

Methodology Report

Polymer Photovoltaic Cell Using $\text{TiO}_2/\text{G-PEDOT}$ Nanocomplex Film as Electrode

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Using $\text{TiO}_2/\text{G-PEDOT}$ (PEDOT/PSS doped with glycerol) nanocomplex film as a substitute for metal electrode in organic photovoltaic cell is described. Indium tin oxide (ITO) worked as cathode and $\text{TiO}_2/\text{G-PEDOT}$ nanocomplex works as anode. The thickness of TiO_2 layer in nanocomplex greatly affects the act of this nonmetallic electrode of the device. To enhance its performance, this inverted organic photovoltaic cell uses another TiO_2 layer as electron selective layer contacted to ITO coated glass substrates. All films made by solution processing techniques are coated on the transparent substrate (glass) with a conducting film ITO. The efficiency of this solar cell is compared with the conventional device using Al as electrode.

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1. INTRODUCTION

Organic photovoltaic devices offer great technological potential as a renewable and alternative source of electrical energy. Efforts focusing on improving the efficiency of solar cell and reducing their manufacturing cost are going on. Among various thin film techniques, solution-processed organic photovoltaic cells have considerable potential for becoming a true low-cost technology since their production demand solution-based deposition methods. And it brings a brilliant prospect that large-scale plastic photovoltaic device will be produced by industrial technology, such as screen-printing, ink-inject, spin coating, or dip coating. In order to prepare organic solar cell by solution process, many methods are attempted to replace one of the electrodes by using polymer electrode [1–3]. Commonly, polymer solar cells are constructed by sandwiching an active layer between two coplanar electrodes [4–6]. The bottom electrode (anode) is usually made of a transparent substrate (glass) coated with a conducting film such as indium tin oxide (ITO). The upper electrode (cathode) is usually formed by vacuum deposition of low work function (WF) metals like aluminum (Al) and calcium (Ca) on top of the active layer.

Many efforts have been made to investigate polymer anode. So far, PEDOT/PSS is widely accepted as a good hole-conducting layer when used in photovoltaic devices. Moreover, various treatments can be employed

to enhance the quality of the surface morphology and conductivity of PEDOT/PSS layer [7, 8]. The conductivity of PEDOT/PSS could be enhanced by doping glycerol, sorbitol, DMSO and so on [9–11]. And these modified PEDOT/PSS have been successfully applied in polymer light-emitting devices and organic photovoltaic cells as electrodes to replace ITO to reduce the cost of devices [3, 12–14]. In this paper, we have explored another method to form organic photovoltaic cells. We use $\text{TiO}_2/\text{G-PEDOT}$ nanocomplex film in photovoltaic cells to displace metal electrode. The interests of using conductive polymer as electrode originate from its simple film-forming techniques. The conductive polymer in solution can be easily shaped into different geometric drawings, and after baking it becomes conductive film. The manipulation and equipment could be simplified since, rather than high-vacuum evaporation system, and the facility we need is an ordinary vacuum-annealing oven equipped with mechanism pump and heater only. Moreover, using polymer electrode to replace metal film is a useful attempt towards flexible plastic large-scale photovoltaic cells.

2. EXPERIMENTAL

The device architectures are shown in Figure 1. The structure of our solution-processed photovoltaic cell is

