

## ELECTRICAL AND OPTICAL PROPERTIES OF THE HYBRID TiO<sub>2</sub> NANOCRYSTALS – MEH-PPV THIN FILMS

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**Abstract.** *Recently, the conjugated polymer – inorganic nanocomposites have been increasingly studied because of their enhanced optical and electronic properties as well as their potential application in developing optoelectronic devices. In this study nanocomposite materials thin films based on poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and nanocrystalline TiO<sub>2</sub> (nc-TiO<sub>2</sub>) have been fabricated. The photoluminescence (PL) spectra of pure MEH-PPV and nanohybrid films have shown that the excitation at a 377 nm wavelength leads to the strongly enhanced performance in photoluminescent intensity due to the compositions of TiO<sub>2</sub> component. Current-voltage (I-V) characteristics of multi-layer device Al//MEH-PPV:nc-TiO<sub>2</sub>//PEDOT:PSS//ITO//glass were investigated. The results show that the hybrid MEH-PPV:nc-TiO<sub>2</sub> materials with high concentrations of TiO<sub>2</sub> (> 25%) can be expected to be a good candidate for photovoltaic solar cell applications whereas those with lower concentrations of TiO<sub>2</sub> are more suitable for organic light-emitting diodes (OLEDs).*

### I. INTRODUCTION

Over the last decade, conjugated polymers have attracted great interest due to most of the polymers can be processed from solution at room temperature and 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. In recent years, incorporation of semiconductor nano-particles in an 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 nanocomposite thin films based on poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and nanocrystalline TiO<sub>2</sub> (nc-TiO<sub>2</sub>) have been fabricated. Enhanced performance in these optical and electrical properties of that nanohybrid material depending on the compositions of nc-TiO<sub>2</sub> was investigated.

## II. 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-TiO<sub>2</sub> have been fabricated by dispersing 5 nm TiO<sub>2</sub> 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-TiO<sub>2</sub>//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 60 s. Then the pristine MEH-PPV or the MEH-PPV blended with nc-TiO<sub>2</sub> (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 120 s, the spin speed is 1500 rpm, the acceleration time is 20 s 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 10<sup>-3</sup> 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) S-4800. 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.

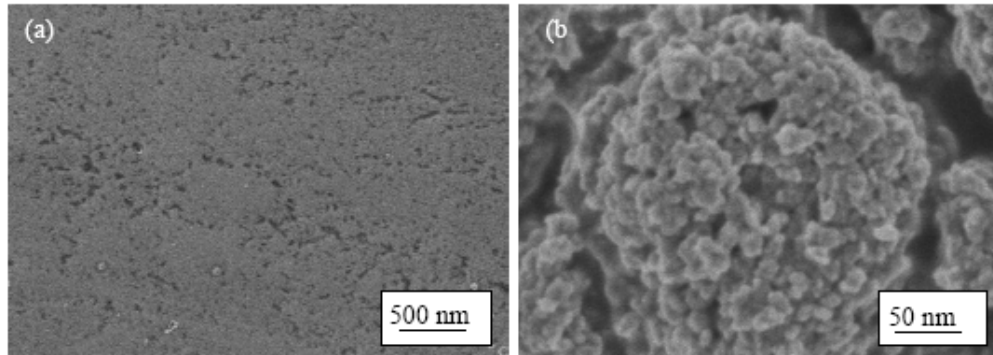
## III. RESULTS AND DISCUSSION

### III.1. Morphology of the hybrid TiO<sub>2</sub> nanocrystals – MEH-PPV thin film

As shown in Fig. 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 TiO<sub>2</sub> nanoparticles became large-sized and agglomerated in the composite films as the percentage of TiO<sub>2</sub> increases, which resulted in more highly interpenetrated networks of TiO<sub>2</sub> produced at higher concentrations. Some large clusters were observed in case of the highest concentration of nc-TiO<sub>2</sub> (50 wt%) in MEH-PPV hybrid films, as seen in Fig. 1b.

