Improved efficiency and lifetime in small molecule organic solar cells with optimized conductive polymer electrodes

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We report on efficient and stable ITO-free small molecule organic solar cells with conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) electrodes using a post-treatment process, causing selective removal of PSS. The solar cells with post-treated PEDOT:PSS electrodes show significantly improved short circuit current densities and efficiencies compared to untreated devices. Moreover, the removal of PSS by the post-treatment significantly improves the lifetime of devices, which are more resistant to loss of fill factor compared to untreated devices. © *2011 American Institute of Physics*. [doi:10.1063/1.3634015]

The performance of organic solar cells (OSCs) has recently been greatly improved, opening the path towards an alternative renewable energy source. To realize the main advantages of OSCs, low cost and flexible devices, the development of electrodes is of great importance. The high cost, brittleness, and high temperature processing of indium tin oxide (ITO), commonly used in photovoltaic applications, drive a search for alternative electrode technologies. So far, conductive polymers,[1] silver nanowires,[2] thin metal layers,[3] carbon nanotubes,[4] and graphenes[5] have been investigated as alternatives to ITO for OSCs. The conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is in particular regarded as a promising electrode material because of its good optoelectronic properties and mechanical flexibility.[6] Several studies have investigated PEDOT:PSS electrodes for application in OSCs and organic light emitting diodes (OLEDs).[1,7]

In a previous study, we reported ITO-free OSCs fabricated on optimized PEDOT:PSS electrodes, using a solvent post-treatment process, resulting in very conductive electrodes.[1] The OSCs with post-treated PEDOT:PSS electrodes showed comparable efficiencies to ITO electrodes. In addition, it was shown that the solvent post-treatment removed insulating and hygroscopic PSS from PEDOT:PSS layers, improving the conductivity and air stability of the films. While the research for ITO-free OSCs with PEDOT:PSS electrodes have mainly been focused on device performance, the stability of devices has been studied far less, despite of the acidic and hygroscopic nature of PEDOT:PSS, which are potential stability issues.[8,9]

In this work, we report the effect of post-treated PEDOT:PSS on the lifetime of ZnPc:fullerene C_{60} bulk heterojunction small molecule OSCs. It is observed that the post-treatment does not only improve the conductivity of PEDOT:PSS but also significantly enhances the lifetime of devices as well as the short circuit current density and efficiency of OSCs. We attribute these effects to the removal of insulating and hygroscopic PSS by the solvent post-treatment.

PEDOT:PSS (Clevios PH1000 with 6 vol. % of ethylene glycol) is spin-coated on glass substrates, pre-treated in oxygen plasma, at 1500–5000 rpm for 30 s. Subsequently, spin-coated films are annealed on a hot plate at 120 °C for 15 min in ambient. For the solvent post-treatment, some of the samples are immersed in an ethylene glycol bath for 15 min and are subsequently annealed at 120 °C for 15 min, as described in detail previously.[1] The sheet resistance of films is examined by a four point probe setup with a source measurement unit (Keithley 2400). The thickness of the films is measured by a surface profilometer (Veeco Dektak 150). Transmittance is examined by a spectrophotometer (Perkin Elmer Lambda 900).

The PEDOT:PSS electrodes are thermally heated at 110 °C for 1 h in a vacuum chamber directly before device evaporation to remove residual water in the polymer. Devices are fabricated by thermal evaporation in a high vacuum chamber (K. J. Lesker, U.K.) at a base pressure of around 10^{-8} mbar. The layer sequence for devices is as follows (bottom to top): PEDOT:PSS as a bottom electrode/1 nm 2,2′-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6TCNNQ) as a hole injection layer/50 nm 5 or 10 wt. % F6TCNNQ doped hole transport layer (HTL)/30 nm mixed zinc phthalocyanine (ZnPc):fullerene C_{60} (ratio of 1:2) as an absorber layer/40 nm C_{60} as an additional absorber layer/6 nm BPhen as an exciton blocking layer/100 nm Al as a top electrode. MeO-TPD (N,N,N′,N′-tetrakis(4-methoxyphenyl)-benzidine), BF-DPB (N,N′-((diphenyl-N,N′-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine), and Di-NPD (N,N′-diphenyl-N,N′-bis(4′-(N,N-bis(naphth-1-yl)-amino)-biphenyl-4-yl)-benzidine) are used as HTLs. After evaporation, all devices are encapsulated with cover glass using epoxy glue and additionally getter material is placed in the cover glass cavity. The active areas are 6.7–7.6 mm^2 measured using an optical microscope. The current-voltage characteristics are obtained with a source measurement unit (Keithley Instruments) under an AM 1.5G sun simulator (Steuernagel SC1200). The values of short circuit

