

Study on Electrical and Optical Properties of the Hybrid Nanocrystalline TiO₂ and Conjugated Polymer Thin Films

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Abstract. Recently, the conjugated polymer – inorganic nanocomposites have been increasingly studied due to the potential applications of these advanced materials in developing optoelectronic devices. In this work nanocomposite materials thin films based on poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and nanocrystalline TiO₂ (nc-TiO₂) have been fabricated. The photoluminescence (PL) spectra of pure MEH-PPV and nanohybrid films have shown that the excitation at a 470 nm wavelength leads to the strong quenching in photoluminescent intensity due to the compositions of TiO₂ component. Current-voltage (I-V) characteristics of multi-layer device with structure of Al//MEH-PPV:nc-TiO₂//PEDOT:PSS//ITO//glass were investigated. The obtained results suggest the application of the hybrid MEH-PPV:nc-TiO₂ materials in polymeric solar cells.

Keywords: Nanocomposite, photoluminescence, titanium dioxide, polymeric solar cell.

1 Introduction

Conjugated polymers have attracted great interest due to their potential application in developing large scopes, flexible, lightweight and low cost organic light emitting diodes (OLEDs) and organic solar cells (OSCs) [1,2]. Unfortunately, the electrical and optical properties of these polymers do not compare to those of inorganic semiconductor materials, thus, polymer-based devices have performed poorly in common. Therefore, incorporation of semiconductor nano-particles in a polymer matrix has been increasingly studied and has opened up the potential to improve the performance of these devices. Hybrid organic–inorganic materials can combine the advantages of the film forming properties of polymers with those of the unique properties of inorganic nanoparticles. In this work, the nanohybrid thin films based

on poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and nanocrystalline TiO₂ (nc-TiO₂) have been fabricated. The absorption and photoluminescence properties of that nanohybrid material depending on the compositions of nc-TiO₂ was investigated. Current-voltage (I-V) characteristics of the device based on the hybrid MEH-PPV:nc-TiO₂ materials were also observed.

2 Experimental

MEH-PPV solution was prepared by dissolving MEH-PPV powder (product of Aldrich, USA) in chloroform with a ratio as 2 mg of MEH-PPV in 1 ml of chloroform. The hybrid organic-inorganic materials based on MEH-PPV and nc-TiO₂ have been fabricated by dispersing 5 nm TiO₂ powder (product of Aldrich, USA) with various ratios (10, 25 and 50 wt% relative to MEH-PPV) in as-prepared MEH-PPV solution.

The device with structure of Al//MEH-PPV:nc-TiO₂//PEDOT:PSS//ITO//glass was fabricated as following procedure. The optically transparent and electrically conductive indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30Ω/ was ultrasonically cleaned in a series of solvents (ethanol, acetone and deionized water). A hole injection buffer layer of polyethylenedioxy-thiophene : polystyrene sulfonate (PEDOT:PSS) was spin-coated on the ITO substrate at spin rates ranging of 2000 rpm for 60s. Then the pristine MEH-PPV or the MEH-PPV blended with nc-TiO₂ (10, 25 and 50 wt% relative to MEH-PPV) was spin-coated on the top of PEDOT:PSS thin film layer. The spin coating was carried-out in gaseous nitrogen with a set-up procedure as follow. The delay time is 120s, the spin speed is 1500 rpm, the acceleration time is 20s and the relaxation time is 5 min. The thickness of the polymer layer is controlled both by spin speed and by the concentration of polymer in the solvent. After spin-coating the samples were put into a vacuum oven for removing the solvent from the polymer film at 150°C in a vacuum of 10⁶ torr for 2 hours. For current-voltage (I-V) testing, an aluminum alloy layer was vacuum deposited by thermal evaporation on the hybrid film to complete the device.

The surface morphology of samples was investigated by using a "Hitachi" Field Emission Scanning Electron Microscopy (FE-SEM). The thickness of all thin films was examined by an alpha step surface profile monitor. The Ultraviolet-visible (UV-vis) absorption spectra was performed by using a Jasco UV-VIS-NIR V570 spectrometer. Photoluminescence (PL) spectra were carried-out by using a FL3-2 spectrophotometer and current-voltage (I-V) characteristics were measured on an Auto-Lab Potentiostat PGS-30.

