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**UV-induced Oxygen Removal for Photostable High Efficiency PTB7-Th:
PC₇₁BM Photovoltaic Cells**

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ABSTRACT: Solution-processed ZnO sol-gel or nanoparticles are widely used as the electron transporting layer (ETL) in optoelectronic devices. However, chemisorbed oxygen on the ZnO layer surface has been shown to be detrimental for the device performance as well as stability. Herein, we demonstrate that a chemisorbed oxygen removal based on a UV illumination of the ZnO surface layer under a nitrogen atmosphere can, simultaneously, improve power conversion efficiency and photostability of PTB7-Th: PC₇₁BM based inverted polymer solar cells. By a systematic study of such UV illumination procedure, we obtained optimal conditions where, both, the cell efficiency and stability were improved. We fabricated cells with a power conversion efficiency higher than 9.8%, and with a T₈₀ lifetime larger than 500 hours, corresponding to about a 2.5-fold enhancement relative to non-UV treated ZnO reference devices.

KEYWORDS: Polymer solar cells, PTB7-Th, photo-stability, sol-gel ZnO, molecular oxygen

1. INTRODUCTION

As it has been noted in several occasions, the sunlight to electricity conversion remains as one of the most viable alternatives to, simultaneously, satisfy an ever increasing energy demand with the fight against the global warming attributed to an extensive use of fossil fuels.^{1, 2} Presently, the exponential decrease in silicon module fabrication costs makes such technology the most competitive one to fit into the traditional large scale electricity production system. However, in other applications that may require flexibility, semi-transparency, or light weight, the organic photovoltaics (OPV) is, certainly, one of the most promising candidates.³⁻⁶ In single junction devices of the poly[[2, 6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-*b*;3,3-*b'*]dithiophene][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7-Th) polymer, power conversion efficiencies (PCEs) exceeding 10% have been reported in several occasions.⁷⁻¹³ Contrary to some hybrid material based solar cells which exhibit a high dispersion in their performance, the reproducibility of the PV parameters for PTB7-Th or PTB7 based cells is remarkable.¹⁴ Yet, several studies have shown that such PTB7 or PTB7-Th based cells exhibit a poor stability under different environmental conditions.¹⁵⁻¹⁷ The physics underlying the degradation dynamics is not fully understood, but molecular oxygen has been seen to be one of the corrosive agents that may strongly affect and degrade the composition of the blend active layer.¹⁹⁻²² A passive isolation from such corrosive elements has been shown to enhance the lifetime of the OPV cells, however, an active removal of the oxygen has never been implemented to demonstrate a cell lifetime increase.

In the present study, we report an effective approach to, simultaneously, improve device efficiency and photo-stability by removing chemisorbed oxygen on the ZnO electron transporting layer (ETL). This is achieved by ultraviolet (UV, 254 nm) irradiation on the ZnO layer in a N₂-filled glovebox (hereafter as UVN treatment). Such treatment was performed prior to the deposition of the photoactive layer, which is composed of the PTB7-Th polymer as donor and [6, 6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) molecule the acceptor. By

incorporating the UVN-treated ZnO ETL, the cell reached a top PCE of 9.83% and showed close to a 2.5 times prolonged lifetime (~ 540 hours) relative to non-UVN treated ZnO devices. Such lifetimes obtained for cells subject to an ISOS-L-1 degradation test²³ correspond to one of the few cases where high efficiency polymer solar cells exhibit a remarkable photo-stability.

2. RESULTS AND DISCUSSION

In the study we consider the performance and degradation dynamics of encapsulated cells under a continuous 1 Sun illumination. As indicated above, such performance is strongly dependent on the electron transporting and photoactive layers. In the inverted architecture devices we fabricated, such layers were a 20 nm sol-gel deposited ZnO ETL and a 95 ± 5 nm bulk heterojunction blends of PTB7-Th:PC₇₁BM, as seen in **Figure 1A**. The chemical composition of the donor and acceptor materials is shown in **Figure 1B**. In several of the fabricated devices the interfacial properties of the ZnO layer were tailored with the UVN treatment described above. Unless otherwise specified, a glass-on-glass encapsulation was applied in the glovebox to all devices before testing them in ambient air. Additional details on the device fabrication procedure are given in the experimental section.