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current density are normalized to 100 mW/cm^2 with respect to a silicon reference diode, calibrated by Fraunhofer ISE (Freiburg, Germany), and are not corrected for spectral mismatch. The ageing experiments are carried out by a self-made setup, described elsewhere.[10] The devices, encapsulated with glass, are heated to ~50 °C and illuminated by white light emitting diodes (LEDs) (Philipps Lumileds, LUXEON LXK2-PWC4-0220) with an intensity of about 3 suns (270–291 mW/cm^2) or 5 suns (500–503 mW/cm^2) in ambient air.[10]

As a result of the solvent post-treatment, the PEDOT:PSS film thicknesses significantly decrease for all films by 27%–39% accompanied by an increase in conductivity by 36%–65%, while the transmittance in visible range hardly changes (less than 0.5%, consistent with our previous study).[1] Figure 1 shows the optical absorption spectra of PEDOT:PSS films prepared at different spin-coating speeds. Regardless of the post-treatment, an almost constant absorption is observed in the visible range, indicating that the post-treatment barely removes PEDOT. In contrast, a large change in the strong absorption peak at the wavelength of 225 nm, attributed the substituted phenyl groups in the PSS, is observed.[11,12] This strongly indicates the evidence of PSS depletion by the solvent post-treatment process, as discussed before.[1] A rough estimation of the amount of PSS removed by the solvent post-treatment is described in supplementary material.[15]

OSCs with different types of HTL layers are prepared to investigate the influence of the post-treatment on the PEDOT:PSS/HTL interface as well as device performances. Figure 2 shows the typical current-voltage (*I-V*) curves of solar cells with PEDOT:PSS electrodes (PEDOT_OSCs) having an HTL of Di-NPD with solvent post-treated and untreated electrodes. The highest power conversion efficiency (PCE) of 2.7% is observed in the device with Di-NPD accompanied by the post-treatment. Devices with MeO-TPD and BF-DPB show a PCE of around 2.6% (see supplementary material). The highest occupied molecular orbital (HOMO) levels of MeO-TPD, BF-DPB, and Di-NPD are −5.1 eV, −5.25 eV, and −5.35 eV, respectively (measured by ultraviolet photoelectron spectroscopy (UPS)).[13] The p-doping in HTL shifts the Fermi energy level closer towards the HOMO level of the HTL.[14] Considering these effects, charge injection and extraction barriers are minimized at the

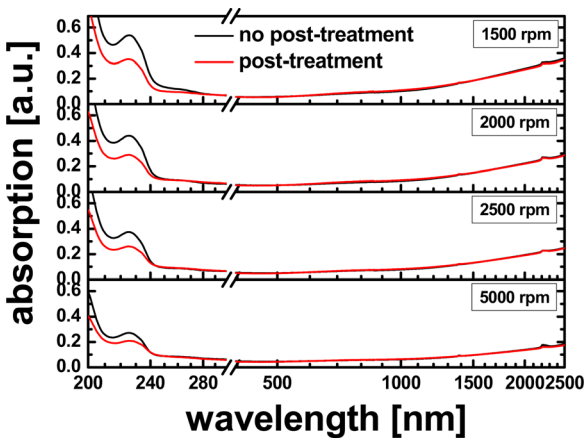

FIG. 1. (Color online) Absorption spectra of PEDOT:PSS thin films with and without the solvent post-treatment with respect to the spin-coating speed.

