Post-Processing Treatments in Hybrid Polymer/Titanium Dioxide Multilayer Solar Cells

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We report on a study of post-processing treatments in hybrid solar cells based on poly(3-hexylthiophene) (P3HT) being in contact with nanocrystalline TiO_2 films. The power conversion efficiency of the hybrid polymer/TiO_2 solar cells is increased over three-fold through the simultaneous application of external bias voltage and UV illumination. These treatments enhance short-circuit current density, J_{SC}, from 1 mA/cm^2 to over 3 mA/cm^2 under simulated air mass (AM) 1.5 conditions (100 mW cm^{-2}) and lead to a peak external quantum efficiency of over 16%. The AM 1.5 open circuit voltage reaches 0.47 V and the fill factor reaches 0.53, resulting in an overall power conversion efficiency of 0.74%. The improved performance following UV exposure is correlated to a slowing of over one order of magnitude in the dynamics of charge recombination as monitored by transient optical spectroscopy. We further demonstrate that while the UV radiation present in a simulated AM 1.5 solar spectrum is sufficient to cause the increase in the J_{SC} and efficiency after two hours of exposure, no change results from exposure to the same spectrum when a UV blocking filter is used. We propose that UV exposure modifies the nature or density of surface trapping species in the nanocrystalline TiO_2, resulting in reduced recombination rates and a higher efficiency of collection of photogenerated charges.

Keywords: Solar Cells, Post Processing, Polymer, TiO_2, Illumination, Photovoltaics.

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1. INTRODUCTION

Solar cells based on soluble conjugated polymers are of great interest because of the potential low cost of production by solution processing.[1–10] Distributed heterojunctions based on blends of poly(3-hexylthiophene) (P3HT) with fullerene derivatives have been among the best studied devices and, to date, have yielded efficiencies of over 6.5% when a metal oxide anode is used to reduce interfacial losses.[11] However, the use of fullerenes as electron acceptors has some disadvantages, such as segregation of the components during ageing[11] and relatively poor photostability. Metal oxides such as TiO_2, ZnO, and SnO_2 are promising as alternative electron acceptors. They offer good electron transport properties, excellent physical and chemical stability, and fabrication via facile techniques.

Promising power conversion efficiencies of over 1% have been reported[5] for hybrid bulk heterojunction solar cells based on blend films of a conjugated polymer and TiO_2 nanorods capped with organic ligands. It has been shown, however, that charges collect in TiO_2:polymer blend films are limited by interparticle transport as well as by the effects of trap states associated with the TiO_2 nanoparticles.[12] Further, the difficulty of controlling the morphology of the blend and the tendency toward phase segregation over time mean that the blend solar cells are not ideal for durable devices. These difficulties can be overcome by using rigid metal oxide nanostructures, which may be filled with a soluble organic donor material, and which present a direct, and electrically connected path for photogenerated electrons to migrate to the collecting electrode. However, the overall performance of such devices is disappointing due to the poor charge collection efficiency, which results from low short circuit current densities ($J_{SC} \sim 1$ mA/cm^2).[13, 14] If the activity of the trap states in a porous metal oxide network is controlled, the charge collection efficiency in the devices can be improved. It has been shown that the performance of polymer-based solar cells is highly dependent on the effects of traps in hybrid TiO_2/polymer solar cells,[15–18] while the effect of the electrical bias is related to the polymer–fullerene blend solar cells.[6]

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In this study, we show how post-fabrication treatment of a TiO_2/polymer solar cell using UV irradiation and electrical bias results in large improvements in short-circuit current density, J_{SC}, and that the improvement is correlated to a slowing down of the interfacial charge recombination rate. We focus on nanostructured heterojunction devices made from well-connected, rigid, porous titanium metal oxide films filled with regioregular P3HT as the solution-processible, hole-transporting component.