Prior to such solar cell fabrication, and with the aim to evaluate the stability of the photoactive layer, we measured the optical transmittance of an ITO/photo-active film when irradiated under AM 1.5G with 100 mW/cm^2 light intensity in ambient air, shown in **Figure 1C**. After 5 hours of continuous illumination, an increase in the transmittance spectra was seen in the 500 nm to 800 nm range, but no change was found in the 300 nm to 450 nm range, such wavelength ranges were ascribed to the PTB7-Th and PC₇₁BM components, respectively. Such increase in transmission in the former wavelength range indicates that the π -conjugated

PTB7-Th backbone is easily damaged with the combined exposure to air and light. However, such conjugated backbone part of the polymer, showed an excellent photo-stability when encapsulated in the glove-box. As shown in **Figure 1D**, no change in the transmittance spectra was observed after 500 hours of a continuous full-sun light-aging experiment. One may conclude that long term photo-stable PTB7-Th: PC₇₁BM cells can be obtained if the oxygen content within the device is kept at an extremely low level.²⁰

2.1. Influence of UVN Treatment on Device Performance.

The current density–voltage (J – V) characteristics for UVN treated and non-UVN treated (reference) cells measured under AM 1.5G solar illumination at 100 mW/cm² are shown in **Figure 2A**. The reference exhibited an average initial PCE of 8.94± 0.16%, while the UVN-treated ZnO devices showed a 7% higher average efficiency of 9.54 ± 0.16%, being 9.83% the highest PCE obtained. The initial photovoltaic parameters for the reference and UVN-treated ZnO devices are shown in **Table 1**. The UVN-treated ZnO interlayer leads to a slight improvement in the fill factor (FF) and a significant enhancement in the short-circuit current (J_{sc}). The latter one is confirmed by the external quantum efficiency (EQE) measurement, shown in **Figure 2B**, where UVN treated ZnO cells exhibit an enhanced efficiency throughout the full spectral range.

It is generally accepted that the surface of a ZnO film contains many oxygen vacancies (or Zn²⁺), which are deep electron-donating sites.²⁴ The electrons in these sites (around 1 eV below the conduction band) are likely to interact with molecular oxygen from the ambient air during film preparation, leading to the formation of chemisorbed O₂^{•−} species, as schematically illustrated in **Figure 2C**.²⁵ This typically results in a high density of surface defects and thus an undesirable energy barrier for electron transport and extraction. We confirmed the presence of such energy barrier for the untreated ZnO cells illuminating them with a GG475 filtered

AM1.5 G source. In that event, an s-shape can be seen in the J - V curves shown in **Figure S1A**. Upon illumination with UV light above the band gap of ZnO, electron-hole pairs are generated and free holes are likely to migrate and recombine with the near trapped electrons. Consequently, the O_2^- species are neutralized and detached from the ZnO film.²⁶⁻²⁸ In the event that such UV-treated ZnO layers are placed again in ambient air the reverse process occurs within minutes. We completed a cell with such UVN treated ZnO layer but placed in air, and observed a performance no different than the reference cell. Therefore, to avoid oxygen re-absorption we implemented the UV treatment in an inert atmosphere (O_2 content < 10 ppm) and kept the cells in this atmosphere until completed.²⁹ As shown in **Figure S1B** no barrier is seen for such UVN-treated cells.

Given the complexity of ZnO Surfaces³⁰, the type of UV-treatment applied may also result in the desorption of hydroxyl groups³¹ or the destruction of organic solvent residues³². However, such changes may have a smaller effect in the degradation dynamics for the type blend under consideration. Indeed, as it was recently demonstrated oxygen is a major source in the destruction of the PTB7 polymer conjugation.¹⁶ In addition, it has been shown that the combined effect of light and oxygen strongly reduces electronic properties in the $PC_{71}BM$ phase.³³

We investigated the effect of the UVN exposure time on the device performance. As shown in **Figure 2D**, the largest improvement in FF was obtained for a 20 min exposure while enhancements in J_{sc} were observed for all UVN-treated devices when compared to reference cells. Provided that the V_{oc} did not change except for exposure times larger than 20 min, as seen in **Figure 2E**, we concluded that the 20 min UVN treatment led to the largest PCE as seen in **Table S1**. Such optimal performance was attributed to enhanced conductivity of the ZnO ETL and reduced interface recombination^{29,34}, which was confirmed by the I- V

