

## Fabrication and Morphological Characterization of Hybrid Polymeric Solar Cells Based on P3HT and Inorganic Nanocrystal Blends

(Fabrikasi dan Pencirian Morfologi Sel Suria Polimer Hibrid Berasaskan Adunan P3HT dan Nanohablur Tak Organik)

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### ABSTRACT

*In this research we investigated the effect of composition on the fabrication and morphological characteristics of a hybrid polymeric solar cell which consists of an electron donating conjugated polymer, namely is poly(3-hexylthiophene) (P3HT) combined with an electron-accepting component, which is a type of inorganic compound of TiO<sub>2</sub> nanocrystals. The composition of TiO<sub>2</sub> in the blends is varied and the optimum performance of the devices are studied. The optical and morphological characterizations are carried out via UV-Visible absorption spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The electrical characteristics of the devices are measured by using Keithley 2400 SMU and solar simulator with light intensity of 100 mW/cm<sup>2</sup>.*

*Keywords: Blend thin film; composition effect; hybrid polymer solar cell; P3HT; TiO<sub>2</sub>*

### ABSTRAK

*Kajian ini dijalankan bagi kesan komposisi terhadap fabrikasi dan ciri morfologi sel suria polimer hibrid yang mengandungi adunan satu bahan penderma elektron polimer terkonjugat poli(3-heksiltiofena) (P3HT) dan satu penerima elektron bahan tak organik dalam bentuk nanohablur, TiO<sub>2</sub>. Kajian dilakukan terhadap komposisi TiO<sub>2</sub> dalam adunan dan prestasi optimum bagi sel suria ini. Ciri-ciri optik dan morfologi filem nipis ini dikaji melalui penggunaan spektroskopi serapan ultraungu-cahaya nampak, pembelauan sinar-X, mikroskopi daya atom, dan mikroskopi elektron daya imbasan. Pencirian elektrik ke atas peranti sel suria ini diukur menggunakan alat Keithley 2400 SMU dan simulasi suria dengan keamatan cahaya sebanyak 100 mW/cm<sup>2</sup>.*

*Kata kunci: Adunan filem nipis; solar sel polimer hibrid; P3HT; TiO<sub>2</sub>; kesan komposisi*

### INTRODUCTION

Organic photovoltaic is considered as one of the best renewable source of energy that can be used widely in the future due to their peculiar advantages, such as low cost, easy fabrication, light weight and mechanically flexible. However, the power conversion efficiencies are limited by the low carrier mobility of the organic materials compared to inorganic materials. In achieving higher performance of organic solar cell, hybrid polymeric solar cell, a subclass of bulk heterojunction (BHJ) devices, which employs a conjugated polymer-like regioregular poly(3-hexylthiophene) (P3HT) as electron donor and an inorganic semiconductor nanocrystal as electron acceptor deserves deep investigation (Brabec et al. 20018; Hoppe & Sariciftci 2004; Yu et al. 1995; Yu & Peng 200).

Inorganic nanocrystals such as TiO<sub>2</sub> (Kwong et al. 2004a) offer several advantages such as size tunability and having high absorption coefficients (Huynh et al. 1999). Typically, the performance of solar cells can be improved by controlling the morphology of the films (Brabec et al. 2001) which is significantly influenced by processing conditions like blend composition, type of solvent, spin

speed and so on. Thus, the investigation of the effect of certain processing conditions on the fabrication and morphological characterization of the hybrid polymeric solar cells is crucial.

In this work, we investigated the effect of TiO<sub>2</sub> composition on the physical and electrical characteristics of the P3HT:TiO<sub>2</sub> blend films and devices. Most of the reported data in the literature review of the P3HT:TiO<sub>2</sub>, the films are prepared from chlorine based solvents such as chloroform (Wang & Wang 2007) or non-chlorinated solvents such as xylene (Yu et al. 2008). However, the polymer films prepared in highly volatile chlorinated solvent such as chloroform are known to produce a rough film.

