

# Effects of Postproduction Treatment on Plastic Solar Cells\*\*

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Efficiencies of organic solar cells based on an interpenetrating network of a conjugated polymer and a fullerene as donor and acceptor materials still need to be improved for commercial use. We have developed a postproduction treatment that improves the performance of solar cells based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) by means of a tempering cycle at elevated temperatures in which an external voltage is simultaneously applied, resulting in a significant increase of the short-circuit current. Using this postproduction treatment, an enhancement of the short-circuit current density,  $I_{sc}$ , to 8.5 mA cm<sup>-2</sup> under illumination with white light at an illumination intensity of 800 W m<sup>-2</sup> and an increase in external quantum efficiency (IPCE, incident photon to collected electron efficiency) to 70 % are demonstrated.

## 1. Introduction

Polymer photovoltaic devices offer great technological potential as a renewable, alternative source of electrical energy. The demand for inexpensive renewable energy sources is the driving force behind new approaches in the development of low-cost photovoltaic devices. In the last couple of years, increased effort has been put into the development of solar cells based on organic molecules and conjugated polymers.<sup>[1–10]</sup> The mechanical flexibility and low weight of plastic materials make them attractive for photovoltaic applications; similarly, the easy thin-film casting technology for solar cells based on soluble conjugated polymers and fullerenes<sup>[11,12]</sup> could lead to a reduction of the production costs of large-area polymer solar cells. Even the bandgap of the polymer can be varied due to the flexibility of organic synthesis, and thus the chemical tailoring of desired properties is possible; for example, polymers that absorb light at different wavelengths can be produced. Because of these advantages, the development of polymer solar cells will have a major impact.

For the generation of electrical power by absorption of photons it is necessary to spatially separate the electron–hole (e–h) pair generated by photoexcitation before recombination processes can take place. In conjugated polymers, the stabilization of the photoexcited e–h pair can be achieved by blending the polymer with an acceptor molecule, which has an electron affinity that is larger than the electron affinity of the polymer, but still smaller than its ionization potential. In addition, the highest occupied molecular orbital (HOMO) of the acceptor should be lower than the HOMO of the conjugated polymer.

Under these conditions it is energetically favorable for the photoexcited conjugated polymer to transfer an electron to the acceptor molecule. The hole remains in the polymer valence band, which is the lowest available energy state for the hole. Such a photoinduced charge transfer from the conjugated polymer to the fullerene has been observed to occur in approximately 50 fs,<sup>[13]</sup> whereas the recombination is hindered and takes place in a microsecond regime.<sup>[14]</sup> Therefore the charges live long enough to be collected at the electrodes.

An important step towards efficient organic solar cells was the development of the bulk-heterojunction concept,<sup>[2]</sup> where polymer and fullerene form a three-dimensional photoactive matrix with a large charge generation interface. This ensures charge creation throughout the whole bulk of the photoactive layer. Using this concept, plastic solar cells with a power conversion efficiency of 2.5 % under AM1.5 (AM = air mass) irradiation were demonstrated.<sup>[15]</sup>

To further improve the power conversion efficiency of polymer solar cells, we have developed a postproduction treatment for plastic solar cell devices. By annealing the devices and simultaneously applying an external voltage we can improve the characteristics of plastic solar cells based on poly(3-hexyl thiophene) (P3HT) as electron donor material and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM), a soluble C<sub>60</sub> derivative, as electron acceptor material. The chemical structures of the investigated materials are shown in Figure 1, while Figure 2 gives a schematic view of the device geometry.

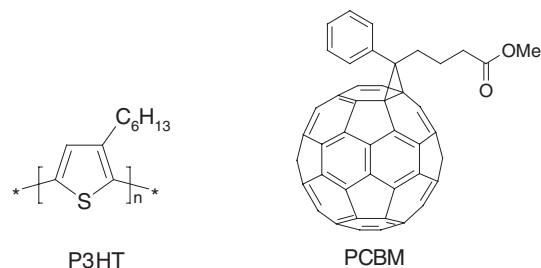


Fig. 1. Chemical structure of poly(3-hexyl thiophene), P3HT, and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester, PCBM.

