

TiO₂ Nanoparticles mixed MEH-PPV Hybrid Absorbing Layer

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ABSTRACT

Hybrid absorber layers having surfactant free CdTe nanoparticles dispersed in poly (2-methoxy, 5-(2-ethyl-hexyloxy)-p-phenyl vinylene) (MEH-PPV) were deposited using spin coating technique. ¹HNMR spectra showed the chemical attachment of TiO₂ nanoparticles to alkoxy group of MEH-PPV. Photoluminescence (PL) measurement confirmed the PL quenching, which is a measure of the degree of dispersion of nanoparticles in the MEH-PPV matrix. This also confirmed that the required dissociation of excitons is taking place. The charge transfer between the polymer and nanoparticles was further confirmed with the help of cyclic voltammetry.

Keywords: MEH-PPV, TiO₂ nanoparticles, hybrid, surfactant free, dispersion

1 INTRODUCTION

Conjugated polymers can exhibit modulation in their electronic properties by molecular engineering, making devices cell processing easy and leading to a low manufacturing cost [1-2]. But for solar cells compared to inorganic semiconductors, polymeric materials have low carrier mobilities and narrow optical absorption spectrum, which cause an inefficient charge generation and transport [3]. This problem can be overcome by mixing inorganic nanoparticles with the polymer and the use of such hybrid material has the potential of bridging the efficiency gap that exists between organic and inorganic semiconductor materials [3]. The properties of hybrid device depend on the quality of dispersion of nanoparticles in the polymer matrix.

The present article reports on the optimization of different process parameters to get the proper dispersion of nanoparticles in the polymer matrix and also explains the chemical interaction between the two materials. TiO₂ nanoparticles are being used for hybrid thin films deposition because these nanoparticles have shown higher photo and environmental stability [4]. Hybrid solar cell devices based on other oxide nanoparticles are reported with low open circuit voltage [5-6]. There are no experimental reports on the role of chemical interaction between TiO₂ nanoparticles and MEH-PPV. In our process, the two materials (surfactant free TiO₂ nanoparticles and poly (2-methoxy, 5-(2-ethyl-hexyloxy)-p-phenyl vinylene) (MEH-PPV)) are mixed in different wt. ratios and a heat

treatment is given to the solution to get a proper mixing or homogeneity.

2 EXPERIMENTAL DETAILS

TiO₂ nanoparticles had been synthesized using solvothermal method [7]. MEH-PPV (Sigma Aldrich) was dissolved in chloroform whereas TiO₂ and MEH-PPV were dissolved in a mixed (1-8 % volume) pyridine-chloroform solution. The solution was stirred for 48 hours and then spin coated in air on glass substrates using Milman-6000 spin coater at 1000 rpm. The samples details are given in table I.

Table 1 Samples details of TiO₂ mixed MEH-PPV hybrid thin films

Materials	Composition (weight ratio)	Sample Name
TiO ₂ : MEH-PPV	0 : 3	MT 0
	20 : 3	MT 20
	30 : 3	MT 30
	40 : 3	MT 40

¹HNMR spectra of solutions were recorded using Bruker Topspin 300 MHz. Chemical shifts are referred to tetramethylsilane for ¹H. All ¹HNMR spectra measurements were done in CDCl₃ at room temperature. Optical absorption study of the spin coated films was carried out with Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer. Photoluminescence measurement was carried out at room temperature. The samples were excited with 532 nm wavelength and the PL signal was detected with a Si detector using a 0.46 m Jobin-Yvon grating monochromator (in the wavelength region of 540–900 nm). Cyclic voltammetry (CV) measurements were recorded on a Princeton Applied Research potentiostat model PAR EG &G - G263 A. A FTO coated glass substrate had been used as a counter electrode. In CV measurement, the potential has been recorded versus a Ag / 0.01 M AgNO₃ + 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) acetonitrile reference electrode at room temperature with a scan rate set at 20 mV/sec. TBAPF₆ dissolved in acetonitrile (0.1M) is used as the supporting electrolyte.