Previously we reported the formation of blend film based on P3HT and [6,6]-phenyl C<sub>60</sub> butyric acid methyl ester (PCBM) using a cosolvent of chloroform and dichlorobenzene (Yusli et al. 2009). Nevertheless, the nanocrystal is not soluble in dichlorobenzene. It is important to slow down the film formation by mixing both chlorinated and non-chlorinated solvents. Hence, the aim of our research work is to fabricate the P3HT:TiO<sub>2</sub> films

using cosolvent of both chlorinated and nonchlorinated based solvents, namely chloroform ( $\text{CHCl}_3$ ) and dimethyl sulfoxide (DMSO). Furthermore, the optimum composition of  $\text{TiO}_2$  in the polymer blends is investigated.

#### EXPERIMENTAL DETAILS

The thin film consists of a blend of regioregular poly(3-hexylthiophene) (P3HT), and titanium dioxide ( $\text{TiO}_2$ ) nanocrystals with particle size less than 100 nm (solid spherical particles, anatase/rutile structures). Both were purchased from Sigma-Aldrich. The chemical structures of P3HT and  $\text{TiO}_2$  are shown in the inset of Figure 1. The pure P3HT,  $\text{TiO}_2$  and P3HT: $\text{TiO}_2$  blend solutions with different composition of  $\text{TiO}_2$  (with 5%  $\text{TiO}_2$ , 10%  $\text{TiO}_2$ , 15%  $\text{TiO}_2$ , 20%  $\text{TiO}_2$ ) were prepared in a mixture solvent consisted of  $\text{CHCl}_3$  and DMSO at a solution concentration of 10 mg/mL.

The design of the solar cell was in the form of a sandwich structure of the blend film between an anode electrode of indium tin oxide (ITO) and a metal cathode of aluminium. The ITO substrates were ultrasonically cleaned in DECON<sup>TM</sup> foam solution, deionised water, acetone, and ethanol solution sequentially. A buffer layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on top of the ITO before being annealed at 110°C for 20 min to reduce the roughness of ITO surface. Then, the blend P3HT: $\text{TiO}_2$  solutions were spin-coated onto the PEDOT:PSS layer at spin speed of 2000 rpm for 30 s to produce homogeneous thin films. Finally, a ~100 nm thick aluminium layer was deposited on the films by thermal evaporation at  $5 \times 10^{-5}$  Pa, defining an area of 0.38 cm<sup>2</sup>. The final device construction of ITO/PEDOT:PSS/P3HT: $\text{TiO}_2$ /Al is illustrated in the inset of Figure 4. Absorption spectra measurements for the blend thin films were obtained using Jasco V-570 UV/VIS/NIR spectrophotometer. A Siemens

D5000 X-ray diffractometer was used to record the X-ray diffraction (XRD) patterns. A Veeco D300 Atomic force microscope was used to study the surface morphology of the films. The current-voltage characteristics of the devices were measured using a Keithley 2400 sourcemeter under the AM1.5G-filtered irradiation (100 mW/cm<sup>2</sup>) from a Oriel 67005 solar simulator.

#### RESULTS AND DISCUSSION

Figure 1 shows the absorption coefficient spectra of the pure P3HT,  $\text{TiO}_2$  and P3HT: $\text{TiO}_2$  blend films with different composition of  $\text{TiO}_2$ . It can be seen that the pure P3HT exhibits a strong absorption in the visible wavelength range from 450 to 650 nm, whereas the nanocrystals of  $\text{TiO}_2$  absorb light in the UV wavelength range from 200 to 300 nm. The absorption spectra of the P3HT: $\text{TiO}_2$  blends show the overlapping absorption spectra of pure P3HT and  $\text{TiO}_2$ . As the  $\text{TiO}_2$  content increases, the magnitude of the absorption coefficient at wavelength larger than 400 nm decreases, which can be attributed to the reduction in the volume occupied by benzene ring of the P3HT polymer within the blend film. For higher  $\text{TiO}_2$  content, the absorption in red band of the P3HT is reduced while absorption in the blue region is increased. This suggests that the existence of  $\text{TiO}_2$  in film has disrupted the intermolecular packing structure of P3HT chains, which may reduce the contribution of P3HT to the light absorption in the visible wavelength range (Kim et al. 2005).