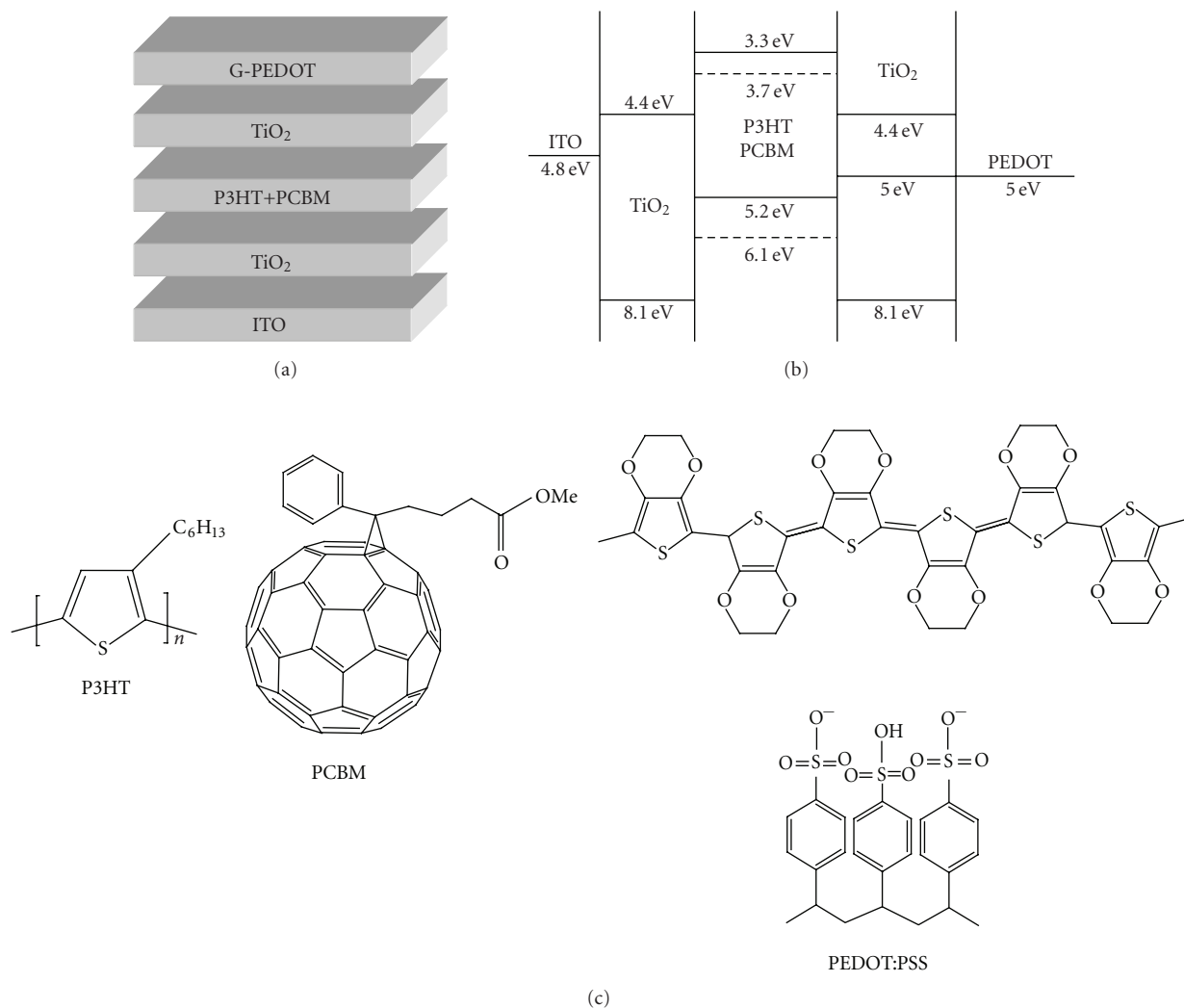


FIGURE 1: (a) The device structures of the solution processed photovoltaic cell. (b) The energy levels of the single components of photovoltaic cell. (c) Molecular structures of the active materials and conductive polymer: P3HT, PCBM, PEDOT:PSS.

ITO/TiO₂/P3HT + PCBM/TiO₂/G-PEDOT. TiO₂ sol-gel solution, which is described at the back of this part, was spin coated on a precleaned ITO glass substrate at 7000 rpm to form about 40 nm layer. Subsequently, during 5 minutes in wet air of about 80% relative humidity at room temperature, the precursor converted to TiO₂ by hydrolysis. Thin films of a blend of P3HT: PCBM with a weight ratio of 1 : 0.8 were spin coated at 1000 rpm from a 10 mg/mL methylbenzene solution and the thin film of TiO₂ is deposited again by spin TiO₂ sol-gel solution. Solid films are formed after 1-hour vacuum annealing at 80°C. At last, G-PEDOT is dropped on the device in order to form thick film. The layer of G-PEDOT is about 20 μm, which is semitransparent and conductive. The photovoltaic device was finished by vacuum annealing at 120°C for half an hour to remove solvent.

