Efficient polymer-based interpenetrated network photovoltaic cells

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Organic solar cells based on an interpenetrated network of conjugated polymer as donor and fullerene derivative as acceptor materials have a great potential for improving efficiency. We fabricated a device based on a composite of poly(2-methoxy-5-(2′-ethylhexyloxy)-1, 4-phenylenevinylene and [6,6]-phenyl C60 butyric acid methyl ester. Surface treatment, insertion of interfacial layers, and improvement of the morphology of the active layer significantly increase the photovoltaic performances of the structure. We obtain an open circuit voltage of 0.87 V and short circuit current density of 8.4 mA/cm^2 under 100 mW/cm^2 air-mass 1.5 solar simulator illumination, yielding a 2.9% power conversion efficiency. © *2004 American Institute of Physics.*
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Poly para-phenylenevinylene (PPV) and its derivatives are widely studied owing to their semiconducting and luminescence properties. Within the class of PPVs, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) exhibits characteristics such as solubility that make it particularly favorable for optoelectronic device fabrication. The discovery of photoinduced electron transfer from a conjugated polymer as donor to buckminsterfullerene C$_{60}$ as an acceptor,[1] provided a molecular approach to high efficiency photovoltaic conversion. Indeed, for photovoltaic (PV) cells made with pure conjugated polymer, energy conversion efficiencies were typically $\eta = 10^{-3} - 10^{-2}\%$, too low to be used in practical application,[2] whereas, with the addition of fullerene, the composite material exhibits a significant photovoltaic effect.[3]

In the following, we report on the systematic optimization of photovoltaic (PV) cells made with MEH-PPV:PCBM composite films. Many attempts for making efficient PV cells using such combination have been published, yet with limited efficiency.[4–6] Our systematic optimization procedure yields highly reproductive devices presenting the same efficiency characteristics as previously reported devices built using the so-called interpenetrated network principle using MDMO-PPV as a semiconducting polymer.[7]

We fabricated photovoltaic cells using MEH-PPV: [6,6]-phenyl C60 butyric acid methyl ester (PCBM) cast from solution, with different concentrations of PCBM, as an active layer. The photovoltaic devices consist of five layers as shown in Fig. 1(a). They were prepared according to the following procedure.

The indium-tin-oxide (ITO)-coated glass substrate, purchased from SOLEMS, with 50 $\Omega/\square$ sheet resistance, was first cleaned in ultrasonic bath for 10 min in Deconex detergent, distilled water and in acetone two times, and was dried in an oven at 100 °C. UV-Ozone treatment was then performed for 15 min. A film of poly(ethylene dioxythiophene) (PEDOT-Baytron P®) was coated on the treated ITO substrates and was then dried for 5 min at 100 °C. The thickness of the PEDOT layer was approximately ~30 nm. The photoactive layer was deposited on top of the PEDOT film by spin coating a solution of the MEH-PPV:PCBM composite with different weight ratio from 1:3 to 1:4. The thickness of the photoactive layer was approximately ~120 nm.

Solution of the conjugated polymer MEH-PPV (purchased from ADS) with the fullerene derivative PCBM synthesized according to literature procedures[8] was prepared with 1,2-dichlorobenzene solvent in the appropriate weight ratio of MEH-PPV to PCBM. The concentration of MEH-PPV was 7 mg/ml. The chemical structure of the donor (MEH-PPV) and the acceptor (PCBM) materials is shown in Fig. 1(b).

The bilayer cathode consisting in 100 mn A1 on top of 0.6 nm LiF[9,10] was thermally evaporated through a shadow
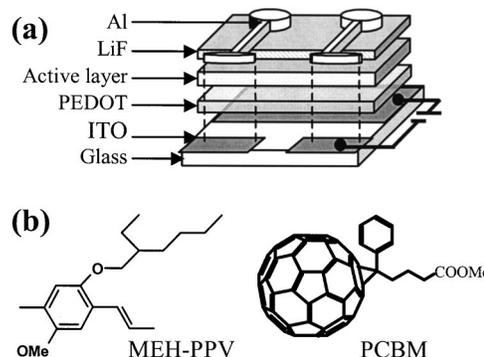

FIG. 1. (a) Device structure of the plastic solar cell. (b) Chemical structure of MEH-PPV and PCBM.