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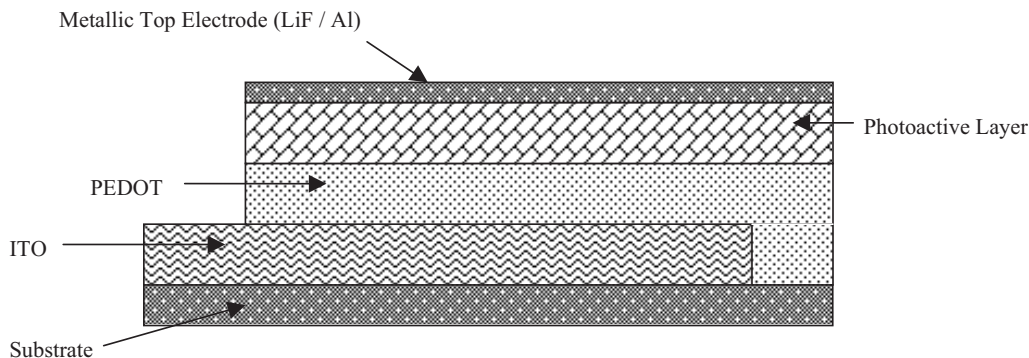


Fig. 2. Structure of the polymer photovoltaic devices.

## 2. Results and Discussion

The low mobility of the charges inside the photoactive matrix of polymer solar cells is one of the factors limiting the cells' efficiency. From the literature it is known that when a polythiophene is annealed to a temperature higher than its glass transition temperature, an enhanced crystallization of the polymer takes place.<sup>[16]</sup> Along with this enhanced crystallization of the polymer, the hole conductivity of the polythiophene increases dramatically.<sup>[17]</sup> During the heat treatment above the glass transition temperature of the polymer, the polymer chains are more mobile. A simultaneously applied external potential difference (electric field) greater than the open-circuit voltage ( $V_{oc}$ ) of the device injects additional charges into the polymer bulk, and is therefore presumed to support an orientation of the polymer chains inside the photoactive matrix in the direction of the electric field. This is expected to yield enhanced conductivity for charges across the polymer matrix. A similar orientation effect was observed for polymer-based organic light-emitting diodes (OLEDs) when subjected to an external electric field and temperature simultaneously.<sup>[18]</sup>

Figure 3 shows the current–voltage behavior of P3HT–PCBM solar cells under illumination with white light at an irradiation intensity of  $800 \text{ W m}^{-2}$ . The photovoltaic element without any postproduction treatment (filled squares) has  $V_{oc}$  of  $\sim 300 \text{ mV}$ , a short-circuit current density ( $I_{sc}$ ) of  $\sim 2.5 \text{ mA cm}^{-2}$ , and a calculated filling factor (FF) of 0.4.<sup>[19]</sup> The overall efficiency for this solar cell is therefore 0.4%. If this kind of solar cell is heated to  $75^\circ\text{C}$  for 4 min (open circles) the  $V_{oc}$  rises to 500 mV and the  $I_{sc}$  increases to  $7.5 \text{ mA cm}^{-2}$ . The filling factor for this cell has a value of 0.57. Therefore the efficiency under white light illumination is 2.5%. A polymer solar cell after postproduction treatment in which it is annealed (at  $75^\circ\text{C}$ ) and simultaneously subjected to an external voltage greater than the open-circuit voltage (in our case 2.7 V) gives a current–voltage behavior as shown in Figure 3 (open triangles) with an  $V_{oc}$  of 550 mV, a  $I_{sc}$  of  $8.5 \text{ mA cm}^{-2}$ , a FF of 0.6, and an overall efficiency of 3.5% under illumination with white light at an intensity of  $800 \text{ W m}^{-2}$ . In Figure 4 the improvement of the performance of the photovoltaic devices with the postproduction treatment is shown by comparing the dark and illuminated  $I$ – $V$