Current-voltage curves were recorded by Keithley 2410 source-measure unit. The photocurrent was obtained with Keithley 2410 unit by illumination with an intensity of 80 mW/cm² from an Xe lamp (71LX150). The photocurrent

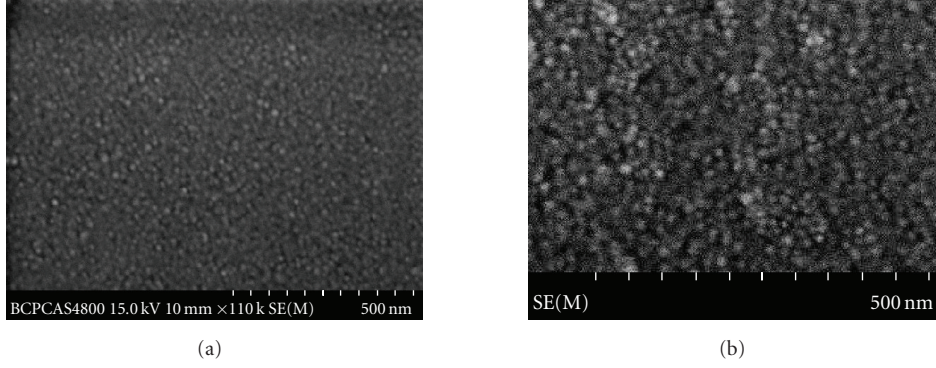
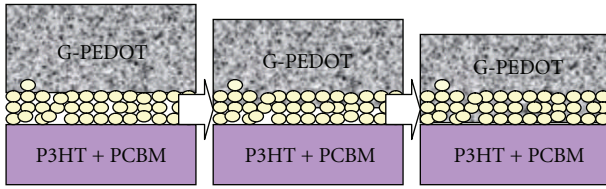
spectral responses were corrected according to the spectral distribution of the illuminating light.

The sol-gel procedure for producing TiO₂ is as follows: titanium isopropoxide (Ti[OCH(CH₃)₂]₄, 10 mL) was prepared as a precursor and mixed with ethanol (CH₃CH₂OH, 40 mL). Put the mixture into a conical flask. And then acetic acid (CH₃COOH, 4 mL) mixed with pure water (H₂O, 2 mL) was dropped into conical flask slowly. The mixed solution was under magnetic stirring for 2 hours. The sol-solution was formed after two days placed in a hermetic cuvette.

3. RESULTS AND DISCUSSION

3.1. TiO₂/G-PEDOT Nanocomplex Anode

The conductivity of PEDOT/PSS used in our device is enhanced by doping 6 wt% glycerol [15]. The surface sheet resistance of a 20-μm thick PEDOT:PSS film fabricated with this addition of 6 wt% glycerol is decreased to nearly 30 (Ω/

FIGURE 2: SEM image of TiO_2 film on ITO substrate.FIGURE 3: Illustration showing the forming process of $\text{TiO}_2/\text{G-PEDOT}$ nanocomplex electrode.

□). In our experiment process, there is a problem that G-PEDOT can hardly spread on P3HT:PCBM layer because of P3HT:PCBM layer's hydrophobic. TiO_2 layer was added to connect the two layers. It changes the P3HT:PCBM layer's surface into hydrophilic. The testing results show that PEDOT/PSS layer is used as anode. G-PEDOT layer is supposed to be cathode because TiO_2 is a perfect hole-blocking layer [16]. But the fact proves to be opposite. In order to testify the function of TiO_2 layer used in this place, a series of tentative experiments and tests have been done and a model of anode was elicited.