3 RESULTS AND DISCUSSION

Figure 1 shows the ^1H NMR spectra for (a) MEH-PPV solution and (b) TiO_2 nanoparticles dispersed in MEH-PPV solution. ^1H NMR spectra show the main characteristics peaks corresponding to pristine MEH-PPV [8]. There is broadening in the width of the peak corresponding to alkoxy site located at $\delta = 3.96$ ppm and also the peaks corresponding to alkyl sites located at lower δ values. The broadening in the peaks corresponds to benzene ring is not understood. The intensity ratio between the benzene ring and the alkoxy group site is found to be 1:0.75. This suppression in the intensity of the alkoxy group site is observed due to the strong interaction between the $-\text{OCH}_3$ (alkoxy group) and the O-Ti-O bonds (TiO_2 is being an alkoxide). Also it can be due to the fact that more electronegativity of O element is added to this particular site which results in the decrease in the peak intensity. It indicates that the nanoparticles are preferentially attached to this site. The peaks at lower δ are also observed to have more broadening in comparison to ^1H NMR spectra of other nanoparticles blend solutions. This can be due to the interaction between the alkyl group and the O-Ti-O. The entropic effect contributes more in case of TiO_2 mixed polymer solution in comparison to CdTe [9] & CdSe [10] mixed MEH-PPV solutions. This can yield a better interaction between the polymer and nanoparticles which can then give a better solar cell performance. ^1H NMR measurements on blend solution confirm that the alkoxy site of MEH-PPV is the preferential site for the nanoparticles attachment or in other words, it can be concluded that it is the functionalization site for this particular class of polymeric materials.

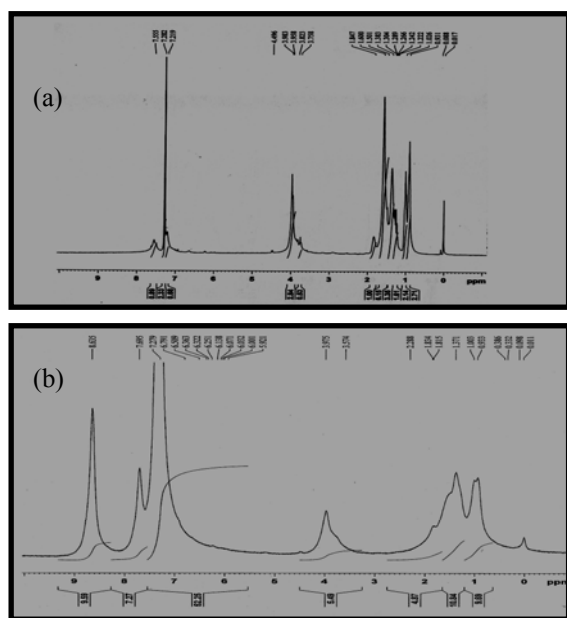


Figure 1: NMR spectra for the solutions (a) dispersed in MEH-PPV and (b) 40 mg TiO_2 nanoparticles dispersed in MEH-PPV.

Figure 2 shows the SEM micrographs for the TiO_2 mixed MEH-PPV films. The film MT 20 shows highly porous surface morphology which is due to the agglomeration of nanoparticles. The TiO_2 nanoparticles aggregate more easily in comparison to other materials like (CdTe [9] and CdSe [10]) nanoparticles due to the porous nature of this material. But as the amount of nanoparticles increases, the improvement in surface morphology can be observed from the micrographs for films MT 30 and MT 40, respectively. This can be one of the reason for more PL quenching in these hybrid films.

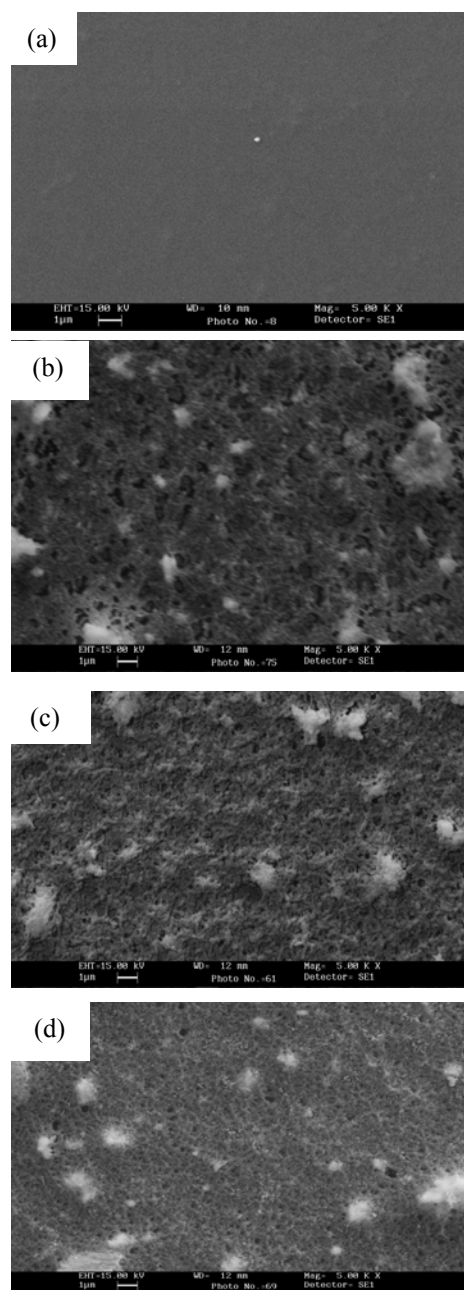


Figure 2: Scanning electron micrographs of TiO_2 mixed MEH-PPV thin films (a) MT 0, (b) MT 20, (c) MT 30 and (d) MT 40.