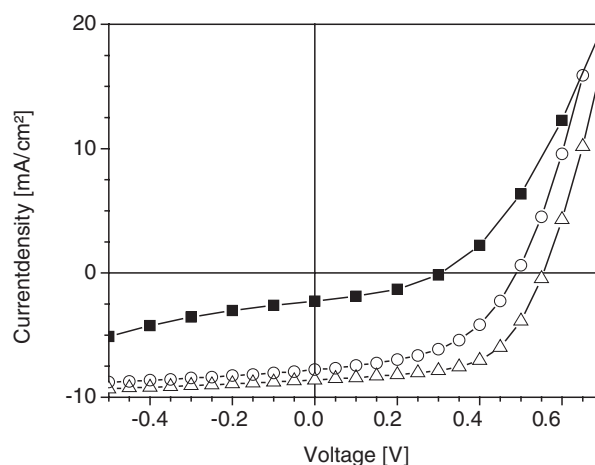


Fig. 3. Current–voltage ( $I$ – $V$ ) curves of P3HT–PCBM solar cells under illumination with white light at an irradiation intensity of  $800 \text{ W m}^{-2}$ : as-produced solar cell (filled squares), annealed solar cell (open circles), and cell simultaneously treated by annealing and applying an external electric field (open triangles).

curves of the differently treated solar cells. The dark  $I$ – $V$  curve of the untreated solar cell shows only a small rectification of around  $10^1$ , indicating that the performance of the device is at least partly limited by shunts. The rectification of the annealed solar cell is approximately  $10^3$  and increases once more to approximately  $10^4$  when an external voltage is applied during annealing. In the same way, the open circuit voltage rises from 300 mV to 560 mV. The increase of the open-circuit voltage and the filling factor (0.4 to 0.6) of the postproduction-treated solar cells can be explained by burning of shunts, whereas the increase in the short-circuit current indicates an enhancement of the mobility of the charge carriers inside the photoactive layer. We presume that this is due to an enhanced crystallization of the polymer during the annealing process and an additional orientational effect due to a simultaneously applied external voltage.

In Figure 5 the results of the IPCE (incident photon to collected electron efficiency) measurements for all three kinds of devices are shown. The external quantum efficiency for the as-produced device (open triangles) shows a maximum of  $\sim 25\%$  at a wavelength of 420 nm. Using a temperature treatment without external voltage (open squares) the IPCE is more than

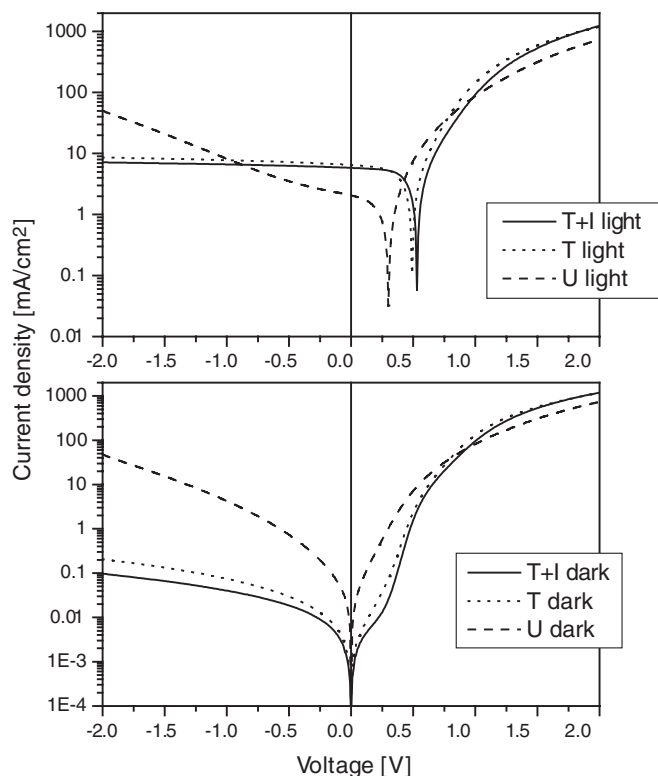


Fig. 4. Dark and illuminated ( $800 \text{ W m}^{-2}$  white light)  $I$ - $V$  curves of different postproduction-treated P3HT/PCBM solar cells: U (untreated), T (annealed), T+I (simultaneous application of heat and external voltage).