2. EXPERIMENTAL DETAILS

Six devices were fabricated from an indium tin oxide (ITO) substrate to check for reproducibility, as described in Ref. [9]. Each device (with a 4.2 mm^2 active area) consists of four layers on top of the ITO substrate; namely, a dense TiO_2 hole-blocking layer (HBL), a porous nanocrystalline TiO_2 layer, a dip-coated polymer layer, and a spin-coated polymer layer. The thicknesses of the layers in each device were (unless stated otherwise) as follows: HBL ($\sim$30 nm), porous TiO_2 ($\sim$220 nm), dip- and spin-coated polymer ($\sim$130 nm), poly(styrenesulfonate)-doped poly(ethylenedioxy thiophene) (PEDOT) ($\sim$40 nm), and Au ($\sim$100 nm). The HBL is required to prevent shunt paths between the polymer and the ITO substrate. In this study, we used TiO_2 paste received from Dyesol. For film deposition, colloidal TiO_2 ($\sim$20 nm diameter) paste was dissolved in tetrahydrofuran (THF) (110 mg/ml) and deposited by spin coating followed by sintering at 450 °C. The active layers were annealed at 140 °C for two hours under dry nitrogen prior to the deposition of PEDOT and Au. Current density–voltage (J–V) and external quantum efficiency (EQE) measurements were made in vacuum, as described in Ref. [9]. Photoinduced charge-transfer yield and recombination kinetics were measured on ITO/HBL/porous TiO_2/polymer samples (without top contact) using nanosecond–millisecond transient optical spectroscopy, as described in Ref. [9].

3. RESULTS AND DISCUSSION

Figure 1(a) shows the EQE spectra of an ITO/dense TiO_2 (30 nm)/porous TiO_2 (220 nm)/P3HT^d/P3HT^s (130 nm)/PEDOT/Au device measured immediately after fabrication (as prepared), after taking the dark-current measurement by applying an external bias from -1 V to 1 V (biased device) and after continuous illumination under simulated air mass (AM) 1.5 irradiation for two hours at short circuit. The figure shows that the peak EQE of the solar cell increases from 12% to 16% after applying the external bias from -1 V to 1 V in the dark. A similar effect has been reported for P3HT–fullerene bulk hetero-junction devices[6] and other reports show that externally applied bias is capable of improving hole mobility in conjugated polymers.[19] External biasing of a device appears

to enhance charge collection by helping to orient the polymer chain inside the porous TiO_2 network in the direction of the electric field.

Although the illuminated device shows similar peak efficiencies to the biased device at the maximum absorption of the polymer, the irradiated device shows enhanced quantum efficiency in the UV region due to enhanced photogeneration in the TiO_2. Integrating the product of the measured EQE with the photon flux density of the AM 1.5 solar spectrum yields a maximum J_{SC} of approximately 3.05, 3.79, and 4.00 mA cm^{-2} for the fresh, the biased, and the illuminated devices, respectively. However, the measured values under AM 1.5 conditions are about 25% lower than the expected value. This is consistent with the sub-linear dependence of J_{SC} on illumination intensity (Fig. 1(c)), which indicates that bimolecular recombination is significant at short circuit. The J_{SC} returned to its original value at low light intensities after the highest intensity was applied. This confirms that the results are not affected by the direction of the intensity scan.

Figure 1(b) shows the J–V characteristics for an ITO/dense TiO_2 (30 nm)/porous TiO_2 (220 nm)/P3HT^d/P3HT^s (130 nm)/PEDOT/Au device under simulated AM 1.5 illumination (100 mW cm^{-2}). J–V characteristics of the sample, which was kept at low vacuum in a sample chamber, were recorded every ten minutes under continuous illumination over a period of two hours. The J_{SC} increases from 1.1 mAcm^{-2} to over 3 mAcm^{-2} while the open-circuit voltage (V_{OC}) increases from 0.43 V to 0.47 V. The increase in V_{OC} is expected for the given increase in J_{SC}. The overall efficiency increases three-fold to 0.74% from 0.24% (Fig. 2(a)). The efficiency of the solar cell remains constant for more than a period of 30 minutes of continuous illumination after two hours of illumination under AM 1.5 conditions at bias (see Fig. 2(b)). We observed no increment in the performance of the device that did not undergo continuous bias. Electrical bias and irradiation are essential to get the observed increase in J_{SC}.

To determine the origin of the light-soaking effect, we investigated the effect of simulated AM 1.5 illumination with and without a UV-blocking filter (admitting light of $\lambda > 400$ nm) on the J–V characteristics of a similar device after applying external bias. No increase in J_{SC} or efficiency with illumination time was observed when the UV-blocking filter was used (Fig. 2(b)). However, both J_{SC} and efficiency increased for two hours after the UV-blocking filter was removed. These observations clearly show that the UV part of the solar spectrum in the range 300–400 nm is responsible for the increase in J_{SC}.