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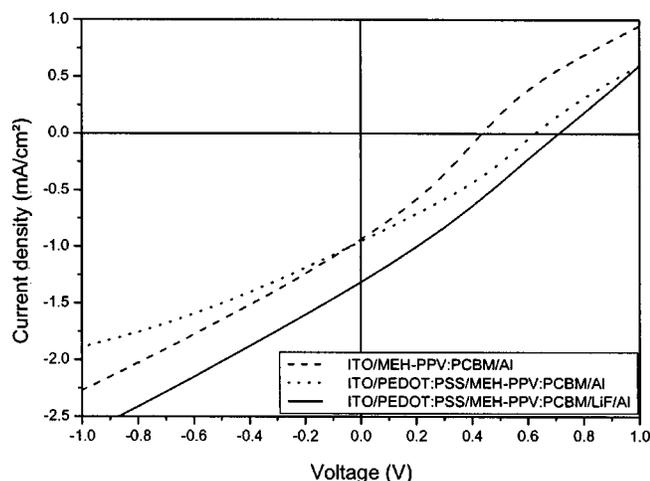Appl. Phys. Lett., Vol. 84, No. 12, 22 March 2004

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FIG. 2. Interface effect on the $J-V$ characteristics of devices with an active layer of MEH-PPV:PCBM (1:3 by wt.), that is spin coated from chlorobenzene: without interface layer (dashes), with a PEDOT layer at the anode (dots), with PEDOT and LiF layers (continuous line).

mask on the active layer in a vacuum of 10^{-6} mbar, resulting in cells with an active area of 34 mm^2.

We used a Keithley 236 unit to capture the $J-V$ current–voltage characteristics, in dark and under illumination with an AM1.5 solar simulator (Steuernagel Solar constant 575). The devices were illuminated through the transparent ITO anode. The incident photon to current efficiency (IPCE) was measured at a chopping frequency of 100 Hz with a lock-in amplifier (Perkin Elmer 7225) during illumination with the monochromatic light from a tungsten lamp (Acton Spectra Pro150), using the relation:

$$IPCE(\%) = 1240 * I_{sc}/(\lambda * I_p),$$

with I_{sc} [$\mu A/cm^2$] the short circuit current density at wavelength λ (nm) and I_p [mW/cm^2] the incident light intensity at this wavelength.

In Fig. 2, the current density–voltage ($J-V$) characteristics under white light (40 mW/cm^2) of photovoltaic devices made from a blend of MEH-PPV:PCBM with insertion of two interfacial layers at the polymer contact with anode and cathode are compared. We see that the interfacial PEDOT layer at the anode leads to an increase of the open circuit voltage (V_{oc}) from 0.4 to 0.66 V. It is mostly attributed to the high work function of PEDOT ($\sim$5.1 eV) with respect to that of ITO (4.4$\sim$4.7 eV).[11] The PEDOT layer does not change the value of the short circuit current density ($J_{sc} \sim$1.2 mA/cm^2). This means that $\sim$30 nm of PEDOT between ITO and the active layer do not affect the collection of holes at the anode of the PV devices. Insertion of thin LiF layer at the Al cathode leads to an increase in J_{sc} up to $\sim$1.5 mA/cm^2: It improves the ohmic contact between Al cathode and organic layer.[9] It is worth noting also that the fill factor (FF) is increased by the addition of both PEDOT and LiF interfacial layers. This tendency must be attributed to better ohmic contacts at the electrodes and suppression of a counter diode at the anode. The point is that the polymer blend contains both donor and acceptor materials in separated phases. Both have opposite behaviors at the contact electrodes. The interfaces must be adapted to make both ohmic contact with one material and rectifying contact with the other.
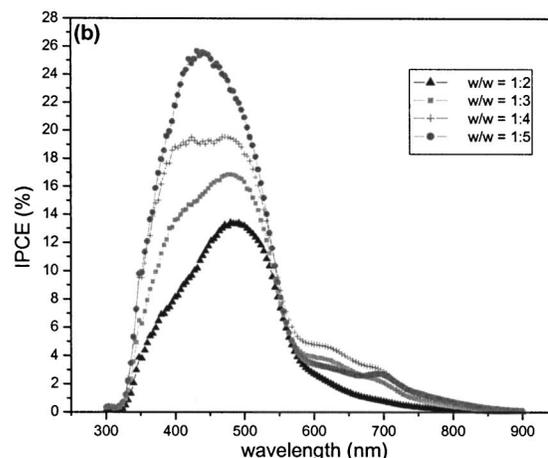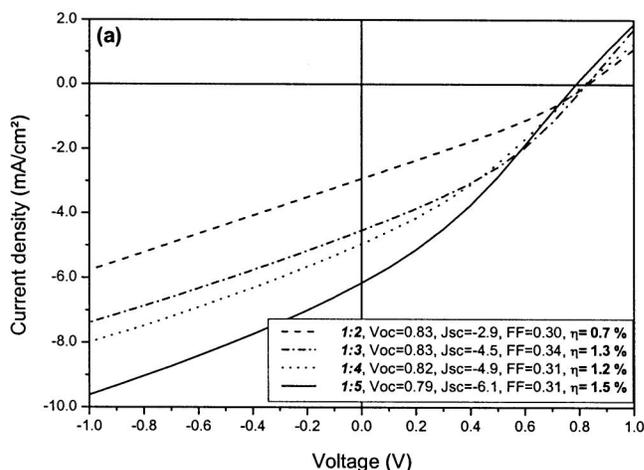

