The influence of the composition of P3HT:TiO$_2$ on the characteristics of hybrid polymer solar cell

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Abstract. In this paper, a study on the fabrication of hybrid polymer solar cells based on organic semiconductor materials P3HT (poly-3-hexylthiophene) and inorganic semiconductor materials TiO$_2$ (titanium dioxide) has been carried out. The study is focused on the influence of the composition of P3HT and TiO$_2$ on the optical and electrical characteristics of hybrid polymer solar cells. The composition of P3HT and TiO$_2$ are varied with ratios of (1:1), (2:1), and (1:2), respectively, in a concentration of 10 mg/ml. The optical characterization using a UV-Vis spectrometer shows that the higher absorption of the active layer results from the (1:1) ratio of P3HT:TiO$_2$. Based on the electrical characterization, using solar simulator on hybrid polymer solar cells, can be concluded that a mass ratio of P3HT:TiO$_2$ (1:1) gives the best performance, with an open-circuit voltage of 0.2437 volts, a short-circuit current of 0.0029 milliamperes, a maximum power of 0.0002 milliwatts, and a power conversion efficiency of 0.00006%, at the light intensity of 500 W/m$^2$.

1. Introduction
Polymer-based solar cells could be good candidates for the next generation of the photovoltaic device due to their various advantages particularly such as low cost and excellent mechanical property. Polymeric materials could be deposited by the solution-based technique or electrochemical polymerization onto printable, flexible and large-scale film, promising for various applications and commercialization of solar cells [1]. However, the disadvantages of polymer solar cells are seriously hindering their performance as follows (i) the poor spectral match between the absorption of the polymer layer and the solar emission results in relatively low current density and energy conversion efficiency; (ii) the extremely large binding energy of photogenerated quasi-one-dimensional excitons (0.4 eV) in conjugated polymers makes direct dissociation of excitons into free carriers very inefficient; (iii) the short diffusion length of 10 nm leads to high recombination, low photocurrents and energy conversion efficiency; (iv) the conversion efficiency is also limited in single layer diodes by the surface of the electrode/polymer contact where the local electric field induces charge separation; (v) allow resistance towards oxygen, high temperature and UV light, etc. causes poor stability and degradation [1].

One promising alternative approach to overcome the problems is to use a nanostructured inorganic semiconductor as the electron-transport component. Electron-transporting metal oxide such as
titanium dioxide (TiO$_2$), tin oxide (SnO$_2$), and zinc oxide (ZnO) is attractive materials in this content on account of their low cost, good stability, ease of fabrication, and their potential that exists for controlling their film morphology on the nanoscale [2].

Hybrid polymer-inorganic solar cells offer the opportunity to combine the beneficial properties of the two materials in charge generation and transport with easy and cheap processing in large areas [3]. The use of two materials with complementary donor and acceptor electronic properties is crucial to the operation of the hybrid polymer solar cell, because photoexcitation of a conjugated polymer provides a bound electron-hole pair or exciton rather than free charges. This exciton can be dissociated efficiently at the interface with a second material via a hole or electron transfer to produce the free charges that generate the photovoltaic effect [4-5]. Compared to organic-fullerene cells, hybrid polymer solar cells may have the advantages of being morphologically more stable and being able to utilize the high charge carrier mobility of the inorganic material. Of course, the challenges for hybrid polymer solar cells remain to create a morphology in which the inorganic and polymeric materials are intimately mixed on a nanometer scale but with continuous phases [4]. In recent years, various solution processed bulk heterojunction hybrid polymer solar cells have been explored [6]. Many of these methods aim at creating an intimately mixed bulk-heterojunction microstructure of the two materials on a nanometer scale, ensuring efficient charge generation at the interface and effective percolating pathways for photogenerated electrons and holes to the electrodes [3].