There are several possible reasons for the increase in J_{SC} of the hybrid TiO_2/polymer solar cells under AM 1.5 illumination with an electrical bias. The effect may be due to an improvement in the transport properties of porous TiO_2, P3HT, and/or the TiO_2/P3HT composite under illumination. Since the effect of illumination is not found in
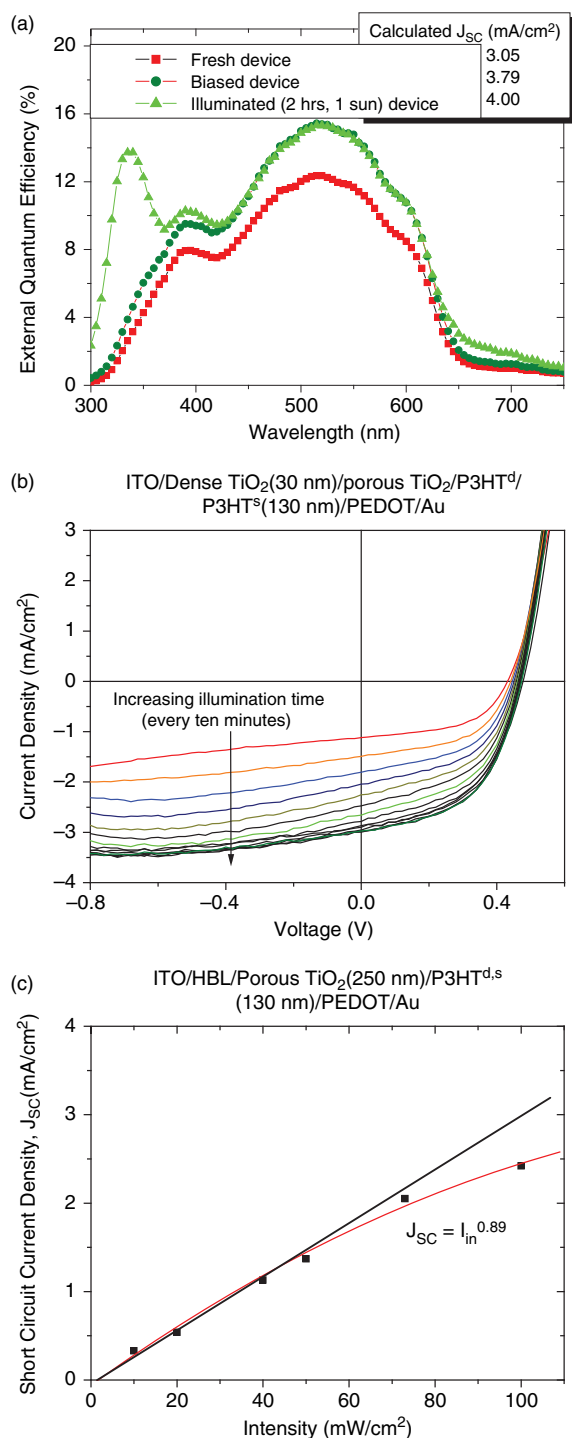
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(a)

(b) ITO/Dense TiO$_2$(30 nm)/porous TiO$_2$/P3HT^d/
P3HT^s(130 nm)/PEDOT/Au

(c) ITO/HBL/Porous TiO$_2$(250 nm)/P3HT^{d,s}
(130 nm)/PEDOT/Au

$$J_{SC} = I_{in}^{0.89}$$

Fig. 1. (a) External quantum efficiency spectra of a device (ITO/dense TiO$_2$(30 nm)/porous TiO$_2$(220 nm)/P3HT^d/P3HT^s(130 nm)/PEDOT/Au) as prepared (square symbols), after applied external voltage (circle symbols) and after continuous illumination for two hours (triangle symbols) at approximately 6 μW/cm^2. (b) Current density versus voltage characteristics of device (ITO/dense TiO$_2$(30 nm)/porous TiO$_2$(220 nm)/P3HT^d/P3HT^s(130 nm)/PEDOT/Au) after basing under Air Mass (AM) 1.5 conditions (1 sun). J–V characteristics were recorded every ten minutes under continuous illumination for two hours. (c) Short-circuit current density versus illumination intensity of the fresh device (ITO/dense TiO$_2$(30 nm)/porous TiO$_2$(250 nm)/P3HT^d/P3HT^s(130 nm)/PEDOT/Au.