Figure 2 shows the XRD patterns of pure P3HT, and blend film with 5%  $\text{TiO}_2$  and 10%  $\text{TiO}_2$  (other results with different content of  $\text{TiO}_2$  are not shown due to the spectral overlapping). For spin-coated P3HT: $\text{TiO}_2$  blend film, a crystalline peak at  $2\theta \approx 5.4^\circ$  in the diffractogram, which corresponds to the first-order reflection is observed

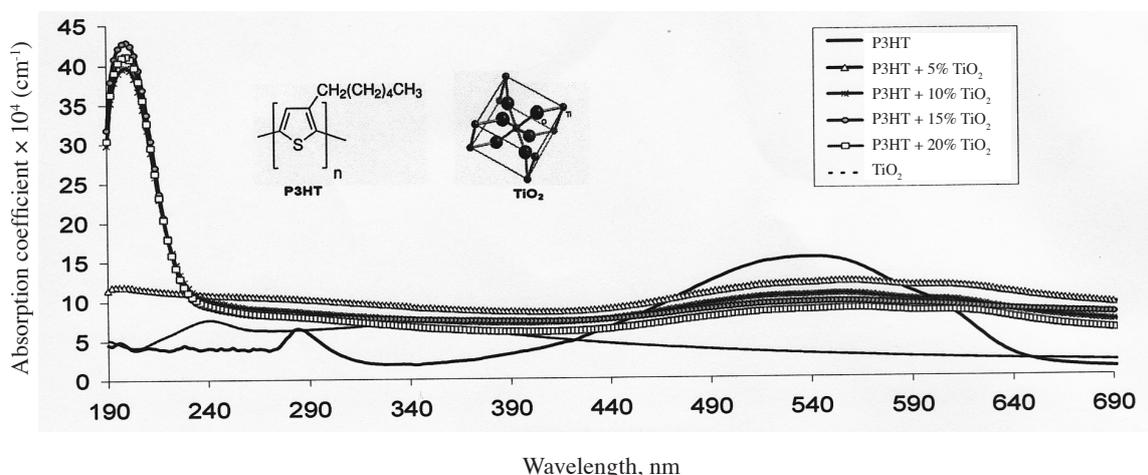


FIGURE 1. Absorption coefficient spectra of pure P3HT,  $\text{TiO}_2$  and P3HT: $\text{TiO}_2$  blend thin films with different composition of  $\text{TiO}_2$ . The film thickness of pure P3HT,  $\text{TiO}_2$  and blends with 5%  $\text{TiO}_2$ , 10%  $\text{TiO}_2$ , 15%  $\text{TiO}_2$ , and 20%  $\text{TiO}_2$  is (43.4, 23.4, 48.3, 44.2, 37.4, and 40.7)  $\pm$  0.1 nm, respectively. The inset shows the chemical structures of P3HT and  $\text{TiO}_2$

(Zhokhavets et al. 2006). This peak may be attributed to the partial crystallinity possessed by P3HT chains which disperse within the domains of  $\text{TiO}_2$  in film. The XRD patterns indicate that the blend film with 5%  $\text{TiO}_2$  shows the highest value of intensity peak. This may attribute to the incorporation of optimum amount of  $\text{TiO}_2$  nanocrystals into polymer that has significantly enhanced the crystallinity of the film. However, the excess  $\text{TiO}_2$  content in film may destruct the ordering of the P3HT chain, causing a decreased XRD intensity. The crystal peaks of  $\text{TiO}_2$  in powder form are confirmed by XRD pattern shown in the inset of Figure 2. For  $\text{TiO}_2$ , the major phase is rutile phase ( $27.5^\circ$ ,  $36.0^\circ$ ,  $41.2^\circ$ ,  $44.1^\circ$ ,  $54.2^\circ$ , and  $56.8^\circ$ ), with the minor anatase phase ( $25.2^\circ$ ,  $37.9^\circ$ , and  $48.0^\circ$ ). The diffraction peak at  $2\theta \approx 41.2^\circ$  shows the highest intensity, which corresponds to the (111) plane of the  $\text{TiO}_2$  structure. Our XRD result of  $\text{TiO}_2$  nanocrystal is in agreement to the other reports (Wang et al. 2009).