Figure 3 shows the absorption spectra for TiO₂ nanoparticles mixed MEH-PPV thin films. For all the films, the peak at ~ 500 nm is attributed to π - π^* transition of the conjugated polymer [11]. Addition of nanoparticles to MEH-PPV results in an increase in optical absorption which will help in light harvesting. This increase in absorption is observed because of the scattering from the TiO₂ nanoparticles present in the MEH-PPV matrix. Further, the absorption edge for the MEH-PPV-TiO₂ hybrid film is slightly red shifted in comparison to MEH-PPV film and the absorption peak at ~ 500 is broadened. The peak broadening and the red shift in absorption spectra for the hybrid films (having TiO₂ nanoparticles) are observed because of the aggregation of polymer chain or as the result of relatively long conjugated chains or the minimal possibility of ground state charge transfer at the interface [12-14].

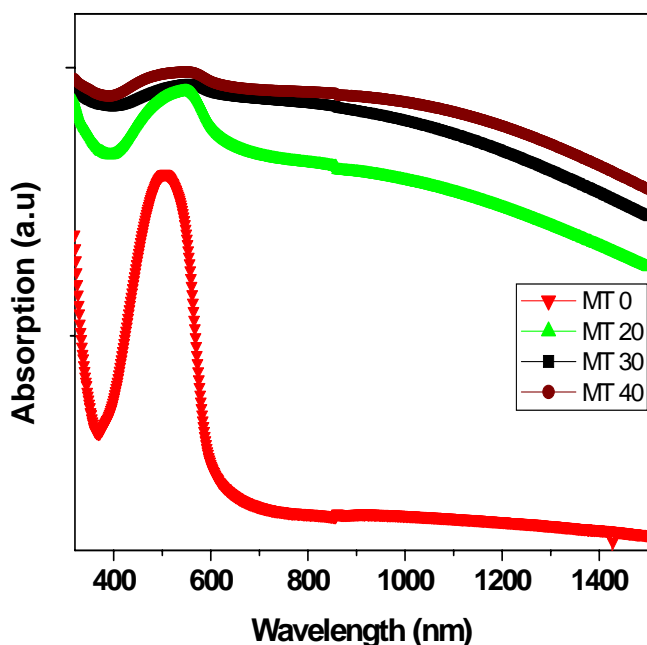


Figure 3: Absorption spectra for the hybrid thin films having TiO₂ mixed MEH-PPV.

PL measurement has been performed on the hybrid thin films to check the photoinduced charge transfer between the nanoparticles and polymer. From Figure 4, it is observed that as the amount of TiO₂ increases, PL quenching increases for the hybrid films [13]. Beyond 30 mg the degree of PL quenching increases significantly for the MT40 film. This implies that TiO₂ at lower concentration in the composite films (MT 20 and MT 30) is not able to provide the required polymer-nanoparticles interfacial properties for the charge dissociation. For film MT 40, SEM and PL measurements are in good accord where the more nanoparticles come into close proximity and provide the continuous path for electron transfer leading to higher PL quenching in comparison to other

films. This also suggests that TiO₂ at this weight ratio is able to provide the required polymer-TiO₂ interpenetrating network for efficient charge transport which can be seen from the densely packed connected network in the plane of the film MT 40 (Fig. 2 (d)). If the amount of TiO₂ nanoparticles is increased more than 40 mg, PL may be quenched further. However, the surface morphology becomes highly porous. This would result in higher series resistance of the hybrid films which would be a barrier for having better solar cell properties.

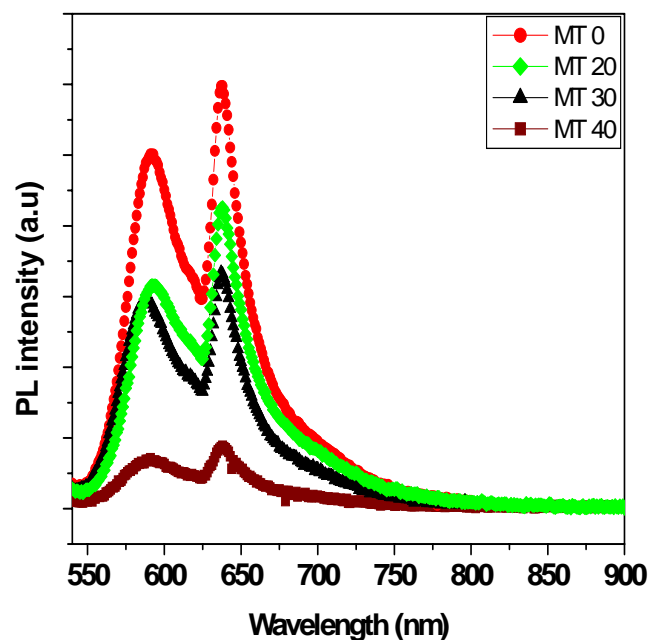


Figure 4: Photoluminescence spectra for the hybrid thin films having TiO₂ mixed MEH-PPV.