(a) ITO/Dense TiO$_2$(30 nm)/porous TiO$_2$/P3HT^d/
P3HT^s(130 nm)/PEDOT/Au

(b) ITO/Dense TiO$_2$(25 nm)/porous TiO$_2$/P3HT^d/
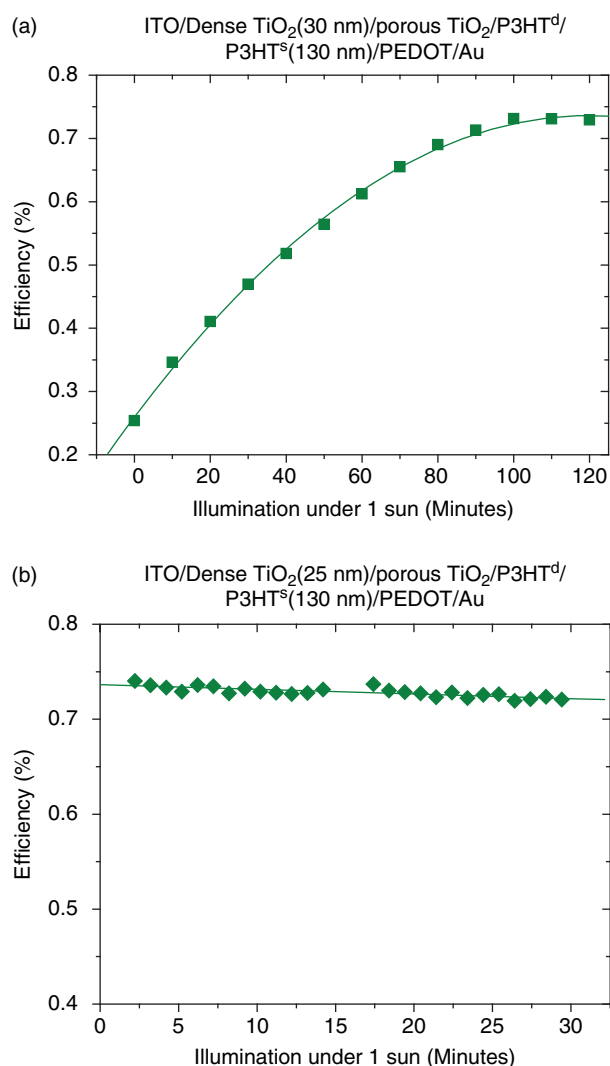P3HT^s(130 nm)/PEDOT/Au

Fig. 2. (a) Efficiency of the ITO/dense TiO$_2$(30 nm)/porous TiO$_2$(220 nm)/P3HT^d/P3HT^s(130 nm)/PEDOT/Au device as a function of exposure time to AM 1.5 illumination (100 mWcm^{-2}, 1 sun). (b) Efficiency of the same device as a function of time after the two-hour illumination period has been completed.

P3HT–fullerene solar cells, a change in the transport properties of the P3HT due to illumination can be ruled out. This effect could therefore be due to a change in recombination kinetics at the polymer–TiO$_2$ interface or in the transport properties of the TiO$_2$. To find whether a change in recombination at the interface is responsible for this effect, we monitored the charge recombination kinetics following band-gap excitation of TiO$_2$ under vacuum using UV light source with a maximum emission wavelength of 254 nm.