The surface of TiO_2 can be seen from Figure 2. Nano-size TiO_2 grains have been arranged compactly in a neat plane with porosity, which enables the electrolyte (G-PEDOT) to soak into the films slowly. The size of TiO_2 grain is about 20 nm. A schematic diagram (Figure 3), which is based on the SEM photo of TiO_2 , presented to demonstrate the forming of the nanocomplex electrode procedure. Firstly, G-PEDOT solution was laid down on TiO_2 -coated sheets to form the nanocomplex electrodes. G-PEDOT molecules then intruded in TiO_2 layer through the interstices slowly while solution was removed by vacuum heating. If the thickness of TiO_2 layer is appropriate, G-PEDOT molecules would finally go to the bottom of TiO_2 layer by the time the solution was completely removed and attach the surface of P3HT:PCBM film. Otherwise, if the thickness of TiO_2 layer is too thick, the interstices of TiO_2 layer would be partly filled by G-PEDOT.

A series of experiments showed that the appropriate thickness of TiO_2 layer is 90 nm. Accordingly, the device with appropriate thickness showed the highest performance (figure can be seen in Figure 4): $J_{sc} = 5.7 \text{ mA/cm}^2$ V_{oc}

$= 0.59 \text{ V}$ $FF = 0.33$ $\eta = 1.38\%$. On the other hand, the TiO_2 layer is partly filled by G-PEDOT and exhibits n -type character for some extend when the TiO_2 layer is too thick. The performance of device is reduced; $J_{sc} = 3.8 \text{ mA/cm}^2$ $V_{oc} = 0.44 \text{ V}$ $FF = 0.30$ $\eta = 0.64\%$. In addition, with decreasing the TiO_2 layer, performance of devices were then lessened at last, because the active layer is affected by G-PEDOT solution, when the TiO_2 layer is too thin.

In conclusion, the thickness of TiO_2 layer in nanocomplex anode greatly affects the performance of device, since the thickness of TiO_2 layer determined the form of $\text{TiO}_2/\text{G-PEDOT}$ nanocomplex. The introduced TiO_2 can connect two different components firmly just like ligament connecting bone and muscle. In other words, TiO_2 grains were embedded G-PEDOT and anchored it on the active layers.

3.2. Function of TiO_2 Contacted to ITO

It is known that TiO_2 layer is used as electron selective film to enhance the performance of organic photovoltaic cell [16]. And the TiO_2 layer which is contacted to ITO in inverted device also has the function of electron selection, which is the same case in our device [17].

From the data showed in Figure 5, it can be seen that without the TiO_2 layer connected to ITO, the device performance is low; $J_{sc} = 0.03 \text{ mA/cm}^2$ $V_{oc} = 0.22 \text{ V}$ $FF = 0.25$ $\eta = 0.0016\%$. By contrast, the device performance, which is using another TiO_2 layer contact to ITO anode, proved to be $J_{sc} = 5.7 \text{ mA/cm}^2$ $V_{oc} = 0.59 \text{ V}$ $FF = 0.33$ $\eta = 1.38\%$. Low performance is mainly due to the inefficiency of electron collection, since the work function of ITO is not suitable (the energy levels of the single components of photovoltaic cell are shown in Figure 1(b)). By adding TiO_2 film, the energy levels (demonstrated in Figure 1(b)) satisfy the electronic structure requirements. From what has been discussed above, we draw the conclusion that TiO_2 layer contacted to ITO is working as electron selective layer.

3.3. Devices Performance Comparison

To compare with performance of the all-solution-processed solar cell, the conventional device is prepared (structure:

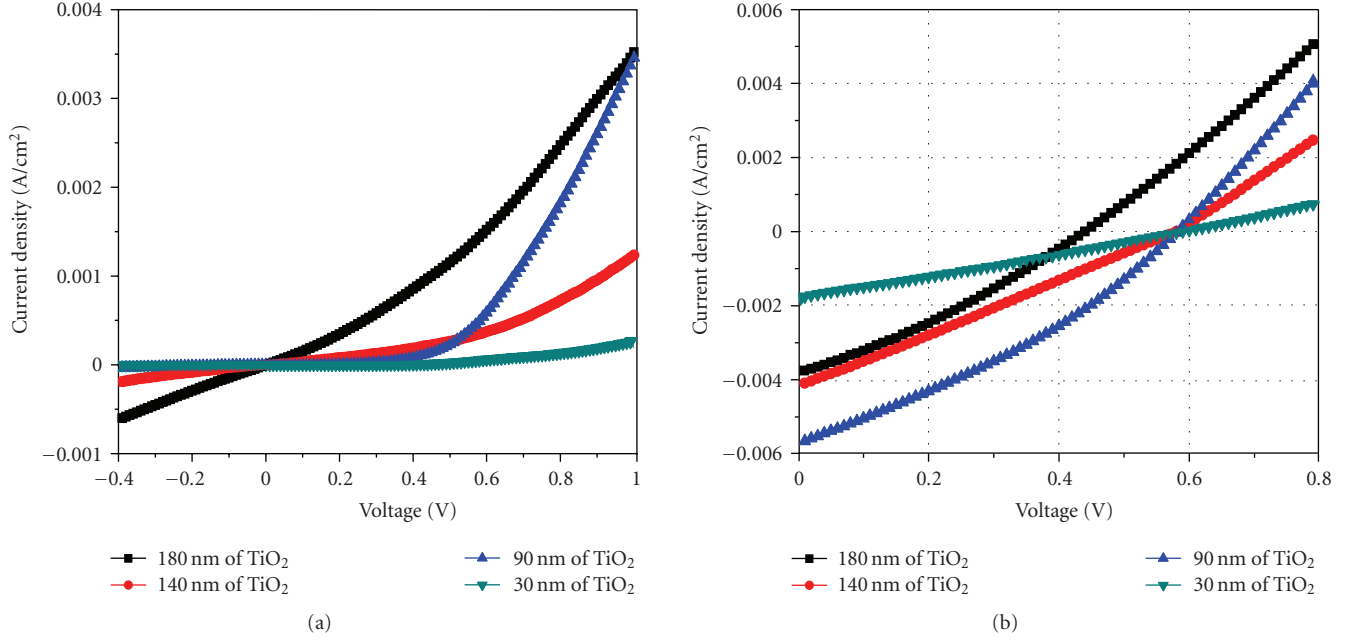


FIGURE 4: (a) I–V characteristics of device in dark condition used different thickness of TiO₂ to construct the TiO₂/G-PEDOT nanocomplex anode. (b) I–V characteristics measured under white illumination (Xe lamp, 80 mW/cm²). Devices' performance: (square) $J_{sc} = 3.8 \text{ mA/cm}^2$ $V_{oc} = 0.44 \text{ V}$ $FF = 0.30$ $\eta = 0.64\%$, (circles) $J_{sc} = 4.1 \text{ mA/cm}^2$ $V_{oc} = 0.59 \text{ V}$ $FF = 0.26$ $\eta = 0.78\%$, (up-triangle) $J_{sc} = 5.7 \text{ mA/cm}^2$ $V_{oc} = 0.59 \text{ V}$ $FF = 0.33$ $\eta = 1.38\%$, and (down-triangle) $J_{sc} = 1.78 \text{ mA/cm}^2$ $V_{oc} = 0.60 \text{ V}$ $FF = 0.26$ $\eta = 0.35\%$.