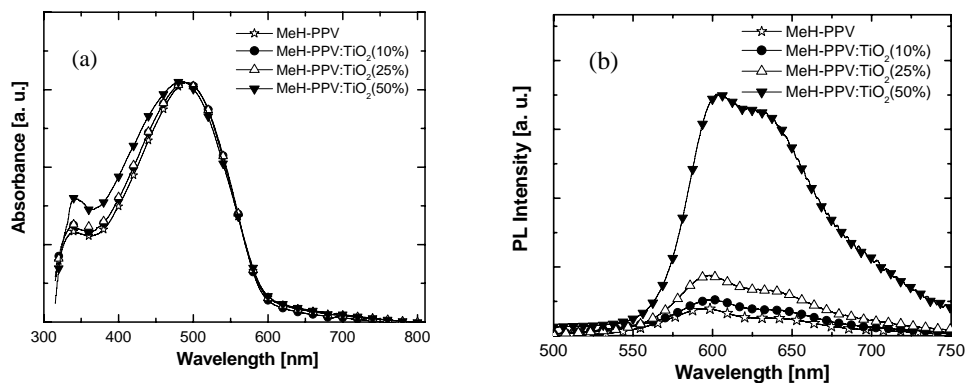
### Photoluminescence of polymeric composites

Fig. 2 shows the absorption spectra (a) and photoluminescence spectra (b) excited at a short wavelength ( $\lambda = 377$  nm) of the MEH-PPV and the hybrid MEH-PPV:nc-TiO<sub>2</sub> respectively. The absorption spectrum of the pristine polymer MEH-PPV shows a peak



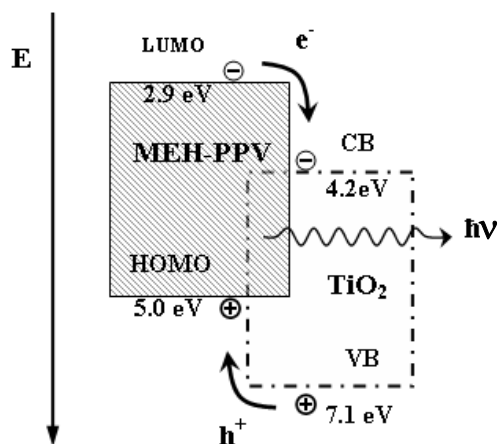
**Fig. 1.** FE-SEM photographs of the MEH-PPV thin film (a) and the hybrid nc-TiO<sub>2</sub> (50wt%) - MEH-PPV thin film (b).

at 490 nm. The broad band peaked at 490 nm is ascribed to the  $\pi$ - $\pi^*$  transitions of the conjugated polymer as shown in [3]. Fig. 2(a) reveals that with addition of TiO<sub>2</sub> nanocrystals the absorption peak of MEH-PPV shifts to shorter wavelengths and the optical density of the absorption spectra in the hybrid films increases with respect to the pristine polymer. The observed results might be explained as the absorption of the composite that has increased compared to the pure MEH-PPV due to the absorption of nanocrystal TiO<sub>2</sub> at wavelengths lower than 400 nm. In addition, the amount of TiO<sub>2</sub> increasing from 10% to 50% in the hybrid materials results in the increasing number of interfaces between the two materials. The embedding of TiO<sub>2</sub> 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].



**Fig. 2.** Absorption spectra (a) and photoluminescence spectra (b) of the MEH-PPV and the hybrid TiO<sub>2</sub> nanocrystals - MEH-PPV with various ratios of TiO<sub>2</sub>:MEH-PPV (in wt %), excited at 377 nm.

As shown in Fig. 2(b), the emission spectrum of MEH-PPV is observed the main PL peak at 595 nm and the shoulder at 630 nm. The photoluminescence spectra of hybrid MEH-PPV:nc-TiO<sub>2</sub> were enhanced with an increase of nc-TiO<sub>2</sub> components (10, 25 and 50 wt.%, respectively). The mechanism of the photoluminescence enhancement effect can be explained as follows. The enhancement 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-TiO<sub>2</sub>, charge-space regions are expected to be formed, due to the charge distribution difference between the oxide and the polymer. Under the excitation of a large energy photonic beam, both of conjugated polymer MEH-PPV and TiO<sub>2</sub> nanocrystals were excited. Electrons from the Highest Occupied Molecular Orbital (HOMO) levels of the polymer move toward the Lowest Unoccupied Molecular Orbital (LUMO) and leave holes in the first one. Correspondingly, electrons from the valence band of TiO<sub>2</sub> can jump to the conduction band, creating holes in the first band and resulting in the decrease of the Schottky barrier height in the second band. As a result, the new electron-hole pairs in the emitting layer are generated, leading to an increase of the photoluminescence intensity, as described in the energy-level diagram (Fig. 3).