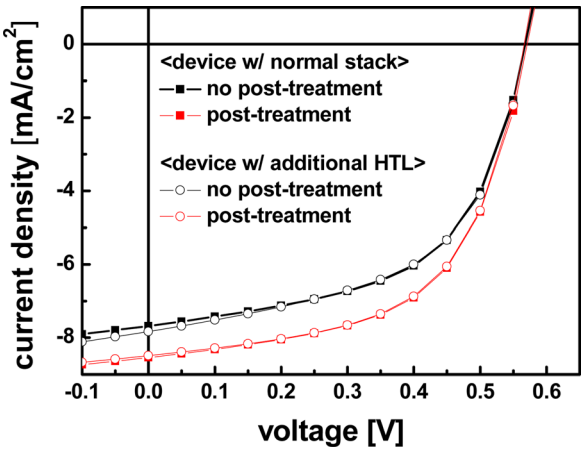

FIG. 2. (Color online) *I-V* curves of OSCs with the HTL of Di-NPD fabricated on the PEDOT:PSS electrodes (full symbols) with and without the solvent post-treatment. Devices with the additional highly p-doped Di-NPD layer between the PEDOT:PSS and the Di-NPD (open symbols).

PEDOT:PSS (work function: ~5.1 eV, as measured by UPS) and HTL interfaces. It is notable that the post-treatment improves the short circuit current density (J_{SC}) for all solar cells, especially for the device with Di-NPD. The J_{SC} increases from 7.5 to 8.3 mA/cm^2 and the fill factor (FF) increases from 55.4% to 56.7% as well as PCE from 2.4% to 2.7%. Similar devices which have an additional 5 nm thick layer of 25 wt.% F6TCNNQ doped Di-NPD between PEDOT:PSS and HTL (5 wt.% F6TCNNQ doped Di-NPD), to observe the influence of interface doping, show similarly enhanced J_{SC} and PCE on the post-treated electrodes as shown in Figure 2. For both types, the reference devices with untreated PEDOT:PSS have almost the same transmittance in the visible region as those with post-treated electrodes, indicating similar incident photon rates on the absorber layer. Injection or extraction barriers at the interface of PEDOT:PSS/doped HTL are low enough for good carrier transport. Considering these points, the improvement of J_{SC}, together with the increase of FF, is likely to be caused by the removal of PSS from the PEDOT:PSS surface, which is known to be PSS rich, and bulk region, being able to collect more photo-generated carriers by eliminating insulating PSS which hinders the carrier extraction at the interface of PEDOT:PSS/HTL electrode.

To investigate the effect of the solvent post-treatment on the lifetime of the devices, ageing measurements are carried out for selected devices. Figure 3 shows the *I-V* curves of PEDOT_OSCs having the HTL of MeO-TPD with and without solvent post-treatment of electrodes under 5 suns over 1000 h, showing the degradation behavior over time. Normalized power outputs at maximum power point are plotted in supplementary material. After 600 h, the untreated device shows a larger power decay compared to the post-treated device, indicating that power loss due to the increase of series resistance with ageing is more significant for the untreated device. Figure 4 shows the behavior of normalized PCE, FF, J_{SC}, and open circuit voltage (V_{OC}) for OSCs in the ageing experiment. The devices are illuminated with an intensity of 3 or 5 suns to accelerate ageing speed. All parameters of devices decrease over time, showing different ageing speeds. The device with the ITO electrode shows a normalized

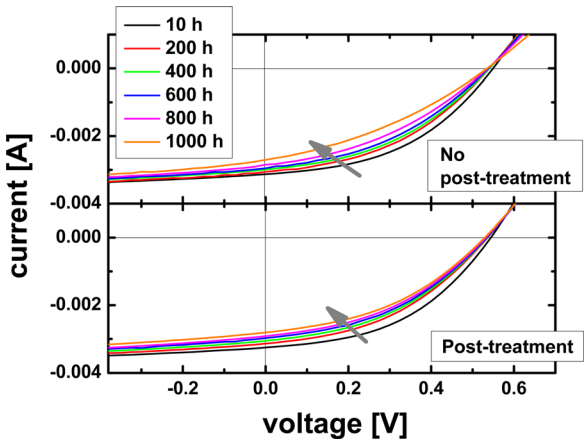

FIG. 3. (Color online) *I-V* curves of OSCs having the HTL of MeO-TPD on the PEDOT:PSS electrodes with and without the post-treatment. The encapsulated devices are heated up to ~50 °C and illuminated by white LEDs equivalent to 5 suns. Normalized power at a maximum power point (MPP) of OSCs is shown in supplementary material.