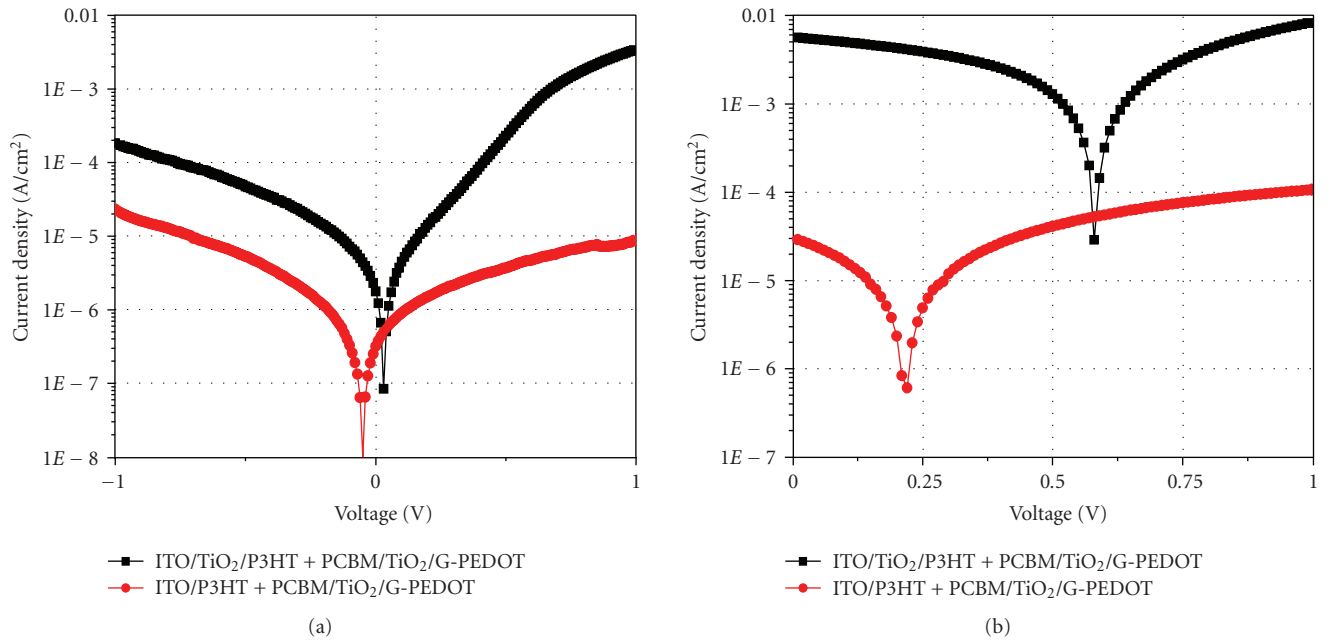


FIGURE 5: I–V characteristics of ITO/TiO₂/P3HT + PCBM/TiO₂/G-PEDOT (square) and ITO/P3HT + PCBM/TiO₂/G-PEDOT (circles). (a) I–V characteristics of device in dark condition. (b) I–V characteristics measured under white illumination (Xe lamp, 80 mW/cm²). Devices' performance: (square) $J_{sc} = 5.7 \text{ mA/cm}^2$ $V_{oc} = 0.59 \text{ V}$ $FF = 0.33$ $\eta = 1.38\%$, (circles) $J_{sc} = 0.03 \text{ mA/cm}^2$ $V_{oc} = 0.22 \text{ V}$ $FF = 0.25$ $\eta = 0.0016\%$.

ITO/PEDOT/P3HT: PCBM/TiO₂/Al, the active layer is annealed 1 hour at 80°C and then at 120°C for half an hour in vacuum). The open-circuit voltage (V_{oc}) and the short-current density J_{sc} measured from the conventional device were 0.58 V and 6.5 mA/cm². In contrast, I–V

characteristics of device with TiO₂/G-PEDOT nanocomplex anode is $V_{oc} = 0.58 \text{ V}$, $J_{sc} = 5.7 \text{ mA/cm}^2$ (as shown in Figure 6). And the efficiency η is 1.38%, compare to the efficiency of conventional device 1.5%. In addition, the result of IPCE (incident photon to collected electron efficiency)

