated poly(2-methoxy-5(2'-ethylhexyloxy)-phenylene vinylene) (MEH-PPV) has attracted a great deal of interests in its applications in PLEDs [9], FETs [10], and solar cells [11] due to its particular structure

and luminescent properties. Its asymmetric alkoxy side chains make MEH-PPV soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, xylene, and toluene. In this work, we studied nanocomposites made by incorporation of the different amount of ZnO nanoparticles in MEH-PPV matrix. Since MEH-PPV is a soluble conjugated polymer, one can incorporate oxide nanoparticles into MEH-PPV directly. We investigated the optical and structural properties of the hybrid materials and discussed the influences of the nature of the behavior of the composites.

2. Experimental Method

MEH-PPV, sodium dodecyl sulfate (SDS), and ZnO nanoparticles were purchased from Sigma-Aldrich and used as supplied. The average molecular weight (M_n) of the polymer ranges from 40,000 to 70,000 g/mol. Five solutions of MEH-PPV in tetrahydrofuran (THF) were mixed with <100 nm diameter of ZnO in different weight percents (0 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%). A certain amount of SDS was added into MEH-PPV:ZnO solutions to

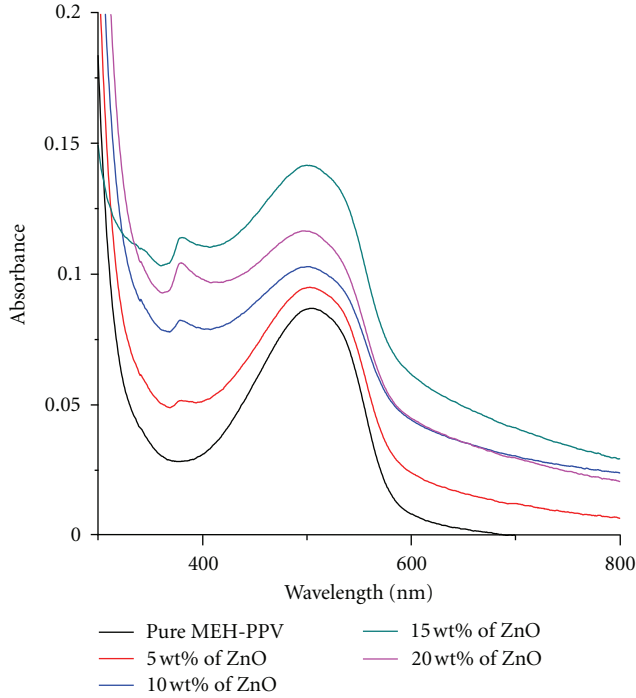


FIGURE 1: UV-Vis absorption spectra of pure MEH-PPV and its nanocomposites.

improve the dispersion of ZnO into the MEH-PPV matrix. Then, the nanocomposite solutions were sonicated for 30 minutes and further stirred for 1 hour. Thin films were obtained by spin coating onto cleaned silicon and glass substrates. This process was repeated for 10 times to yield the required thickness.

Optical characterization of the fresh samples was performed by UV-Vis using JASCO V-670, and the thickness was measured using Veeco Dektak 150. PL measurement was made by using a Fluorolog 3 spectrophotometer. An SEM image was obtained using JEOL JSM-7600F equipped with EDS.

3. Results and Discussion

3.1. UV-Vis Spectra. Figure 1 shows the UV-Vis absorption spectra (300–800 nm) of pure MEH-PPV and its nanocomposite thin films. The absorption peaks of the pure MEH-PPV and its composites are located at ~ 507 nm. These peaks are attributed to π - π^* transition of the conjugated polymer [12]. The addition of ZnO nanoparticles to MEH-PPV shows an increment in the optical absorptions which means that ZnO helps in light harvesting in the visible region. These increments are due to the absorption of ZnO nanoparticles into the MEH-PPV. The increase in absorption is higher as the amount of nanoparticles increases. As the concentration of ZnO nanoparticles increases, the absorption peaks also appear broadened. This may be due to the distribution of energy levels corresponding to the π - π^* transition. The absorption peaks of ZnO nanoparticles appear in the UV region (<400 nm). This peak increases when the amount of