3 Results and Discussion

3.1 Morphology of the Hybrid TiO₂ Nanocrystals – MEH-PPV Thin Film

As shown in figure 1a, homogeneous MEH-PPV film with good quality deposited onto glass substrate from MEH-PPV solution exhibited smooth surface and good film-to-substrate adhesion. On the other hand, it was shown that the TiO₂ nanoparticles became large-sized and agglomerated in the composite films as the percentage of TiO₂

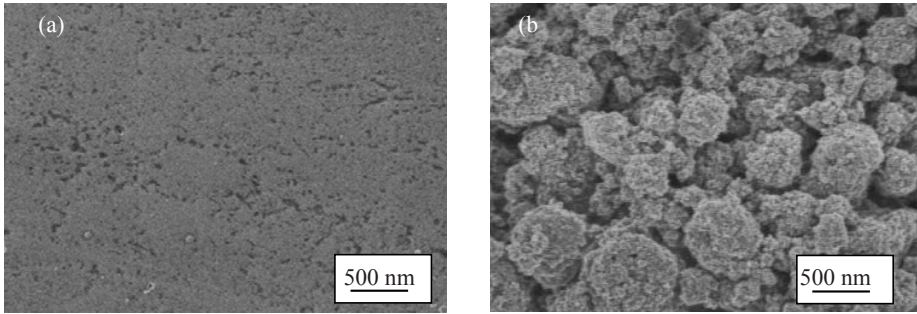


Fig. 1. FE-SEM photographs of the MEH-PPV thin film (a) and the hybrid nc-TiO₂ (50wt%) – MEH-PPV thin film (b)

increases, which resulted in more highly interpenetrated networks of TiO₂ produced at higher concentrations. Some large clusters were observed in case of the highest concentration of nc-TiO₂ (50 wt%) in MEH-PPV hybrid films, as seen in figure 1b.

3.2 Photoluminescence of Polymeric Composites

Figure 2 shows the absorption spectra (a) and photoluminescence spectra (b) excited at a short wavelength ($\lambda = 470$ nm) of the MEH-PPV and the hybrid MEH-PPV:nc-TiO₂ respectively. The absorption spectrum of the pristine polymer MEH-PPV shows a peak at 490 nm. The broad band peaked at 490 nm is ascribed to the $\pi-\pi^*$ transitions of the conjugated polymer as reported in [3]. Figure 2a reveals that with addition of TiO₂ nanocrystals the absorption peak of MEH-PPV shifts to shorter wavelengths and the optical density of the absorption spectra in the hybrid films increase with respect to the pristine polymer. The observed results might be explained that the absorption of the composite has increased compared to the pure MEH-PPV due to the absorption of nanocrystal TiO₂ at wavelengths lower than 400 nm. In addition, the amount of TiO₂

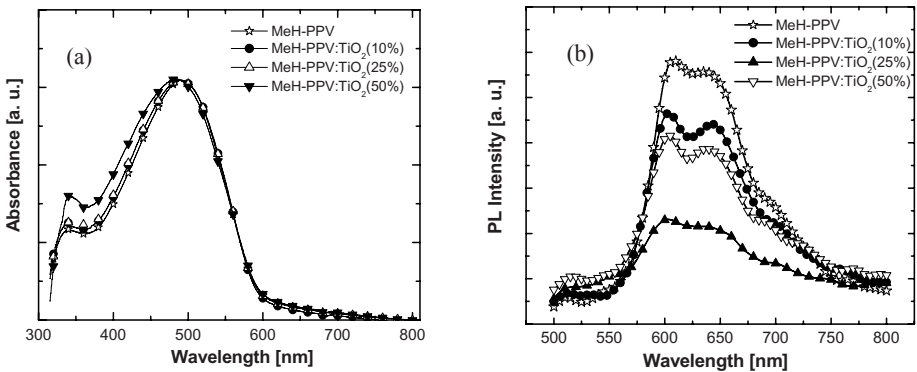


Fig. 2. Absorption spectra (a) and photoluminescence spectra (b) of the MEH-PPV and the hybrid TiO₂ nanocrystals – MEH-PPV with various ratios of TiO₂:MEH-PPV (in wt %), excited at 470 nm