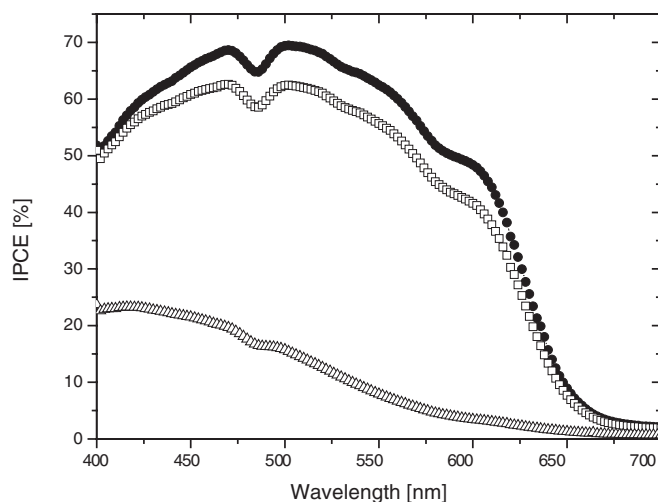


Fig. 5. External quantum efficiency (IPCE) of P3HT-PCBM solar cells: as-produced solar cell (open triangles), annealed solar cell (open squares), and cell simultaneously treated by annealing and applying an external voltage (filled circles).

doubled to  $\sim 60\%$ , while the maximum is shifted to a wavelength of  $500 \text{ nm}$  and broadened up to  $640 \text{ nm}$ . Therefore the increase is huge for the spectral area around  $600\text{--}640 \text{ nm}$ , which is consistent with results found for dye/P3HT blend photovoltaic cells.<sup>[17]</sup> A further improvement of the maximum of the IPCE over the spectral range from  $420 \text{ nm}$  to  $640 \text{ nm}$  can be achieved for devices postproduction-treated simultaneously with temperature and an applied external voltage (sol-

id circles). A maximum in IPCE of  $70\%$  is reached at a wavelength near  $500 \text{ nm}$ . On the other hand, the increase in the absorption of postproduction-treated solar cells is only around  $10\%$  compared to untreated devices. Therefore, we presume this enhancement of the IPCE to originate from an enhancement of the charge carrier mobility of the bulk. The dip at approximately  $480 \text{ nm}$  is an artifact of our measuring equipment and therefore not real.

The influence of the duration of the postproduction treatment on the overall efficiency is plotted in Figure 6. Using a temperature of  $75^\circ\text{C}$ , a maximum in efficiency is found for a duration of the treatment of  $5\text{--}6 \text{ min}$  for annealing only (dashed line) and  $4 \text{ min}$  for simultaneous treatment with temperature and an applied potential (solid line). Longer postproduction treatment times tend to decrease the overall efficiency dramatically again, as can be seen in Figure 6.

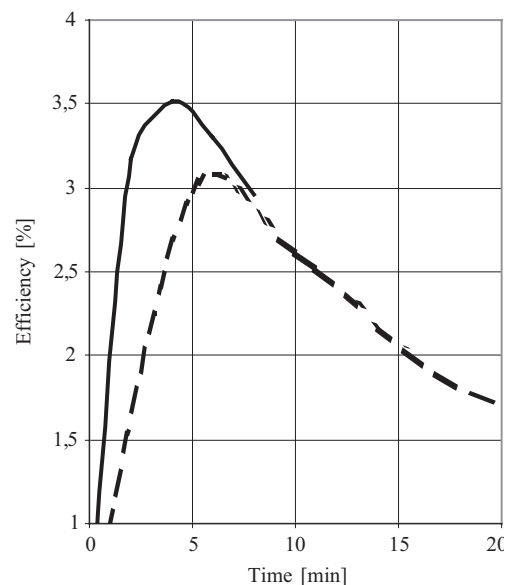


Fig. 6. Influence of the duration of the postproduction treatment on the white-light efficiency ( $800 \text{ W m}^{-2}$ ) for different postproduction treatment methods: annealing (dotted line), annealing plus external voltage (solid line)