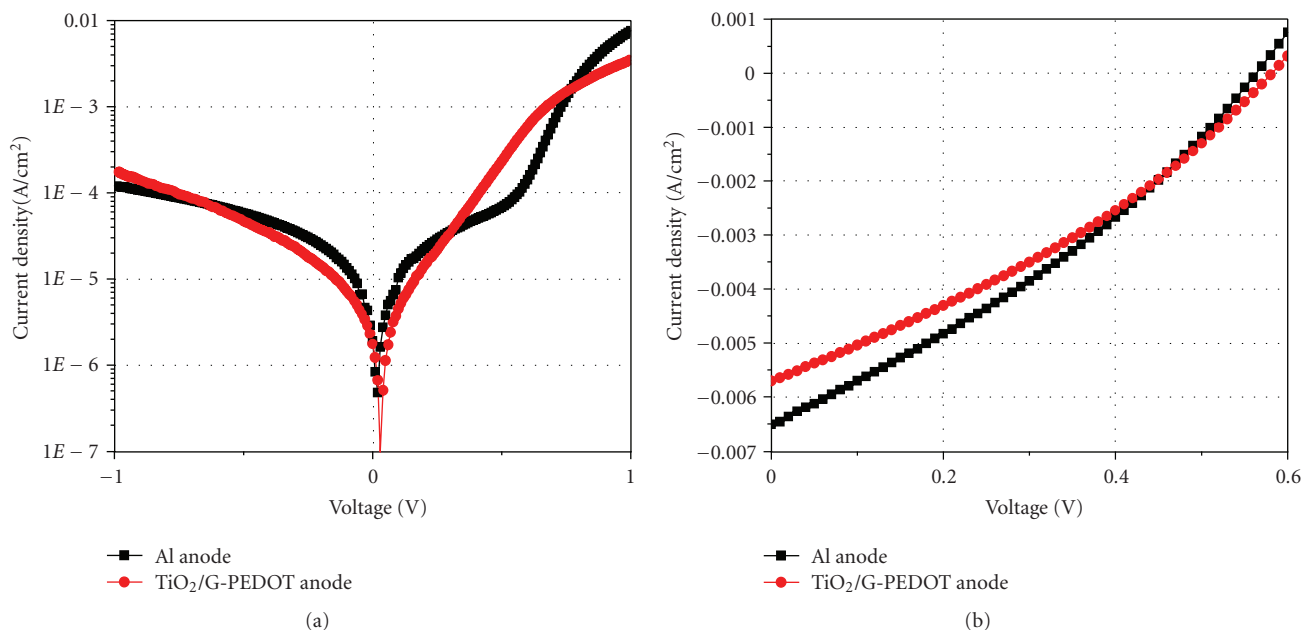


FIGURE 6: I–V characteristics of ITO/PEDOT/P3HT + PCBM/TiO₂/Al (square), and ITO/TiO₂/P3HT + PCBM/TiO₂/G-PEDOT (circles). (a) I–V characteristics of device in dark condition, (b) I–V characteristics measured under white illumination (Xe lamp, 80 mW/cm²). Devices' performance: (square) J_{sc} = 6.5 mA/cm² Voc = 0.58 V FF = 0.32 η = 1.5%, (circles) J_{sc} = 5.7 mA/cm² Voc = 0.59 V FF = 0.33.

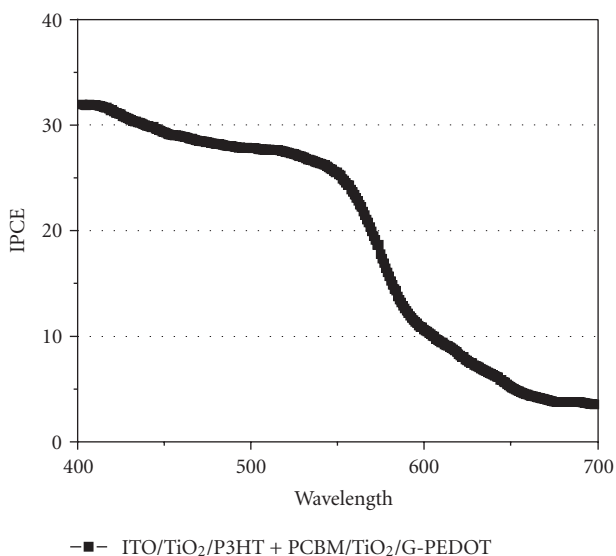


FIGURE 7: IPCE of device used TiO₂/G-PEDOT nanocomplex as anode.

(showed in Figure 7), measurements of the device used TiO₂/G-PEDOT nanocomplex anode shows a maximum of 32.4% at wavelength of 400 nm.

From the data discussed above, we can see that the efficiency of our inverted device almost reaches the level of the conventional device. And the performance of this kind of solar cells is comparable to the device using Al as electrode.

4. CONCLUSION

In summary, compared with common conductive metal, TiO₂/G-PEDOT nanocomplex can be an interesting alternative electrode applied in organic solar cell. The thickness of TiO₂ layer in nanocomplex greatly effects the performance of device. The other TiO₂ layer contacted to ITO works as an electron collection layer to improve the performance of device. The efficiency of photovoltaic devices with polymer anode is comparable to that of conventional devices using Al as electrodes.

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