

Effect of Temperature and Light Intensity on the Performance of Polymer/Fullerene Solar Cells with Titanium Dioxide Nanolayers

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In this work, alternative architecture for polymer/fullerene solar cells has been explored using titanium dioxide nanolayers which invert the polarity of the cell and may relax the necessity to have a hole-collecting buffer layer poly(styrene sulfonate)-doped poly(ethylene dioxy-thiophene) (PEDOT:PSS). This work particularly focuses on the performance of the inverted devices with dense TiO₂ nanolayers as a function of temperature, illumination intensity and time. We find that both temperature and illumination intensity slightly influence the power conversion efficiency of devices with the PEDOT:PSS layer. However, the inverted solar cells without the PEDOT:PSS layer showed very different characteristics regarding the power conversion efficiency which increased significantly with the operating temperature from 30 °C to 65 °C. This was attributed to a consequence from the strong and positive temperature dependence of open-circuit voltage which may be due to a “kink” in the current–voltage characteristics near the open-circuit voltage.

Keywords:

1. INTRODUCTION

Solar cells made from conjugated polymers and fullerene derivatives are promising candidates for photovoltaic conversion due to their mechanical flexibility, light weight, ease of processability and low cost fabrication of large areas.^{1–5} Of various combinations, devices made using blend films of poly(3-hexylthiophene) (P3HT) and soluble fullerene derivative ([6,6]-phenyl-C₆₁-butyric acid methyl ester) (PCBM) deliver reproducible high efficiency >4%, which typically have poly(styrenesulfonate)-doped poly(ethylenedioxythiophene) (PEDOT:PSS) as a hole-collecting buffer layer. However, these solar cells suffer from degradation due to the PEDOT:PSS layer which oxidizes the active material. Alternative architectures for P3HT:PCBM solar cells, which relax the necessity for the PEDOT:PSS layer, are thus become a preferred option.

The P3HT:PCBM incorporated with nanolayers of metal oxides is one such alternative. In these solar cells, the polarity is reversed as compared to the conventional P3HT:PCBM solar cells and are referred to as inverted solar cells. When comparing the P3HT:PCBM solar cell

with the hybrid TiO₂/polymer solar cells, the lower interfacial site is a disadvantage for the latter, but the slower recombination is an advantage.⁶ It may be therefore possible to have the merits of both of these TiO₂:P3HT and P3HT:PCBM in the TiO₂ incorporated P3HT:PCBM inverted solar cell. The charge carrier recombination may be even slower in the inverted solar cells because of the two-step charge carrier separation. Hole blocking is another added advantage offered by the dense TiO₂ nanolayer which enhances the charge transport in the inverted solar cells. Moreover, the TiO₂ nanolayer is an excellent electron transporting non-toxic material which possesses potential for controlling interface morphology, mechanical and chemical stability.⁷

In this work we study the influence of the temperature, illumination intensity and time on the solar cell parameters of the TiO₂/PCBM:P3HT inverted solar cells with or without the PEDOT:PSS nanolayer. A striking feature with the inverted devices without the PEDOT:PSS layer is that the power conversion efficiency depends on a distorted feature in the current–voltage characteristics near the open-circuit voltage. We discuss the possible origin of this so-called “kink” and how it controls the power conversion efficiency.

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2. EXPERIMENTAL DETAILS

Indium-tin oxide (ITO)-coated glass substrates ($\sim 25 \text{ } \Omega/\text{cm}^2$) were first cleaned several times thoroughly in acetone and isopropanol and then annealed to remove any organic residue. They were then blown with nitrogen gas. To prepare the dense TiO_2 nanolayer, precursor solution was prepared using titanium isopropoxide and acetylacetonone as described in the Ref. [8] for the hole blocking purpose. A dense layer of TiO_2 was made on the ITO glass using the spray pyrolysis technique and sintered at $450 \text{ }^\circ\text{C}$ for 30 minutes. Blend solutions were prepared with P3HT and PCBM, purchased from Merck Chemicals Ltd, with a 1:1 weight ratio in chlorobenzene at a solution concentration of 25 mg/ml . These solutions were vigorously stirred for more than 24 hours to maximize mixing. The blend solution of P3HT:PCBM was then spin-coated onto this substrate (1250 rpm) after which the films were annealed at $120 \text{ }^\circ\text{C}$ for 120 minutes in an N_2 environment. Some of the devices were with PEDOT:PSS layer onto this substrate. To make the PEDOT:PSS layer, the aqueous solution of PEDOT:PSS (Baytron) after filtering through a $0.45 \text{ } \mu\text{m}$ filter was heated at $90 \text{ }^\circ\text{C}$ for 5 minutes. It was then spin-coated at 4000 rpm . The substrates were again baked at $100 \text{ }^\circ\text{C}$ for another 5 minutes in the nitrogen environment. Finally, gold top contact was made by thermal evaporation at a pressure better than $5 \times 10^{-6} \text{ Torr}$. After that they were annealed at $120 \text{ }^\circ\text{C}$ for 10 minutes in a home-built annealing box filled with nitrogen. The current–voltage (I – V) measurements (using a Keithley 2400 source meter) of these photovoltaic devices were carried out in a closed cycled cryostat using He gas and in a furnace both in the dark and illumination under white light.