FIG. 3. Dependence on PCBM concentration of the $J-V$ curves under 100 mW/cm^2 AM1.5 illumination (a) and IPCE spectra (b) of PV (ITO/PEDOT/MEH-PPV:PCBM/LiF/Al) cells. MEH-PPV/PCBM ratio is given by weight (w/w). PV parameters are given in the inset of (a) V_{oc} in V and J_{sc} in mA/cm^2.

Figure 3 shows the $J-V$ characteristics and IPCE for various PCBM concentrations under 100 mW/cm^2 illumination. We observe the increase of J_{sc} with PCBM concentration. Higher concentration of PCBM favors the formation of a phase separated interpenetrated network with sizable domains,[12] which in turn favors effective charge separation.[4,5] This is confirmed by IPCE, which also increases with PCBM concentration from 13% to 26% at 500 nm wavelength [Fig. 3(b)]. The feature down to 700 nm in the IPCE may be attributed to PCBM absorption, showing that both compounds fully participate to the photovoltaic effect. The average PV parameters of cells made with a MEH-PPV:PCBM ratio about 1:5 are the following: J_{sc} = 5.8 mA/cm^2, V_{oc}=0.79 V, FF=0.31, η=1.4%. These values are larger than previously reported results using the same polymer.[5]

Figure 4 compares the $J-V$ curves for devices with MEH-PPV:PCBM (1:5 by weight) cast from chlorobenzene (CB), 1,2-dichlorobenzene (ODCB), and toluene (TOL) solution. On average, the CB and ODCB-based devices exhibit a much higher J_{sc} as compared to the toluene-based device (5.7 mA/cm^2 vs 2.4 $\mu A/cm^2$). The average V_{oc} and FF of CB and ODCB-based devices are almost identical, 0.8 V and 0.33, respectively. These yield a conversion efficiency around 1.5%. In contrast, the average V_{oc}, FF, and η of
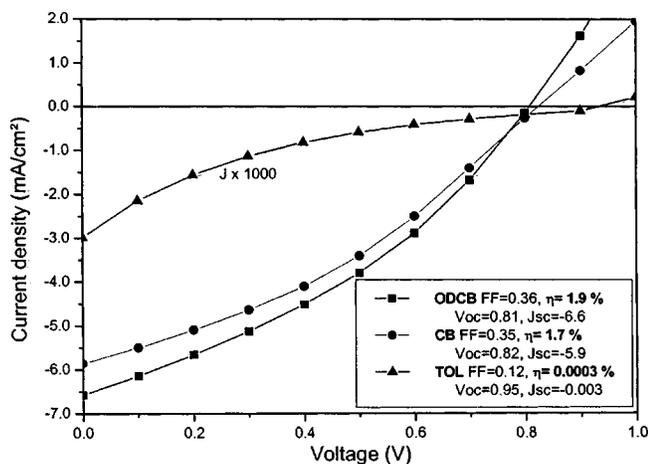
FIG. 4. $J-V$ characteristics under 100 mW/cm^2 AM1.5 illumination of devices with an MEH-PPV:PCBM active layer spin coated from ODCB (squares), TOL (triangles), and CB (circles). Current is multiplied by 1000 to fit in the scale for the toluene device. PV parameters are given in the inset: V_{oc} in V and J_{sc} in mA/cm^2.
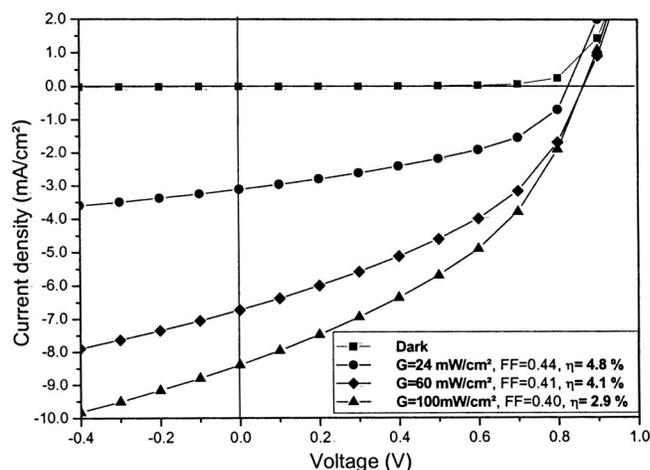

FIG. 5. $J-V$ characteristics under different AM 1.5 solar simulator light intensities G of an optimized MEH-PPV:PCBM device (see the text). PV parameters are given in the inset.