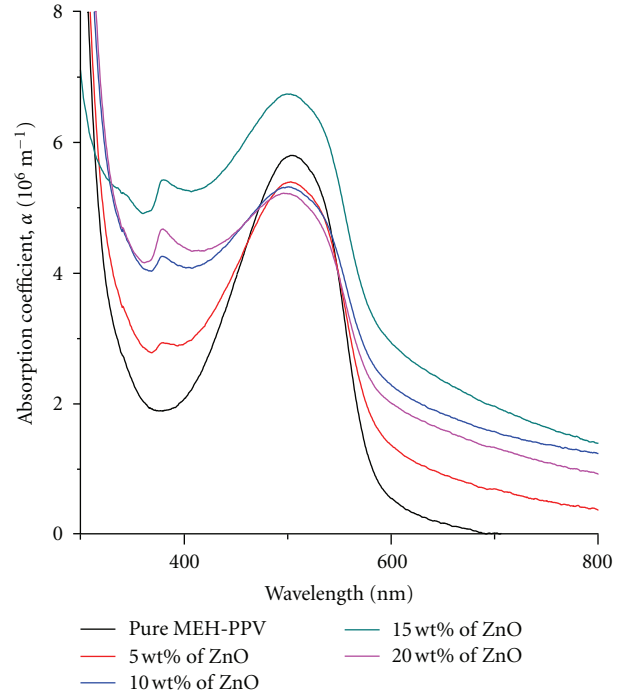


FIGURE 2: Absorption coefficient spectra of pure MEH-PPV and its nanocomposites.

ZnO nanoparticles increases. This could also be due to the nano-size of the ZnO, which could increase the surface area, thus making the absorption stronger. From transmittance data, the absorption coefficient (α) can be calculated. α was obtained through Lambert's law, which is indicated by the following relation:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right). \quad (1)$$

t is the thickness of thin films, and T is the transmittance. Figure 2 shows the α spectra of the pure MEH-PPV and its nanocomposites. α depends on the wavelength of light, which is being absorbed. MEH-PPV:ZnO nanocomposites containing 15 wt% of ZnO have higher absorption coefficient compared to the other samples. The optical bandgap was determined using Tauc's plot. The relationship between direct bandgap and photon energy is given as

$$\alpha h\nu = A(h\nu - E_g)^{1/2}. \quad (2)$$

The extrapolation of the straight-line portion of the $(\alpha h\nu)^2$ versus $h\nu$ for pure MEH-PPV and MEH-PPV:ZnO nanocomposites revealed that the optical bandgap of the nanocomposites, slightly decreases when the amount of ZnO nanoparticles in MEH-PPV increases as seen in Figure 3. The differences in the bandgap values are too small between the pure polymer and its nanocomposites and ZnO nanoparticles apparently do not affect the conjugation length of MEH-PPV. Therefore, addition of ZnO nanoparticles will not affect the structure of the polymer and hence its optical properties. The thickness and optical bandgap of pure MEH-PPV and its nanocomposites are summarized in Table 1.

TABLE 1: The thickness and optical bandgap of pure MEH-PPV and its nanocomposites.

| Sample | Thickness (nm) | Optical bandgap (eV) |
|---------------|----------------|----------------------|
| Pure MEH-PPV | 34.50 | 2.1941 |
| 5 wt% of ZnO | 40.51 | 2.1664 |
| 10 wt% of ZnO | 44.51 | 2.1299 |
| 15 wt% of ZnO | 48.35 | 2.1217 |
| 20 wt% of ZnO | 51.36 | 2.1340 |