The effect of blend composition on the surface morphology of the atomic force microscopy (AFM) images of the pure P3HT,  $\text{TiO}_2$  and P3HT: $\text{TiO}_2$  blend films (here, only blend with 5%  $\text{TiO}_2$  and 10%  $\text{TiO}_2$  are displayed) are shown in Figure 3 (on the left). The root-mean-square (rms) roughness of the pure P3HT,  $\text{TiO}_2$  and blend films with 5%  $\text{TiO}_2$ , 10%  $\text{TiO}_2$ , 15%  $\text{TiO}_2$ , and 20%  $\text{TiO}_2$  are  $(10.6, 7.7, 6.5, 10.1, 25.3, \text{ and } 33.2) \pm 0.1$  nm respectively. Upon blending the P3HT with  $\text{TiO}_2$ , phase separation occurs between the donor and acceptor phase in film, leading to the formation of continuous pathways for charge carrier, and thus increases the interfacial area for the exciton dissociation process. However, the excess  $\text{TiO}_2$  content may lead to the decrease of the P3HT content, forming more  $\text{TiO}_2$ -rich phases (such as blend

with 10%  $\text{TiO}_2$ ) in film that give rise to a larger scale phase separation, and destroy the interpenetrating pathways for hole transport of the polymer P3HT (Kwong et al. 2004b; Yu et al. 2008). It can be proven by the coarser surface morphology possessed by the blend films with higher  $\text{TiO}_2$  content, as the rms roughness value increases from  $(6.5 \text{ to } 33.2) \pm 0.1$  nm.

These results are further supported by the selected scanning electron microscopy (SEM) images of the blend films, as shown in Figure 3(b). The bright areas of the SEM images in Figure 3(b) are interpreted as the  $\text{TiO}_2$  nanocrystals and the darker areas as polymer soft material. The  $\text{TiO}_2$  nanocrystals are randomly distributed in polymer matrix forming an interconnected network. The coarse phase separation can be clearly seen for film with higher  $\text{TiO}_2$  content, which may deteriorate the device performances.

Figure 4 shows the current density-voltage (J-V) characteristic curves and device parameters of the short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and power conversion efficiency (PCE) values of the solar cells that corresponding to the pure P3HT and P3HT: $\text{TiO}_2$  blend film with 5%  $\text{TiO}_2$  as tabulated in Table 1. The  $J_{sc}$  of the device made of pure P3HT is  $0.015 \text{ mA/cm}^2$ , the  $V_{oc}$  is  $0.043 \text{ V}$ , and the FF is 0.27 to produce a PCE of 0.17%. The device for blend film with 5%  $\text{TiO}_2$  performs a better  $J_{sc}$  of  $0.059 \text{ mA/cm}^2$  and the  $V_{oc}$  is  $0.088 \text{ V}$ , and thus the corresponding PCE increases to 1.35%. The improvement of the device efficiency is attributed to the formation of nice carrier transport network in the blend film. Further increase of  $\text{TiO}_2$  in the films will deteriorate the device performances deteriorate, which may due to the poor surface morphology of the blend films.