The cyclic voltammetry measurement is also performed on the hybrid films to further investigate the charge transportation between the two materials and also how the ionic conductivity varies in the hybrid thin films. CV measurement is performed only with the selected composition which is optimized on the basis of optical and surface morphological properties. Figure 5 shows the cyclic voltammograms for TiO₂ nanoparticles and TiO₂ mixed MEH-PPV thin film (MT 40). The oxidation peak is slightly shifted to the higher potential which confirms a slower ionic motion for the hybrid thin films [14], it can be clearly seen from the inset in Fig. 5 (a). In Fig. 5 (b), arrows at -0.015 V & -0.62 V indicate the weak oxidation peaks for the composite film and analogous to these two peaks, there are two reduction peaks at ~ -0.15 V & -0.38 V. These peaks are shifted to higher potential in comparison to TiO₂ nanoparticles CV curve (Fig. 5 (b)). This proves the charge transfer between the nanoparticles and polymer.

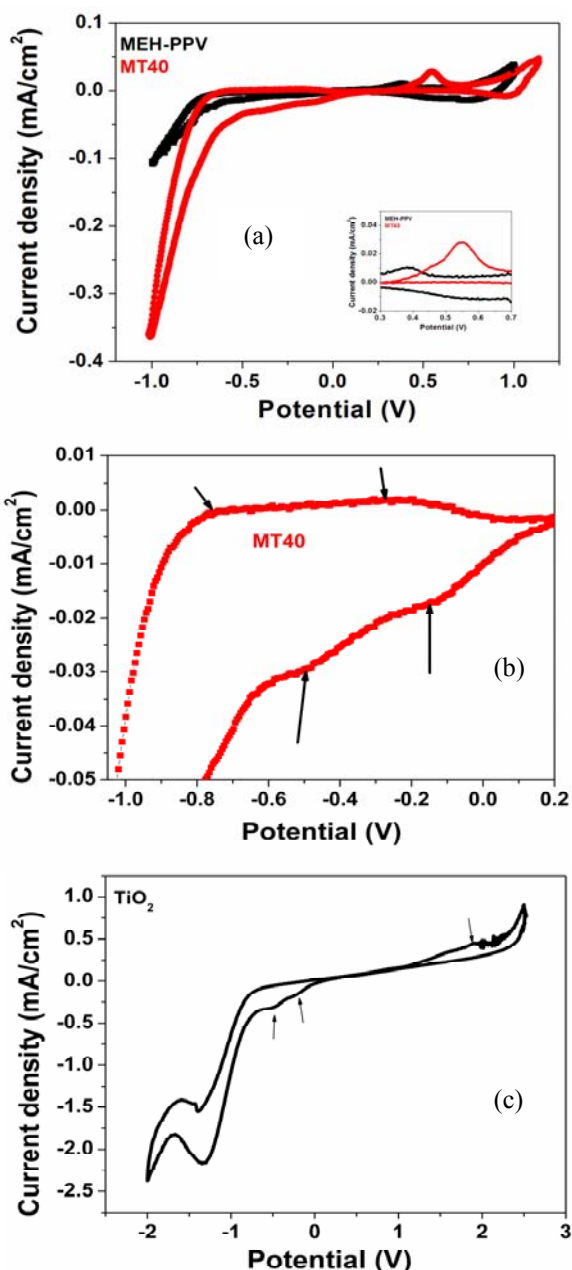


Figure 5: Cyclic voltammograms for the TiO₂ based MEH-PPV blend thin film (a) MT40, (b) selected range of the CV cycle for MT 40 and (c) TiO₂ nanoparticles.

CONCLUSION

Our study shows that solvothermally synthesized TiO₂ nanoparticles can be easily dispersed in MEH-PPV matrix. The hybrid layer deposited with weight ratio 40: 3 shows a stronger interaction which can be useful for making a good absorber layer for solar cell. PL measurements confirm the better dispersion of TiO₂ nanoparticles in MEH-PPV in thin films. The blend solution having proper dispersion of

nanoparticles into polymer matrix can be made by heating the solution before depositing the hybrid absorbing layer.

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