Poly(3-hexylthiophene) or P3HT is a conjugated polymer with a band-gap of approximately 1.9 eV, and now often used as an active layer for polymer solar cells [7]. The highest efficiency of bulk-heterojunction structure of polymer solar cells was made with P3HT as the donor electron [8]. TiO$_2$ is an acceptor because it has a high absorption coefficient and size-tunable [9]. It was also reported that addition of titanium dioxide (TiO$_2$) could not only significantly improve the stability of devices composed of P3HT but also enhanced the charge transfer and thus the efficiency of hybrid solar cells [10]. In this research, hybrid polymer solar cells based on P3HT and TiO$_2$ has been fabricated. In order to obtain the optimum separation of exciton and charges transfer, it is needed to adjust donor/acceptor ratio. Therefore, the research was focused on the variation of P3HT and TiO$_2$ ratios. The correlation between P3HT:TiO$_2$ ratios on the optical and electrical characteristics of the cells under air mass 1.5 illuminations at a light intensity of 500 W/m$^2$ were investigated.

2. Method

Hybrid polymer solar cells were fabricated with the structure of PET/ITO/PEDOT:PSS/P3HT:TiO$_2$/Al/PET. The fabrication process consists of several steps, i.e. ITO etching, PEDOT:PSS spin coating, P3HT:TiO$_2$ spin coating, aluminum evaporating, cells lamination, and characterization.

2.1. ITO etching

The substrate used is an ITO coated PET with a sheet resistance of 60 Ω/square. ITO is a transparent conductive oxide which serves to drain the generated hole. In order to avoid a short circuit of the cell, the ITO pattern was etched partially. A black paint is sprayed on the ITO surface which has been patterned by adhesive tape mask previously. The substrate is then dried in room temperature overnight, and when it has dried the mask is removed. The next step is an etching process which aims to eliminate undesired ITO layer. The etching process is performed by dipping the substrate into 50% HCl solution for 5 minutes. After the undesired ITO layer has disappeared, the substrate is washed in DI water and dried. The remaining paint then removed by immersing the substrate into thinner solution, isopropyl alcohol, and DI water, respectively, for 10 minutes in the ultrasonic bath.

2.2. PEDOT:PSS spin coating

PEDOT:PSS is used as hole transporter and to prevent the diffusion of ITO into the active layer of the solar cell. The spin coating process of PEDOT:PSS is performed by dripping a PEDOT:PSS solution on ITO surface which has been covered with adhesive tape previously as PEDOT:PSS mask pattern
and then rotated at 1000 rpm for 60 seconds. The PEDOT:PSS layer is then dried in a vacuum oven at 120°C for 60 minutes.

2.3. P3HT:TiO2 spin coating
The mixture of P3HT:TiO2 serves as an active layer of the solar cell, so the fusion of these two materials greatly influences the optical and electrical characteristics of solar cells. The mixtures were varied in (1:1), (2:1), and (1:2) ratios, respectively, in a constant concentration of 10 mg/ml. The mixtures were spin coated on PEDOT: PSS layer that have been covered with the masking tape. The spin coating process was done on 1000 rpm for 1 minute. The dried layer is then annealed in a vacuum oven at 120 °C for 10 minutes.

2.4. Aluminum evaporating
Aluminum (Al) layer serves as a cathode in hybrid polymer solar cell devices. The aluminum layer is grown on the surface of the P3HT:TiO2 using shadow mask patterns. The evaporation process is done until the chamber pressure of 5 x 10^{-5} mBar and takes place for 5 minutes to produce an aluminum layer with a thickness of 60 nm.

2.5. Lamination
Lamination process aims to protect the cell from the outside air and moisture. Before laminated, two tabbing wires with 15 mm long are attached to ITO and Al electrodes respectively using Ag paste glue as the external contacts for I-V characterization. The lamination process is done by attaching thermoplastic sealant between device and PET and then clamped using two glasses on both sides. Finally, it is heated in a vacuum oven at 100 °C for 10 minutes.