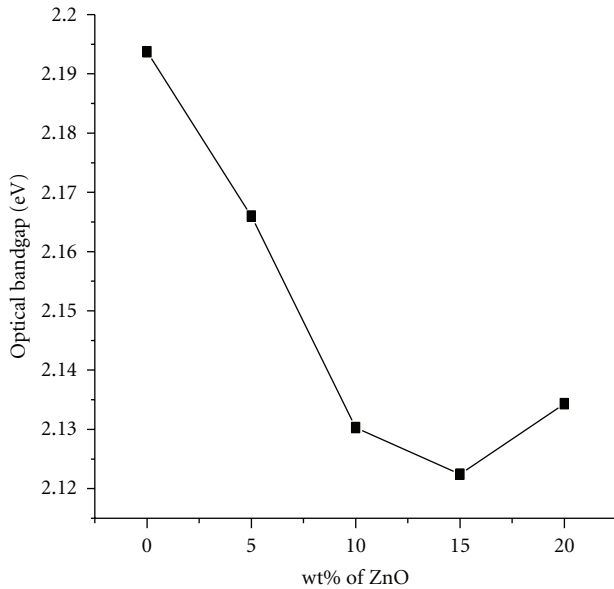


FIGURE 3: Optical bandgap of pure MEH-PPV and its nanocomposites.

3.2. PL Spectra. Figure 4 shows that the PL spectra of pure MEH-PPV and MEH-PPV:ZnO nanocomposites in the wavelength range from 500 to 700 nm. The emission peak of pure MEH-PPV was found to be at 571 nm due to the emission characteristic of PPV backbone, which arises from the relaxation of excited π -electrons to the ground state. The peak for pure MEH-PPV at 617 nm is related to the interchain states [13]. It can be seen that the emission peak increases and slightly red shift as ZnO concentration increases. A maximum emission is found for nanocomposite with 20 wt% of ZnO. This is related to the high-energy transfer from the particles to the polymer. The change in PL emission peak can be explained in two ways: chain separation and charge trapping effect. ZnO is an n-type semiconductor that can trap electrons and allows more holes to recombine through the interface of MEH-PPV and ZnO. Then, the exciton formation inside nanocomposite layer increases and enhances luminescent properties [14]. Furthermore, the red shift in luminescence peak is related with the changes in the conjugation lengths [3]. The red shift occurred due to the formation of nanoparticles agglomeration in the nanocomposites.

3.3. SEM Images. Figures 5(a), 5(b), and 5(c) represent the effect of the different amount of ZnO nanoparticles

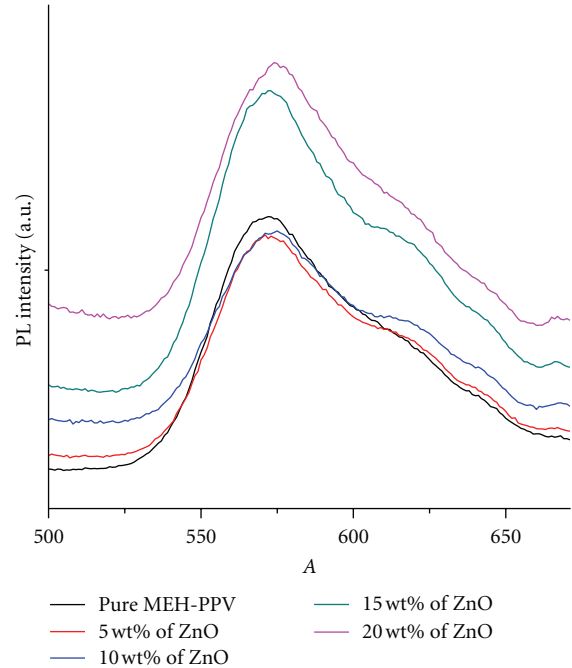


FIGURE 4: PL spectra of pure MEH-PPV and its nanocomposites.