conductivity measurements from diode devices of ITO/ZnO (w/o UVN treatment) (100 nm)/Al, as shown in **Figure S2**. The electrical conductivity under illumination for UVN-treated ZnO film was $\sim 4.16 \times 10^{-4}$ S/m, about 1.5 times higher than the one from as-prepared ZnO film. The current in UVN-treated ZnO film increased by ~ 22 -fold at 1 V in the dark compared to as-prepared ZnO. Such features indicate that the chemisorbed O_2^- defects on ZnO surface were significantly reduced by UVN treatment which led to the enhancement in electron concentration on the ZnO conduction band. However, one should note that UV exposures larger than 20 min increased the carrier concentration in the ZnO ETL to a level where carrier selectivity was lost and the cell electrical properties degraded³⁵. This led to the reduction in FF and V_{oc} seen in **Figure 2E** and to an increase in the series resistance seen in **Table S1**. The UV-induced shunt recombination caused by such very high n-doping ZnO resulted in the tunneling of holes from the adjacent PTB7-Th valence band into the ZnO conduction band.²⁵ Note also that, as seen in **Figure S1**, the UVN pre-treated ZnO cells do not require a UV activation similarly to the Al-doped ZnO (AZO) devices³⁶.

2.2. Effect of UVN Treatment on Device Photostability

As indicated, the finished reference and UVN-treated ZnO devices were subjected to a continuous UV filtered AM1.5G 1 sun aging in an open-circuit configuration in air. The UV light at wavelengths below 400 nm was filtered out using a GG400 filter in order to reduce the undesirable photochemical reactions and burn-in loss³⁷⁻³⁸. An in-depth study on the burn-in degradation dynamics for PTB7-Th: PC₇₁BM based inverted cells will be published elsewhere.³⁹ Beyond 100 hours of light exposure, when the burn-in loss effect becomes marginal, we observe (**Figure 3A and Table 1**) that the performance of UVN-treated cells degrades more than two times slower than the reference cells. The V_{oc} of the reference and UVN-treated ZnO devices was stable within the timescale of degradation considered, as seen in **Figure S3**. The major PCE loss originates from the J_{sc} and FF decays as shown in **Figure**

3B. One may confirm the effectiveness of the active oxygen removal induced by the UV light by comparing the decay dynamics of the UVN-treated cell with cells fabricated using an oxygen-free ETL as the poly [(9,9-bis(3-(*N,N*-dimethylamino)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl-fluorene)] (PFN). In both cases, as seen in **Figure 3A**, the measured decay time beyond 100 hours is close to the one measured for the UVN-treated cell. Indeed, beyond the effect of the burn-in, for all four cases under consideration the device evolution dynamics can be adjusted to a single exponential decay, as seen in **Figure S4**.²³ The decay time for the reference cell was determined to be less than two thousand hours while for the other three cells the decay time is about two times larger, being the decay time for the UVN-treated device the largest one, as seen in **Table S2**. The three cells with a molecular-oxygen-free ETL exhibited T_{80} lifetimes in the 500-550 hours range, while that for the reference T_{80} lifetime for was close to 2.5 times smaller as seen in **Table 1**. T_{80} corresponds to the time it takes for the cell PCE to drop to 80% of its initial value.

To shed some light into what the effect of the molecular oxygen removal is, we investigated the V_{oc} dependence on light intensity, shown in **Figure 4**. The slope of the V_{oc} versus the natural logarithm of the light intensity gives similar slopes for the fresh reference and UVN-treated ZnO devices, implying that a similar mechanism of bimolecular recombination is dominant in fresh cells.⁴¹⁻⁴² After 500 hours of illumination, the slope of the degraded reference cell increased by 1.25, whereas the increase for the UVN-treated ZnO cell was only 1.15. The higher slope seem to indicate a larger increase in the number of Shockley–Read–Hall (SRH) or trap-assisted recombination sites in the reference cells than in the cells where the UVN-treatment is applied. Ascribing the larger slope seen for the aged reference cell to oxygen-induced traps is one possibility,³³ but alternative explanations based on an increase in the density of states disorder may be plausible, too.⁴⁰

It is also worth noting that the oxygen removal approach we implemented for the PTB7-Th: PC₇₁BM cells can also be successfully applied to other high performance low band gap photo-active materials. Simultaneous enhancement in the PCE and photo-stability were also demonstrated for PffBT4T-OD: PC₇₁BM inverted cells⁴³ when the UVN-treated ZnO ETL was incorporated. UVN-treated ZnO devices showed an enhanced average PCE of 9.5% compared to 9.1% for the reference devices without further optimization (See **Table S3**). An enhanced photo-stability indicating a 45% PCE loss for the treated cell over a 60% loss for the untreated one, under a UV-filtered illumination for 120 hours, as seen in **Figure S5**.