Figure 3(a) shows the P3HT polaron absorbance probed at 950 nm as a function of time after laser excitation for a sample before and after UV illumination. The comparison show that the exposure to UV light slows down the charge recombination kinetics by over one order of magnitude. This indicates that the nature of the polymer–TiO$_2$
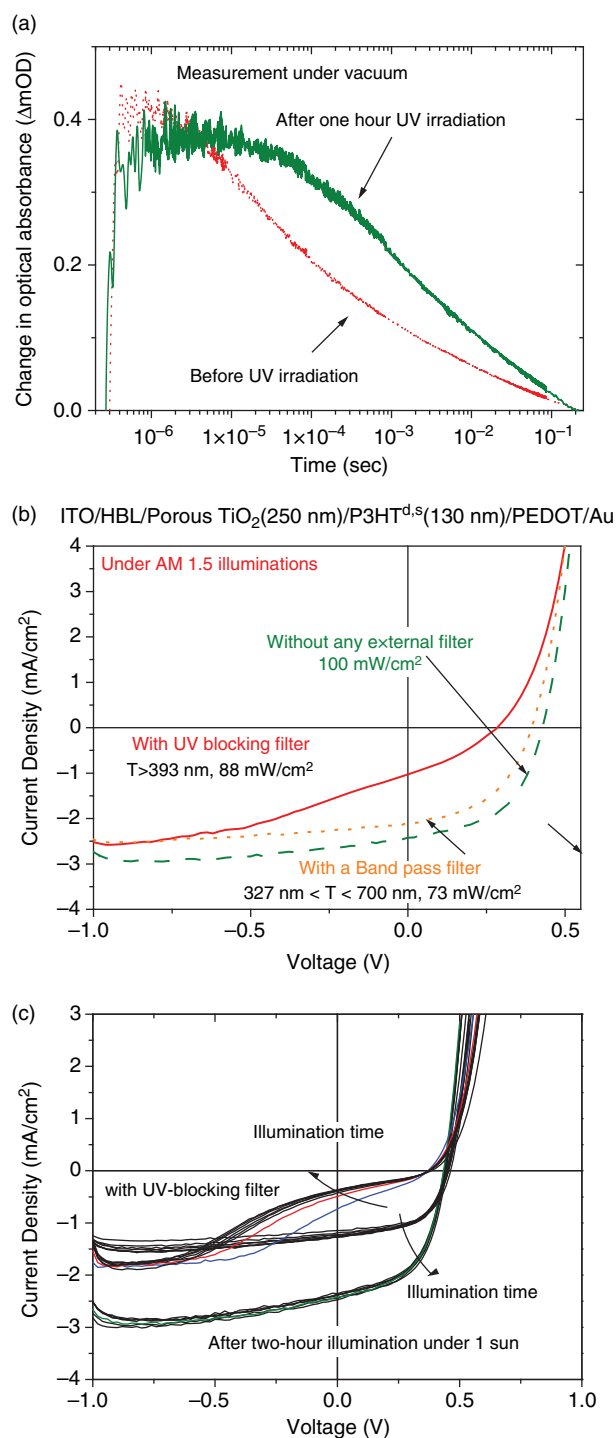
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Fig. 3. (a) Photoinduced change in absorbance at 960 nm (P3HT-hole polaron) for ITO/dense TiO$_2$ (30 nm)/porous TiO$_2$(220 nm)/P3HT^d/P3HT^s (130 nm) under UV irradiation (dashed line), before UV irradiation (dotted line), and after UV irradiation (solid line). The excitation density is ~30 μJ/pulse/cm^2 (corresponding to 1.3×10^{14} incident photons/pulse/cm^2) at 520 nm with all the samples excited through the substrate side. (b) Current density versus voltage characteristics for ITO/dense TiO$_2$(30 nm)/porous TiO$_2$ (220 nm)/P3HT^d/P3HT^s(130 nm)/PEDOT/Au device under AM 1.5 conditions (1 sun) with a UV filter (solid line), without any external filter (dashed line), or with a band-pass filter (dotted line).

interface has been changed by the UV irradiation. Since the wavelength range responsible for the change is capable of band-gap excitation of the TiO$_2$, this suggests that the UV exposure modifies the nature or density of surface defects (acting as recombination centers) in the nanocrystalline TiO$_2$ by stimulating a surface chemical reaction. We noted accelerated kinetics during UV irradiation, which can be explained as the effect of background illumination, as is also seen in polymer–fullerene devices. It is important to note the effect of the history of the UV irradiation on the kinetics: a several-fold slowing down that may explain the higher J_{SC}.

4. CONCLUSION

We report improved efficiency for multilayer hybrid TiO$_2$/polymer solar cells based on nanocrystalline TiO$_2$ and a P3HT polymer. We observe that prolonged UV illumination together with applied electrical bias improves the photocurrent generation efficiency and, hence, the power conversion efficiency of the hybrid TiO$_2$/polymer device. The improvement is assigned to a reduced rate of interfacial charge recombination after the treatment. Our results suggest a strategy for post treatment of polymer–metal oxide hybrid devices, consisting of exposure to UV light and electrical bias. The changes are attributed to the effect of UV exposure on the nature or density of surface defects in the nanocrystalline TiO$_2$. Further studies are needed to clarify the mechanism of the recombination deceleration.

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