### 3. Conclusion

Treating P3HT-PCBM solar cells after the deposition of the aluminum top electrode simultaneously with an applied external potential higher than the open circuit voltage and a temperature higher than the glass transition temperature led to improved overall efficiency. Photovoltaic devices with an external quantum efficiency (IPCE) above  $70\%$  and a power conversion efficiency of around  $3.5\%$  under illumination with white light at an irradiation intensity of  $800 \text{ W m}^{-2}$  were produced. The enhancement of the open-circuit voltage and the filling factor of postproduction-treated devices compared to untreated devices is presumed to result partly from a burning of shunts, while the increase of the short-circuit current is presumed to result from an increase of the charge carrier mobility.

## 4. Experimental

Plastic solar cell devices were prepared according to the following procedure: The indium tin oxide (ITO) coated glass substrate, purchased from Merck, with a surface resistance of  $\sim 15 \Omega/\square$ , was first cleaned by ultrasonication in organic solvents and dried in a nitrogen flow. Afterwards it was coated with a film of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) in aqueous solution, purchased from Bayer AG, using spin-casting technology. The thickness of the PEDOT layer was approximately 100 nm. After the PEDOT film had dried overnight, a photoactive layer with a thickness of 100–120 nm was cast on top of the PEDOT film by spin-coating from a solution of P3HT mixed with a soluble derivative of C<sub>60</sub>, PCBM, using 1,2-dichlorobenzene as the solvent. After a drying period of approximately 1 h, the top electrode, consisting of 0.6 nm LiF and subsequently 60 nm Al, was evaporated in a vacuum better than  $10^{-5}$  mbar. The size of the active area of the solar cells is between 5 and 8 mm<sup>2</sup> and was measured for each device separately using an optical microscope for exact determination.

Following the fabrication of the devices, the solar cells were further treated by annealing and simultaneously applying an external electric field. The devices were placed on a hotplate and a potential applied between the electrodes of the devices for several minutes. Best results were achieved using a temperature of 75 °C, a voltage of 2.7 V forward bias, and a duration of the postproduction treatment of 4 min. Afterwards the devices were cooled to room temperature before the measurements were started. For visualization of the postproduction treatment effect achieved with temperature and a simultaneously applied external voltage, postproduction-treated polymer solar cells were compared on the one hand with untreated polymer solar cells and on the other with polymer solar cells that were annealed only. The whole device preparation, as well as the postproduction treatment and the device characterization, was performed under inert gas (Ar) atmosphere inside a glove box system.

Current versus voltage curves were measured with a Keithley SMU 2400 unit under an illumination intensity of 800 W m<sup>-2</sup> with a Steuernagel solar simulator simulating the AM1.5 sun spectrum. Illumination occurred through the transparent ITO side. The external quantum efficiency, IPCE (incident photon to collected electron efficiency),

$$\text{IPCE} [\%] = 1240 \times I_{\text{sc}}/(\lambda \times I_{\text{P}}) \quad (1)$$

was measured with a lock-in detector after illumination with monochromatic light from a tungsten lamp. In the formula  $I_{\text{sc}}$  [ $\mu\text{A cm}^{-2}$ ] is the short-circuit cur-

rent density measured at the wavelength  $\lambda$  [nm] and  $I_{\text{P}}$  [ $\text{W m}^{-2}$ ] the incident light intensity at this wavelength.

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- [19] Filling factor  $\text{FF} = (V_{\text{max}}I_{\text{max}})/(V_{\text{oc}}I_{\text{sc}})$ , where  $V_{\text{max}}$  and  $I_{\text{max}}$  are respectively voltage and current density at the maximum power point and  $V_{\text{oc}}$  and  $I_{\text{sc}}$  are the open circuit voltage and the short circuit current density, respectively.