3. CONCLUSION

In summary, we have demonstrated that PTB7-Th polymer based cells have the potential to become very stable provided that finished devices are not under the action of strong oxidizing elements like oxygen. We have shown that the light transmission spectrum from an encapsulated PTB7-Th: PC₇₁BM blend layer remains unaltered even when under continuous 1 Sun illumination. However, for a long term stability of such polymer solar devices, isolation from corrosive elements may not be sufficient. An active removal of such elements, which may be embedded in small quantities in the finished device during the fabrication process, must be implemented. The combined effect of such elements and 1 sun illumination provides an irreversible degradation to the devices which show no recovery even when stored in dark for a long time. We demonstrated that the active removal of oxygen molecules adsorbed on the ETL and photoactive material interface increases the lifetime of high performance low band gap polymer cells with improved device initial PV parameters. Finally, it is worth mentioning that the oxygen removal procedure we considered is simple and a low cost implementation for a large scale production of polymer solar panels should be feasible.

4. EXPERIMENTAL SECTION

Materials and device fabrication: The polymer PTB7-Th (Commercial name: PCE-10, Lot No.YY7096, 1-material), and PC₇₁BM (purity > 99%, American Dye Source) were used as received without further purification. The sol-gel ZnO precursor solutions (0.3 M) were prepared according to previously reported method elsewhere.⁴⁴ Solutions of PTB7-Th: PC₇₁BM (1.0:1.5 wt) at a concentration of 10 mg/mL were prepared in chlorobenzene and stirred at 60 °C overnight in N₂-filled glovebox. Processing additive 1, 8-diiodoctane (3% vol) was added into the blends one hour prior to spin-coating. Devices were fabricated by spin-casting ZnO precursor on the pre-cleaned ITO (Lumtec, 135 nm, 15 Ω/sq) and annealing at 180 °C in air for 10 min to form a ca. 20 nm condensed electron transporting layer. The prepared samples were then transferred into a N₂-filled glove box for spin-casting photoactive layer with controlled thickness. While inside the glove box and prior to such spin coating, the samples were annealed for an additional 10 min at 150 °C to remove any adsorbed water molecules. For UVN-treated devices, the ZnO films were subjected to UV (CL-1000 model, 254 nm) illumination in glovebox prior to the deposition of the photoactive layer. For non-ETL device, to alleviate the Schottky-contact energy barrier between ITO and PC₇₁BM, the ITO surface was also UV illuminated in the glovebox for 20 min prior to deposition of the photoactive layer.⁴⁵ PFN interlayer was prepared following the recipe of previous reports.^{9,46} The resulting photoactive films were dried under high vacuum ($< 5 \times 10^{-7}$ mbar) overnight. Finally, MoO₃ (8 nm) and Ag (150 nm) electrodes were sequentially deposited on the active layer through a shadow mask by thermal evaporation ($< 5 \times 10^{-6}$ mbar), which defines the active area of 0.06 cm². The deposition rate for MoO₃ and Ag was 0.5 Å /s and 1 Å/s, respectively. The devices were encapsulated with pre-cleaned glass slides using a UV-curable epoxy (ELC-4908, Electro-Lite Corp) in N₂-filled glovebox.

Characterization and measurements: J – V curves of all devices (including aged cells) were measured with a Keithley 2420 source meter under a 1 sun, AM 1.5G spectrum from a solar simulator (ABET Sol3A, 1000 W/m²). The illumination intensity of the light source (Xenon lamp, 300W, USHIO) was determined using a Hamamatsu silicon photodiode (with KG-5 filter, area=0.1296 cm²) certificated by ISE Fraunhofer. Spectrally resolved EQEs were measured using a bench top QEX10 measurement system supplied by PV Measurements Inc. Photo-degradation tests were carried out under the standard solar simulator with UV-filtered ($\lambda > 400$ nm) one sun illumination in the ambient air. The temperature of the device surface imposed by illumination was 40 ± 5 °C as indicated by a thermocouple placed under the substrate. Transmission spectra of photoactive layers were recorded with a Perkin Elmer Lambda 950 UV/vis spectrometer.