2.6. Characterization
Measurement of the electrical characteristics of the cells was performed by illuminating the cells under AM 1.5 solar spectrum of Oriel solar simulator using a xenon lamp, which is equipped with National Instrument I-V measurement systems at the light intensity of 500 W/m². Characterization of optical properties is carried out using UV-Vis spectrometer, whereas the active layer surface observation is performed using scanning electron microscope (SEM).

3. Result and Discussion
Figure 1 shows 20,000X magnification SEM photographs of surface morphologies of P3HT and TiO2 in ratios of (1:1), (2:1), and (1:2), respectively.

![Figure 1](image)

**Figure 1.** SEM photographs of surface morphologies of P3HT and TiO2 in ratios of 2:1 (a); 1:1 (b); and 1:2 (c).

Based on the results of SEM, the active layer of each sample showed a different morphology. On the entire surface of the layers shows agglomerate structures. The agglomerates may be formed from TiO2 nanoparticles which covered by the P3HT film. Although TiO2 used in this research has a particle size of 25 nm (Aldrich P25), but the distribution of the TiO2 nanoparticles in the P3HT film is not fully
spread. Thus, agglomeration forming cannot be avoided. It is also reported by Yu et al, that the size distribution of the inorganic nanoparticles in the active layer has not been precisely controlled [10]. In the ratio of P3HT:TiO$_2$ (2:1), a smaller agglomerates structure obtained, indicates the most porous surface. The porous surface will cause high absorption of light. In the surface of (1:1) and (1:2) ratios, the structures obtained are relatively similar. The surfaces were formed a larger agglomerates. 

Characterization results of an optical property of hybrid polymer solar cells based on P3HT:TiO$_2$ using UV-Vis spectroscopy are shown in figure 2.

![Figure 2. The absorption spectrum of the active layer varying ratios of P3HT:TiO$_2$.](image)

In figure 2, note that P3HT:TiO$_2$ ratios of (2:1), (1:1), and (1:2) are resulting the similar spectrum in the visible. The maximum peak of the (2:1) ratio is higher compared to (1:1) and (1:2) ratios, in the range of 465-590 nm. However, in the range of 400-465 nm and 590-800 nm, (1:1) ratio has higher absorption, and the average absorption of (1:1) ratio is equal to the (2:1) ratio, which is around 0.4 au. According to the standard spectrum, pure P3HT show strong absorption in the visible wavelength range of 450-650 nm, while pure anatase TiO$_2$ absorbs light in the ultraviolet wavelength range of 200-300 nm [11]. The addition of TiO$_2$ is decreasing the absorption of P3HT and shifts the maximum peak to the shorter wavelength. Kim et al reported that the addition of excess TiO$_2$ into P3HT provides the results for phase separation of larger scale and damages the structure of P3HT chains [12]. The same results were also confirmed by Yun and Sulaiman which showed that the addition of TiO$_2$ in the active layer interferes intermolecular structure of P3HT chains which can reduce the absorption of light contributed by P3HT in the visible wavelength range [11]. This is caused by a reduction in the volume occupied by the benzene ring of the P3HT polymer in the mixed film.

Regarding light absorption by P3HT and charge transport by TiO$_2$, if P3HT is higher than TiO$_2$, more light will be absorbed, and more exciton will be generated. However, at same the time, the electron charge transport towards the cathode will be decreased because of the number of electrons produced is not proportional to the amount of TiO$_2$ particles. The generated electrons will recombine partially and only small portion of electrons will reach the cathode. Conversely, if TiO$_2$ is higher than P3HT, then the exciton will be less generated. As the consequence, free charges will be less generated, although there are many numbers of TiO$_2$ particles, only a few charges are transported toward the cathode. By using a balanced ratio of (1:1) may be the problem above can be improved, although there is a risk of reduction on the light absorbed by P3HT. This can be seen from the absorption spectrum of the (1:1) ratio, although the light absorption in the range of 465-590 nm is lower than the (2:1) ratio, but the absorption in the range of 400-465 nm and 590-800 nm is higher than that of the (2:1) ratio. Although the average absorption of the (1:1) ratio is equal to of the (2:1) ratio, the spectrum of the
(1:1) ratio is broader than that of (2:1) ratio. Therefore, the (1:1) ratio will result in the generation and separation of exciton more efficiently than the others into electrons and holes free-charge.