3. RESULTS AND DISCUSSION

Figure 1 shows that the current density–voltage (J – V) characteristics of an inverted device without PEDOT:PSS (ITO/dense TiO_2 /PCBM:P3HT/Au) in a temperature range varying from $30 \text{ }^\circ\text{C}$ to $75 \text{ }^\circ\text{C}$ prominently differ from the other solar cells in that a ‘kink’ exhibited in the vicinity of the open-circuit voltage, V_{OC} . In this vicinity, the slope of the J – V curve for voltages less than V_{OC} ($V_{\text{OC}} - \Delta V$, infinitesimal ΔV is assumed to be positive) is very sensitive to both the temperature and intensity, compared to for voltages greater than V_{OC} . It should be noted that the inverse of the slope represents series resistance and it follows that the series resistance shifted to a higher value when the applied voltage passed the V_{OC} from $V_{\text{OC}} - \Delta V$ to $V_{\text{OC}} + \Delta V$. The kink cannot be claimed as specific to these types of devices only, but has already been observed in hybrid metal oxide/polymer solar cells and multilayer molecular film copper phthalocyanine (CuPc)/C60 solar cells^{9,10} when there is an energy step at polymer/top contact or bottom contact/copper phthalocyanine (CuPc),⁹

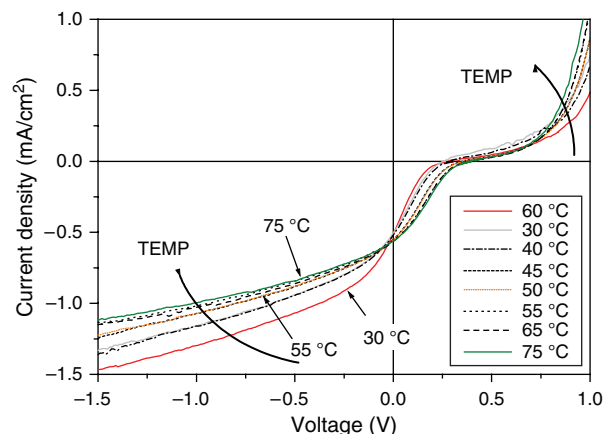


Fig. 1. Current–voltage characteristics of ITO/dense TiO_2 /PCBM:P3HT/Au device at different temperatures and under white light illumination of intensity of 10 mW cm^{-2} .

respectively. A modeling study confirmed that the kink in the current–voltage curve close to the open-circuit may be due to the presence of large interfacial energy steps or low carrier mobilities and a reduction of the open-circuit voltage and crossing of the light and dark current curves when interfacial recombination is strong.¹¹ However, the power conversion efficiency, controlled to a considerable extent by the kink, is the main outcome that distinguishes our present study from earlier observations and studies. Moreover, this kink effect becomes dominant with an increase in temperature or intensity.

Figure 2 shows that the power conversion efficiency of the inverted PCBM:P3HT solar cells with a TiO_2 nanolayer significantly increases (nearly a factor of 3) with temperatures in the range of $30 \text{ }^\circ\text{C}$ to $65 \text{ }^\circ\text{C}$. The strongly temperature-dependent open-circuit voltage with a positive temperature coefficient in the temperature range of $30 \text{ }^\circ\text{C}$ – $65 \text{ }^\circ\text{C}$ is the major underlying reason for this strange behavior in terms of the power conversion efficiency. The very similar trends of temperature responses in relation to power conversion efficiency and the open-circuit voltage (as depicted in Figs. 2 and 3) further support that

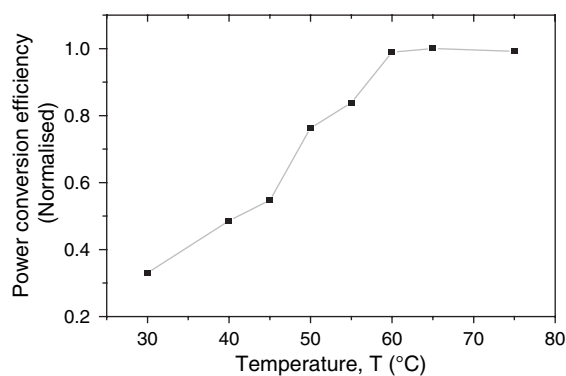


Fig. 2. Normalized power conversion efficiency of ITO/HBL/PCBM:P3HT/Au at different temperatures.

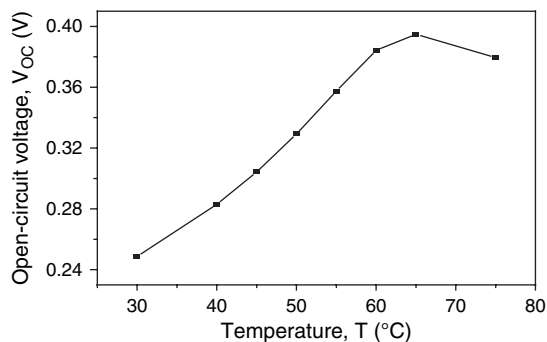


Fig. 3. Open-circuit voltage of the inverted solar cell, ITO/dense TiO_2 /PCBM: P3HT/Au.

the power conversion efficiency mostly relies on the open-circuit voltage.