increasing from 10% to 50% in the hybrid materials results in the increasing number of interfaces between the two materials. The embedding of TiO₂ in polymer matrix prevents the formation of polymer aggregates in the composite films and reduces the polymer conjugation chain length of MEH-PPV, therefore shifted the peak [4,5].

As shown in figure 2b, the emission spectrum of MEH-PPV is observed the main PL peak at 597 nm and the shoulder at 635 nm. The photoluminescence spectra of hybrid MEH-PPV:nc-TiO₂ were decreased with an addition of nc-TiO₂ components (10, 50 and 25 wt.%, respectively). The mechanism of the photoluminescence quenching effect can be explained as follows. The quenching of PL intensity of the composite may be attributed to the presence of interfaces between nanocrystalline oxide particles and polymer. At the interfaces of hybrid MEH-PPV:nc-TiO₂, charge-space regions are expected to be formed. Under the excitation at 470 nm wavelength, electrons from the Highest Occupied Molecular Orbital (HOMO) levels of the conjugated polymer MEH-PPV were excited and jumped to the Lowest Unoccupied Molecular Orbital (LUMO) and leave holes in the first one. Then those electrons transferred to the conduction band (CB) of TiO₂, acting as an electron accepting species. As a result, the electron-hole pairs were separated more effectively, leading to an decrease of the photoluminescence intensity.

3.3 Electrical Properties of the Hybrid Structures

A schematic diagram of our device configuration is shown in figure 3, which consists of a transparent indium-tin-oxide (ITO) conducting electrode, poly(3,4-ethylenedioxythiophene)– poly(styrenesulfonate) (PEDOT:PSS), the MEH-PPV: nc-TiO₂ hybrid film, and an aluminium (Al) electrode. The thickness of the MEH-PPV: nc-TiO₂ hybrid film was estimated to be 180 nm. For the samples, device 0 (D0), device 1 (D1), device 2 (D2), and device 3 (D3), respectively are abbreviated to the heterojunctions samples with MEH-PPV, MEH-PPV:nc-TiO₂ (10 wt.%), MEH-PPV:nc-TiO₂ (25 wt.%) and MEH-PPV:nc-TiO₂ (50 wt.%) used in I-V measurement, as follows:

D0: Al//MEH-PPV //PEDOT: PSS//ITO//glass

D1: Al//MEH-PPV: nc-TiO₂(10wt.%)//PEDOT: PSS//ITO//glass

D2: Al//MEH-PPV: nc-TiO₂(25 wt.%)//PEDOT: PSS//ITO//glass

D3: Al//MEH-PPV: nc-TiO₂(50 wt.%)//PEDOT: PSS//ITO//glass

Figure 4 shows the current–voltage response of the devices with and without nc-TiO₂ particles dispersed in MEH-PPV layer. For a comparison, the slopes of the I-V curves increase significantly and turn-on voltages of nanocomposite devices decrease as the concentration of nc-TiO₂ increases (10, 25 and 50 wt.%, respectively). The I–V characteristic of the MEH-PPV based device (D0) exhibits a turn-on voltage is of around 2.5 V. In case of the nanohybrid devices, a turn-on voltage is approximately 2 V with D1 and D2 devices and no reverse current was observed up to an applied voltage of 2 V. For D3 device although the turn-on voltage is smaller, the current began increasing with voltage right from 0. Therefore in the D3 device the reverse current of the device appeared from starting switch-on voltage and it might be heated up the device. This indicates that the D2 will be the best candidate for a photovoltaic solar cell. The main reason is that the presence of semiconducting oxide particles covered with