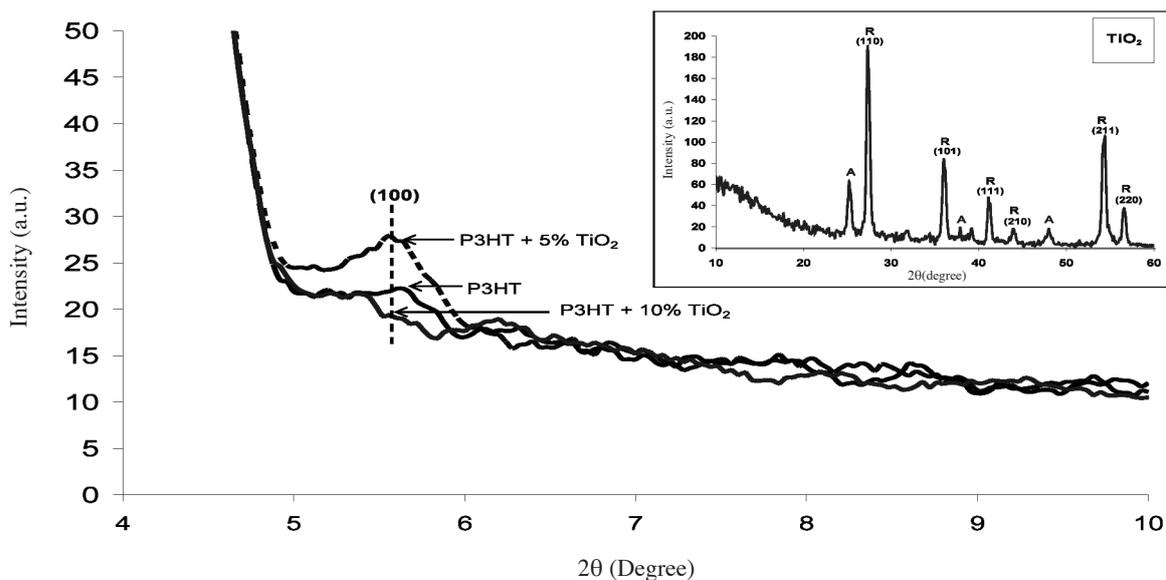


FIGURE 2. X-ray Diffraction of pure P3HT and P3HT: $\text{TiO}_2$  blend films with 5%  $\text{TiO}_2$ . The inset shows the XRD pattern of the  $\text{TiO}_2$  nanocrystals in powder form