For a solar cell that behaves as a non-ideal diode, current density J is given approximately by

$$J = J_{SC} - J_0 [\exp(eV/mkT) - 1] \quad (1)$$

Where J_0 is the dark saturation current density, m is the ideality factor, k is Boltzmann's constant and T the temperature.¹² Open-circuit voltage, V_{OC} , is then related to short-circuit current, J_{SC} through

$$V_{OC} = \frac{mkT}{e} \ln \left[\frac{J_{SC}}{J_0} \right] \quad (2)$$

Substituting for J_0 one could obtain the expression¹¹

$$V_{OC} = a - bT \quad (3)$$

where a and b are constants involving the intrinsic parameters of the active material.

The linear decrease of V_{OC} with temperature as governed by Eq. (3) was observed in several structures. A linear decrease of V_{OC} with average temperature coefficient $dV_{OC}/dT = -(1.40-1.65)$ mV/°C has been reported for typical PCBM/P3HT cells with PEDOT:PSS buffer layer within a temperature range of 30 °C to 60 °C.¹³ However, V_{OC} of the inverted solar cell shows almost linear increase with temperature, having an average temperature coefficient $dV_{OC}/dT = +6.9$ mV/°C violating the non-ideal diode model.

At V_{OC} dark current is compensated by the current under illumination and hence making the zero photocurrent. If the kink effect was not present, there would be no discontinuity of the slopes of $J-V$ curve at the V_{OC} which leads to the decrease in V_{OC} similar to the conventional devices, which is not the real case. This supports the kink-controlled V_{OC} .

It has been reported in the literature about the strong temperature dependence of J_{SC} of the polymer: fullerene solar cells.¹³⁻¹⁵ In our case, J_{SC} exhibits an increasing trend on temperature, attains the maximum around 65 °C and falls down with the further increase in temperature. The

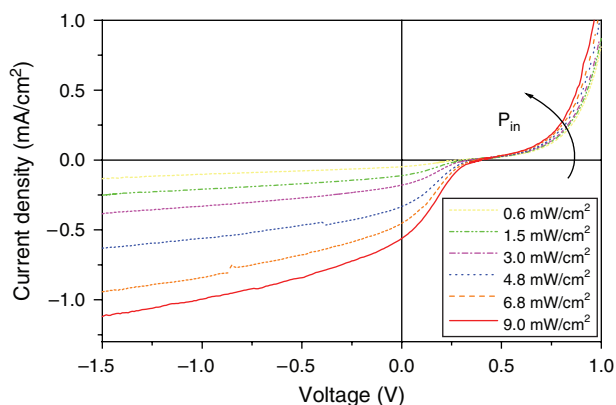


Fig. 4. Current density–voltage characteristics of ITO/HBL/PCBM: P3HT/Au at a temperature of 65 °C under different white light intensities ranging from 0.6 mW/cm² to 9 mW/cm².

fill factor of the polymer: fullerene solar cells is usually low compared to the other structures because of the possible shunt pathways present due the blend nature. In the inverted solar cells, the FF becomes even lower because of the kink.

Figure 4 shows the current density–voltage characteristics of the inverted solar cell at a temperature of 65 °C under different low light intensities. In this intensity range, the scaling exponent is found to be unity which shows that the dominant mechanism for recombination is monomolecular type. A significant deviation from unity for the value for the scaling exponent could be expected when the mode of recombination changes from monomolecular to bimolecular recombination, particularly at higher light intensities. As a consequence of the linear variation of J_{SC} with P_{in} , it follows from Eq. (2) that V_{OC} should exhibit a slope of mkT/q , when plotted as a function of the logarithm of light intensity. The ideality factor of the inverted devices is found between 1.5 and 2.0.

This kink effect becomes dominant at higher temperature and/or intensity. In order to explore the origin of this kink, we examined the $J-V$ characteristic of the device by varying the light intensity and wavelengths. The kink feature persists at different wavelengths, indicating that the kink is not a result of the spatial distribution of the photogeneration rate, and under different light intensity, indicating that it is not due to charge trapping. The kink may however be due to the energy barrier at TiO_2 /fullerene or P3HT/Au interface.

4. CONCLUSION

We find that both temperature and illumination intensity slightly influence the power conversion efficiency of both conventional and inverted solar cells of P3HT:PCBM having a PEDOT:PSS layer. The fact that the power conversion efficiency of the inverted solar cells without PEDOT:PSS is increased over a factor of three within a

30 °C temperature increase is attributed to a consequence from the strong and positive temperature dependence of open-circuit voltage which may be due to a “kink” in the current–voltage characteristics near open-circuit voltage. However, the short-circuit current density and fill factor follows the same trend revealed by the conventional counterparts. We discussed the origin of this kink and how it can control the power conversion efficiency in the inverted devices.

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