on the degree of agglomeration and distribution of ZnO particles in nanocomposites thin films. As an amount of ZnO nanoparticles increases, the agglomeration regions become larger, and the phase separation between ZnO and MEH-PPV for nanocomposites thin films can be seen clearly. However, in this paper, the certain amount of SDS was added to improve the dispersion of ZnO with sonication treatment. Although thin films containing 5 and 20 wt% ZnO nanoparticles show agglomeration regions, the ZnO is evenly distributed. ZnO nanoparticles may be dispersed homogeneously in hydroxyl-containing solvents such as EG and glycerol because there are many hydroxyl groups on the surface of the oxide nanoparticles. In this paper, tetrahydrofuran was used as the solvent and ZnO nanoparticles were agglomerated. This agglomeration can be reduced by modifying the nanoparticles structure by adding some surfactant or wetting agent to obtain homogeneous thin films. Figure 5(d) shows the EDS result of composite containing 20 wt% of ZnO nanoparticles. The ZnO peak clearly shows the present ZnO in the thin films.

4. Conclusion

In this paper, we investigated the optical and morphological properties of MEH-PPV containing different weight percents of ZnO nanoparticles. UV-Vis absorption spectra for MEH-PPV:ZnO are more intensive compared to the pure MEH-PPV. Small amounts of ZnO nanoparticles added into MEH-PPV matrix have no effect on conjugation segments. The optical bandgap also slightly decreases when the amount of ZnO increases. PL spectra show that the emission peak increases and slightly red shift as ZnO concentration increases. SEM images show that the degree of agglomeration increases as the amount of ZnO increases.

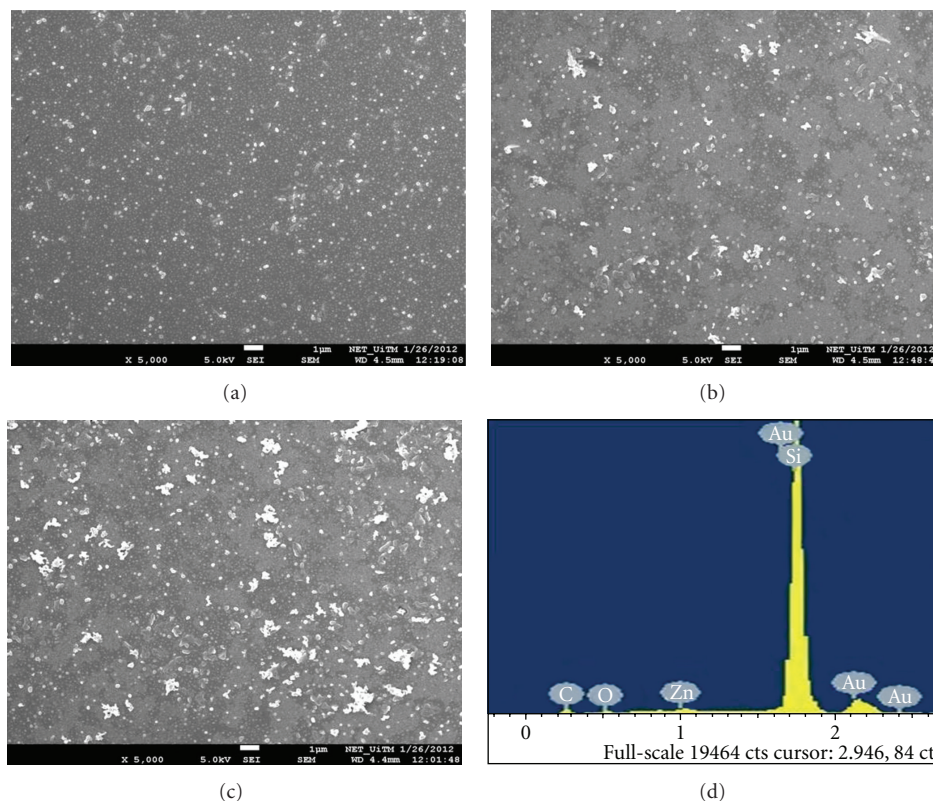


FIGURE 5: SEM images of pure MEH-PPV and its nanocomposites: (a) 0 wt%, (b) 5 wt%, and (c) 20 wt% of ZnO and (d) EDS result of MEH-PPV: 20 wt% of ZnO.

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