efficiency decay of ~3.5% over 800 h under 3 suns with almost stable FF, but a decrease of J_{SC} and V_{OC}. The PEDOT_OSC having an HTL of BF-DPB without the solvent post-treatment shows a PCE decay of 17%, after ~800 h under 3 suns. With the solvent post-treatment, the stability of the PEDOT_OSCs is improved, showing a PCE decay of only 9%. It is shown that the main factor of different ageing behavior in this experiment is the difference rate of the FF decay. Both OSCs show similar trend in loss of J_{SC} and V_{OC}. The device with solvent post-treated PEDOT:PSS is more resistant against FF decay compared to the untreated device. The post-treated device shows a FF decay of only 5%. In contrast, the FF decay of the untreated device is about 11% after ~800 h under 3 suns.

We increase the illumination intensity equivalent up to 5 suns for the PEDOT_OSCs with the HTL of MeO-TPD. The untreated device shows a PCE and FF decay of 33% and 22%, respectively, after 1000 h. In contrast, the PEDOT_OSC with post-treatment shows a remarkably enhanced stability compared to the untreated device, showing a PCE and FF decay of only 20% and 8%, respectively. Both PEDOT_OSCs with and without the post-treatment show a rather similar decrease of J_{SC} and V_{OC}. The improved stability for the post-treated samples can be well explained by the influence of PSS which has a hygroscopic and acidic nature. The PSS depleted samples by solvent post-treatment minimize the residual water in the electrode and decrease its acidity. As a result, water and PSS migration to the organic absorber layer are suppressed and the chemical stability is improved. Therefore, device degradation is slowed down or hindered.

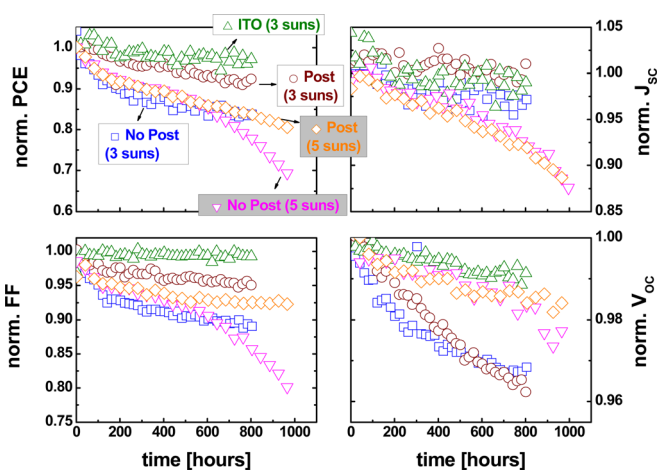

FIG. 4. (Color online) Ageing characteristics of solar cells with ITO or PEDOT:PSS electrodes treated with and without the solvent post-treatment. The encapsulated devices are heated up to ~50 °C and illuminated by white LEDs equivalent to 3 suns or 5 suns. All devices aged at 3 suns have BF-DPB as HTL, the devices aged 5 suns employ a Meo-TPD HTL.

TABLE I. Performance parameters of PEDOT_OSCs with an HTL of Di-NPD with and without solvent post-treatment of the electrodes.

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
No post-treatment				
Di-NPD	0.57	7.5	55.4	2.4
Di-NPD with additional HTL	0.57	7.6	54.1	2.3
Post-treatment				
Di-NPD	0.57	8.3	56.7	2.7
Di-NPD with additional HTL	0.57	8.3	57.2	2.7

In summary, we have demonstrated efficient ITO-free OSCs with optimized PEDOT:PSS polymer electrodes and improved lifetimes. The PEDOT_OSCs show an improvement of J_{SC} and PCE by the solvent post-treatment almost independent of the HTL materials used. In addition, the post-treatment considerably improves the lifetime of devices with a strong reduction in FF decay. These results indicate that the solvent post-treatment for PEDOT:PSS electrodes is a very promising method for the development of low cost and stable ITO-free solar cells.

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[15]See supplementary material at http://dx.doi.org/10.1063/1.3634015 for estimation of the amount of removed PSS, additional I-V curves, and an additional ageing graph are shown.