toluene-based device are 0.93 V, 0.12, and 3×10^{-4}%, respectively. We attribute this difference to the film morphology obtained from toluene, which appears improper to the formation of an interpenetrated network.[7,13]

For devices delivering currents in the range of 6 mA/cm^2 (Fig. 4), the ITO resistance becomes a questionable problem. Using the same preparation procedure as described earlier, we built photovoltaic cells based on MEH-PPV:PCBM (with 1:5 ratio) cast from ODCB, using ITO substrates from MERK with <12 $\Omega/\square$ surface resistance, instead of 50 $\Omega/\square$ for the previous devices. We show in Fig. 5 the evolution of the $J-V$ characteristics of such devices under different illumination intensities. Short circuit current and FF are improved owing to the lower ITO series resistance. Series and shunt resistances of the working devices in Fig. 5 degrade from low to large light intensities owing to poor charge transport characteristics of the polymer.[14] Values of the series and shunt resistances obtained from the slopes of the characteristic under 100 mW/cm^2 illumination, at 1 and 0 V, respectively, are 98 and 735 Ω. We obtain $J_{sc} = 8.4$ mA/cm^2 and $V_{oc} = 0.87$ V with the device in Fig. 5, so that conversion efficiency reaches 2.9%. Even a correction should be added to correct our values obtained with a solar simulator to the true AM 1.5 solar spectrum,[15] it is a significant improvement with respect to the previously reported results.[4–6] It is comparable to the best conversion efficiency obtained with MDMO-PPV:PCBM-based PV cells.[7]

In conclusion, using engineered electrode contacts and improving the deposition conditions as well as the PCBM loading into the polymer film, it is possible to build efficient PV cells using the interpenetrated network concept. This shows that the concept is extremely powerful and robust to build PV cells from polymer blends.[16]

Further improvements require optimization of charge transport and light absorption properties of the devices.[17] But

we can see that PV cells based on MEH-PPV:PCBM have large potentiality with a photocurrent larger than 8 mA/cm^2 under 100 mW/cm^2. Improving the fill factor up to 0.8 could yield a solar conversion efficiency in excess of 5%.

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