Table 1 shows electrical characteristics of hybrid polymer solar cell based on P3HT:TiO$_2$. These data are the results from the calculation of the I-V curve using Labview software facilitated by National Instrument.

**Table 1.** The electrical characteristics of hybrid polymer solar cells based on P3HT:TiO$_2$ by measuring under light intensity conditions of 500W/m$^2$ at room temperature.

| Electrical Characteristics       | P3HT:TiO$_2$ Ratios |
|----------------------------------|---------------------|
|                                 | (2:1)              | (1:1)              | (1: 2)              |
| Open-circuit voltage ($V_{oc}$)  | 0.1615 V           | 0.2437 V           | 0.1211 V            |
| Short-circuit current ($I_{sc}$)  | 0.0020 mA          | 0.0029 mA          | 0.0019 mA           |
| Maximum power ($P_m$)  | 0.0001 mW          | 0.0002 mW          | 0.00004 mW          |
| Power conversion efficiency (PCE) | 0.00002%         | 0.00006%          | 0.00001%           |

From the table, hybrid polymer solar cells using P3HT: the TiO$_2$ ratio of (1:1) gives better electrical characteristics than the others. The (1:1) ratio has an open-circuit voltage of 0.2437 volts, a short-circuit current of 0.0029 milliamperes, a maximum power of 0.0002 milliwatts, and a power conversion efficiency of 0.00006%.

In general, the fabricated cells have low electrical characteristics especially in short-circuit current ($I_{sc}$) and open-circuit voltage ($V_{oc}$). The short-circuit current generated only reach the order of microampere. As a result, the maximum power generated is also reaching the order of microwatt, and the efficiency as well. The photocurrent that is extracted from the solar cell at under short-circuit condition can be affected by several factors [13]. Foremost of them is the light absorption of the active layer and hence the thickness of the film. The absorption of the entire film determines the short-circuit current. However, an optimization of the active layer thickness is also needed. A thicker film result in the lower electric field and charge collection, hence lower short circuit current [13].

The next factor is morphology, the interpenetrating network of polymer donor and inorganic acceptor which determines how easily the exciton gets separated before geminate recombination takes place [12]. In this study, the existence of agglomerates (as seen in the SEM picture) may result in recombination and also, cause external light scattering. Processing parameters such as the choice of solvent, spin speed, and annealing treatment also play key roles in determining the film morphology [14].

Polymer solar cells are highly susceptible to degradation. Degradation processes involving oxygen which is then bonded to the carbon most tip of the alkyl chain P3HT. Then the bond forming reactions will indirectly interfere with the conjugation of P3HT backbone [15]. Environmental condition around the moist sample also causes the penetration of the free molecules to the devices. In addition, the degradation of the devices could be caused by the diffusion of aluminum as electrodes into the active layer, so that the possibility of leakage currents and high resistance [16].

4. Conclusions

Hybrid polymer solar cells based on P3HT and TiO$_2$ with the configuration of PET/ITO/PEDOT:PSS/P3HT:TiO$_2$/Al/PET have been fabricated. The ratio of the P3HT:TiO$_2$ active layer affects the optical and electrical characteristics of polymer solar cells. A (1:1) ratio of P3HT:TiO$_2$ gives the best performance, with an open-circuit voltage of 0.2437 volts, a short-circuit current of 0.0029 milliamperes, a maximum power of 0.0002 milliwatts, and a power conversion efficiency of 0.00006%.

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