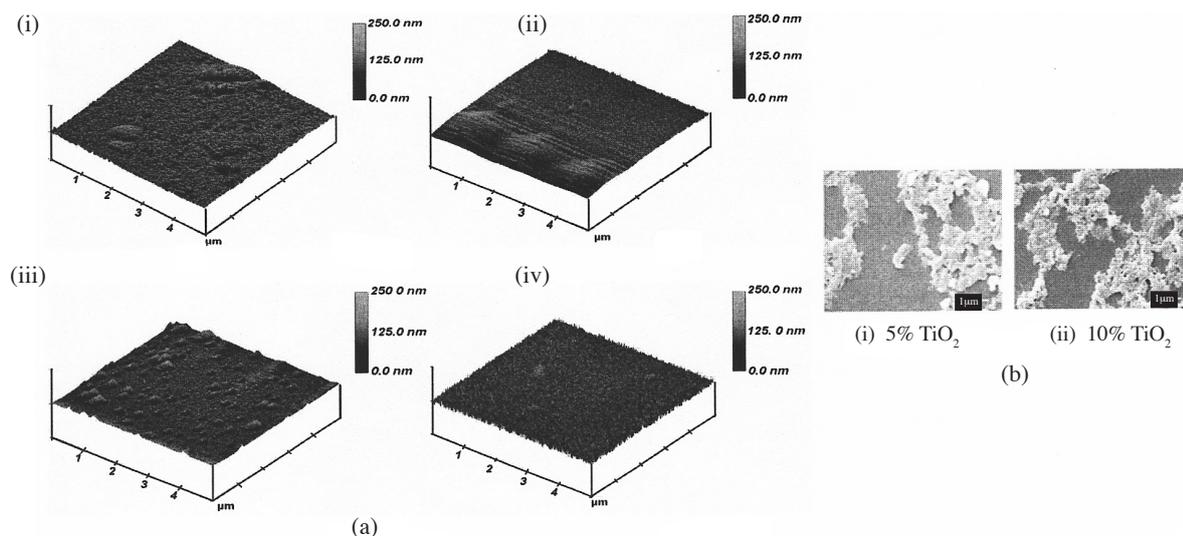


FIGURE 3. (a) 3D atomic force microscopy images of (i) pure P3HT, (ii)  $\text{TiO}_2$ , (iii) P3HT: $\text{TiO}_2$  blend film with 5%  $\text{TiO}_2$ , and (iv) blend film with 10%  $\text{TiO}_2$ ; (b) SEM images of (i) blend film with 5%  $\text{TiO}_2$  and (ii) blend film with 10%  $\text{TiO}_2$

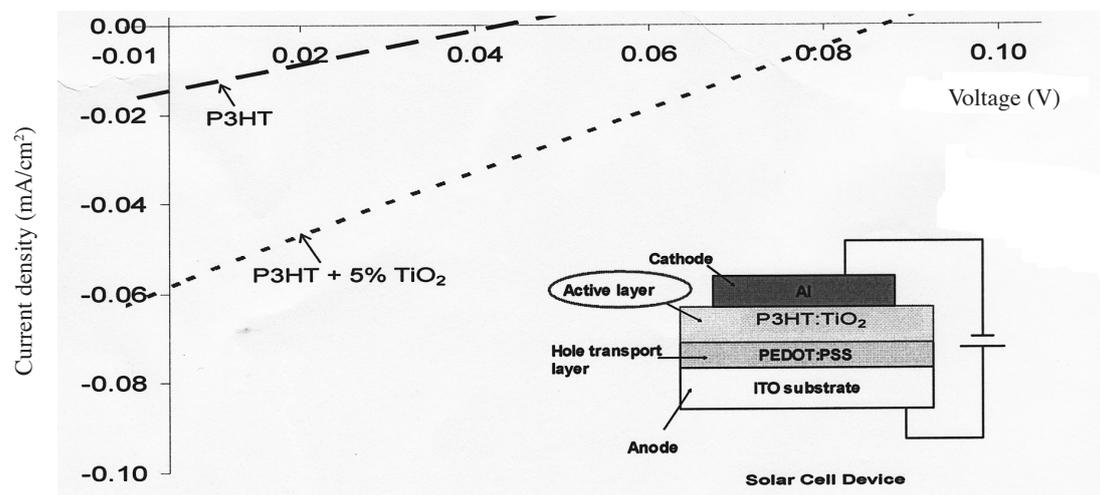


FIGURE 4. J-V plots for pure P3HT and P3HT blend with 5%  $\text{TiO}_2$  solar cells. The inset shows the structure of solar cell device

TABLE 1. The comparison of device characteristics parameters for pure P3HT and P3HT: $\text{TiO}_2$  solar cells with 5%  $\text{TiO}_2$

	P3HT	P3HT+5% $\text{TiO}_2$
$V_{oc}$ (V)	0.043	0.088
$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	0.015	0.059
$V_{max}$ (V)	0.019	0.044
$J_{max}$ ( $\text{mA}/\text{cm}^2$ )	0.009	0.031
FF	0.27	0.26
PCE (%)	0.17	1.35

## CONCLUSIONS

This study shows that the optical, morphological and electrical properties of P3HT: $\text{TiO}_2$  solar cells can be significantly affected by the blend composition. We noted that the performance of the devices are significantly

dependent on the charge transport properties of the blends as well as their surface morphology. The incorporation of optimum amount of  $\text{TiO}_2$  into polymer P3HT may aid in enhancing the crystallinity and providing a more continuous, efficient pathways for charge transport. Hence, the device performance can be improved. We found that the optimum  $\text{TiO}_2$  content is 5% with the power conversion efficiency of the solar device is 1.35%. However, the excess amount of  $\text{TiO}_2$  in blend may destroy the interpenetrating pathways for charge transport properties of the P3HT that lead to the deterioration of solar cell performances.

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