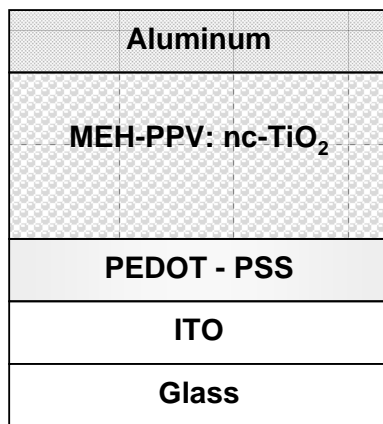
**Fig. 3.** The energy-level diagram of the TiO<sub>2</sub> nanocrystals and MEH-PPV polymer.

### Electrical properties of the hybrid structures

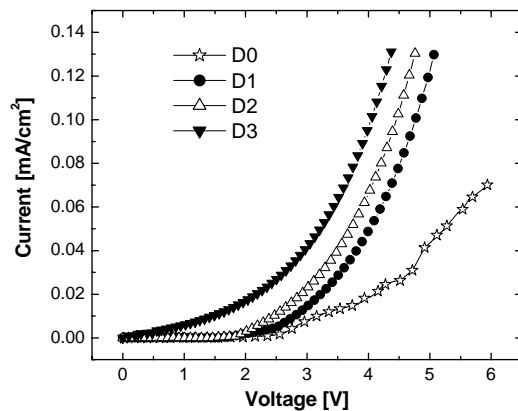
A schematic diagram of our device configuration is shown in Fig. 4, which consists of a transparent indium-tin-oxide (ITO) conducting electrode, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), the MEH-PPV: nc-TiO<sub>2</sub> hybrid film, and an aluminium (Al) electrode. The thickness of the MEH-PPV: nc-TiO<sub>2</sub> 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-TiO<sub>2</sub> (10 wt.%), MEH-PPV:nc-TiO<sub>2</sub> (25 wt.%) and MEH-PPV:nc-TiO<sub>2</sub> (50 wt.%) used in I-V measurement, as follows:

- D0: Al//MEH-PPV //PEDOT:PSS//ITO//glass  
 D1: Al//MEH-PPV:nc-TiO<sub>2</sub>(10 wt.%)//PEDOT:PSS//ITO//glass  
 D2: Al//MEH-PPV:nc-TiO<sub>2</sub>(25 wt.%)//PEDOT:PSS//ITO//glass  
 D3: Al//MEH-PPV:nc-TiO<sub>2</sub>(50 wt.%)//PEDOT:PSS//ITO//glass

Fig. 5 shows the current–voltage response of the devices with and without nc-TiO<sub>2</sub> 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-TiO<sub>2</sub> 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 D3 will be a better candidate for a photovoltaic solar cell than for the OLED. The main reason is that the presence of semiconducting oxide particles covered with conducting polymer in the device produces more highly interpenetrated networks of TiO<sub>2</sub> 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-TiO<sub>2</sub> 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-TiO<sub>2</sub> are a promising material for hybrid organic solar cell applications.



**Fig. 4.** Hybrid organic–inorganic device with structure of Al//MEH-PPV:nc-TiO<sub>2</sub>//PEDOT-PSS//ITO//glass



**Fig. 5.** I-V characteristics of the devices with different ratios of nc-TiO<sub>2</sub> 10, 25 and 50 wt.% and without nc-TiO<sub>2</sub> in MEH-PPV as active layers.

#### IV. CONCLUSION

The nanocomposite hybrid thin films based on conjugated polymer MEH-PPV and TiO<sub>2</sub> nanocrystals were fabricated. The optical and electrical properties of the devices substantially depend on the compositions and morphologies of TiO<sub>2</sub> component in the hybrid layer. The embedded nc-TiO<sub>2</sub> in MEH-PPV resulted in the enhancement 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 the potential application of the hybrid MEH-PPV:nc-TiO<sub>2</sub> materials with high concentrations of TiO<sub>2</sub> (> 25%) in flexible polymeric solar cells while the hybrid materials with lower concentrations of TiO<sub>2</sub> are more appropriate for organic light-emitting diodes (OLEDs).

#### ACKNOWLEDGMENT

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