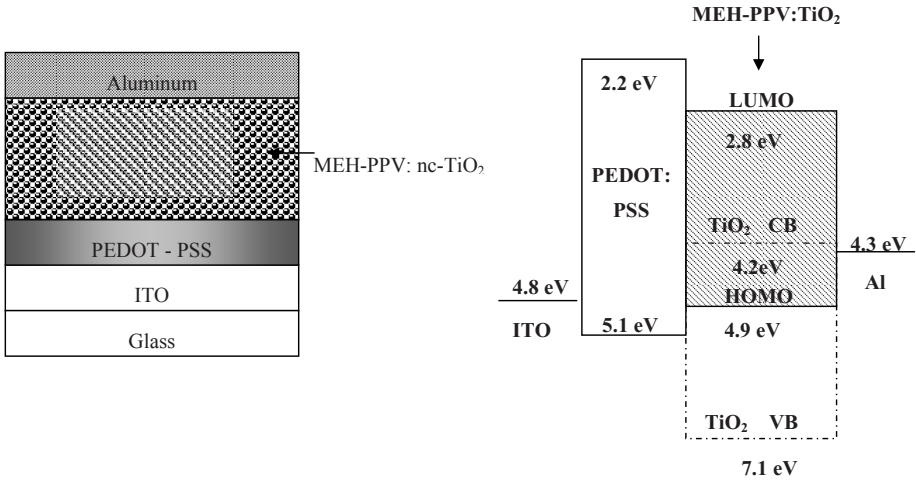


Fig. 3. Hybrid organic–inorganic device with structure of Al//MEH-PPV:nc-TiO₂//PEDOT-PSS //ITO//glass (a) and the energy-level diagram of the device (b)

conducting polymer in the device produces more highly interpenetrated networks of TiO₂ at higher concentrations. Thus, an enhanced charge transport route is desirable to achieve efficient electron conduction. In addition, the rough surface of the MEH-PPV:nc-TiO₂ layer can lead to stronger contact and increased contact area to the Al electrode, which might give rise to an increase in the electrical conductivity. These results suggest that hybrid MEH-PPV:nc-TiO₂ are a promising material for hybrid organic solar cell applications.

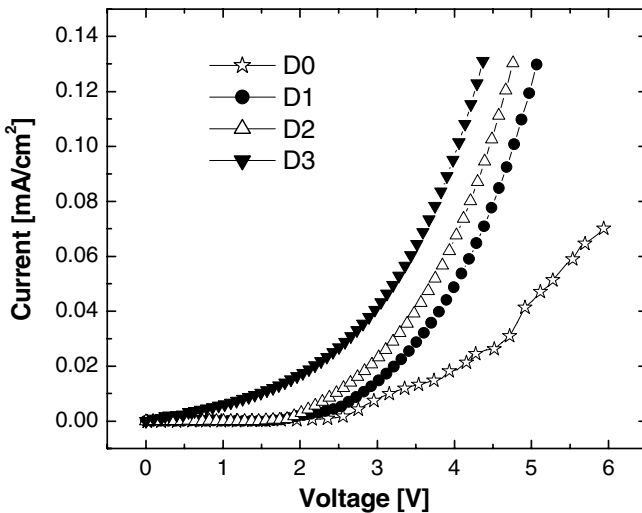


Fig. 4. I-V characteristics of the devices with different ratios of nc-TiO₂ 10, 25 and 50 wt.% and without nc-TiO₂ in MEH-PPV as active layers

4 Conclusion

The nanocomposite hybrid thin films based on conjugated polymer MEH-PPV and TiO₂ nanocrystals were fabricated. The optical and electrical properties of the devices substantially depend on the compositions and morphologies of TiO₂ component in the hybrid layer. The embedded nc-TiO₂ in MEH-PPV resulted in the quenching of the PL spectra of the conjugated polymer and the improvement of I-V characteristics. Combining the PL spectra of the materials with the electrical property of the devices one can see that the hybrid films exhibited the high efficiency of charge transportation in the active layer of the multi-layer device. The obtained results suggest that the hybrid MEH-PPV:nc-TiO₂ materials with the concentration of TiO₂ (25%) can be expected to be a good candidate for photovoltaic solar cell applications.

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