ASSOCIATED CONTENT

Supporting Information. Conductivity measurements on ZnO interlayer with and without UVN-treatment. Single-carrier mobility measurements and double exponential fitting details for stability evolutions. Photovoltaic properties and photostability measurements of PffBT4T-2OD:PC₇₁BM solar cells incorporation of UVN-treatment.

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Notes

The authors declare no competing financial interest

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Figure 1. A) Scanning electron microscopy (SEM) image for the cross-section of the optimal inverted organic cell architecture used here: glass/ITO (140 nm)/sol-gel ZnO (20 nm)/PTB7-Th: PC₇₁BM (95 nm)/MoO₃ (8 nm)/Ag (150 nm). B) Molecular structures of the PTB7-Th donor, and PC₇₁BM acceptor. Transmittance evolution for ITO/PTB7-Th: PC₇₁BM photoactive films without (C) and with (D) glass encapsulation under AM 1.5G one-sun illumination in ambient atmosphere.

Figure 2. The effect of the UVN-treatment on PTB7-Th: PC₇₁BM solar cell performance. A) Current density versus voltage ($J - V$) characteristics of UVN-treated ZnO (solid circles) and reference (open circles) solar cells measured under 1000 W m^{-2} AM 1.5 G illumination. B) External quantum efficiency (EQE) spectra of UVN-treated ZnO (solid circles) and reference (open circles) solar cells. C) Schematic diagram of the sol-gel ZnO film and UV illumination interaction in a N_2 atmosphere. J_{sc} and FF (D), and V_{oc} and PCE (E) as function of the UVN exposure time on ZnO interlayer. Each data point represents the average over 20 devices and the error bars represent standard deviation of these data.

Table 1. Initial and after a 500 h degradation photovoltaic parameters, decay constants and lifetime for reference, UVN treated ZnO, PFN, and no ETL devices.

ETL		Photovoltaic properties ^[a]				Decay constant and lifetime ^[b]	
		J_{sc} (mA/cm^2)	V_{oc} (V)	FF [%]	PCE [%]	τ (h)	T_{80} (h)
ZnO reference	Fresh	16.12 ± 0.20	0.79	70.2 ± 1.0	8.94 ± 0.16 (9.19)	1843.5	~ 190
	Degraded (500 h)	14.70 ± 0.23	0.78	53.8 ± 1.6	6.14 ± 0.24		
UVN- treated ZnO	Fresh	16.92 ± 0.37	0.79	71.5 ± 1.2	9.54 ± 0.16 (9.83)	4181.4	~ 540
	Degraded (500 h)	16.01 ± 0.07	0.79	59.6 ± 0.5	7.68 ± 0.09		
PFN	Fresh	16.80 ± 0.10	0.78	69.2 ± 1.6	9.07 ± 0.17 (9.22)		
	Degraded (500 h)	15.31 ± 0.15	0.79	60.3 ± 0.9	7.26 ± 0.13	3215.1	~ 500
Non-ETL	Fresh	16.37 ± 0.30	0.57	59.7 ± 0.6	5.63 ± 0.16 (5.86)	3071.9	~ 550
	Degraded (500 h)	13.55 ± 0.29	0.60	55.5 ± 2.2	4.52 ± 0.17		

^[a] Photovoltaic parameters measured under full AM1.5G solar illumination at $100 \text{ mW}/\text{cm}^2$. The average values and standard deviations are obtained from over 20 devices for fresh cells and over 8 devices for degraded cells. The best PCE values are shown in parentheses.

^[b] Decay constants and lifetimes are extracted from double-exponential decay fittings of PCE evolution. Aging was carried out under a UV-filtered AM1.5G ($\lambda > 400 \text{ nm}$) one-sun illumination.

Figure 3. A) Normalized PCE time evolution for encapsulated reference, UVN-treated ZnO, PFN, and no-ETL devices subject to a continuous UV filtered AM 1.5G illumination ($\lambda > 400$ nm, 100 mW/cm^2) at $40 \pm 5^\circ \text{C}$. B) Normalized J_{sc} and FF evolution for reference and UVN-treated ZnO devices. Each data point represents the average over 6 devices and the error bars represent standard deviation of these data.

Figure 4. Measured V_{OC} of UVN-treated and reference cells before and after a 500 hour degradation cycle as a function of light intensity (symbols), together with linear fittings to the data (dotted lines).

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