Controlling Surface Enrichment in Polymeric Hole Extraction Layers to Achieve High-Efficiency Organic Photovoltaic Cells

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Introduction

Academia and industry have shown great interest in organic photovoltaic cells (OPVs) based on printable polymeric semiconductors because of their potential as low-cost, lightweight, and flexible devices for sustainable solar energy conversion.[1,2] In recent years, the processing conditions of the PEDOT:PSS layer in OPVs have been modulated by a surface-enriched layer formed on top of the conducting polymer-based hole extraction layer (HEL). This tunes the surface work function of the HEL to better align with the ionization potential of the polymeric photoactive layer. Results show noticeable improvement in device power conversion efficiencies (PCEs) in OPVs. We achieved a 6.1% PCE from the OPV by optimizing the surface-enriched layer.

Results and Discussion

In order to study the contribution of the PSS surface layer to the tuning of the HEL WF, the HEL heat treatment was applied to systems with two different photoactive materials: poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) and poly(N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole):[6,6]-phenyl-C71-butyric acid methyl ester (PC71BM). Thermal annealing at 140 °C for 10 min, while the Yang group did so at 120 °C for 1 h.[6a,b] Kim et al. annealed the PEDOT:PSS layer of all OPV devices at a much higher temperature: 230 °C during 15 min.[6c,4] In addition to these differences in thermal annealing conditions, HELs with different PSS/PEDOT ratios have been used in OPVs. This can improve hole extraction from the photoactive layer due to its relatively high work function (WF) compared to indium-doped tin oxide (ITO; WF = 5.0–5.2 eV) compared to indium-doped tin oxide (ITO; WF = 5.0–5.2 eV). Hole extraction contact is an important issue, especially when the donor material in the photoactive layer has a highest occupied molecular orbital (HOMO) level that is lower than the WF of ITO, relative to the vacuum level.[35] Despite its importance for improving device efficiency the HEL has not been sufficiently studied yet. Many reports on the optimization of device performance lack a detailed investigation of the most-often used polymeric HEL (i.e., PEDOT:PSS). Therefore, the reported optimized processing conditions of the PEDOT:PSS layer in OPVs are different throughout the literature.[8] For example, the group of Heeger and Lee performed thermal annealing at 140 °C for 10 min, while the Yang group did so at 120 °C for 1 h.[6a,b] Kim et al. annealed the PEDOT:PSS layer of all OPV devices at a much higher temperature: 230 °C during 15 min.[6c,4] In addition to these differences in thermal annealing conditions, HELs with different PSS/PEDOT ratios have been used in OPVs. This can improve hole extraction from the photoactive layer (Figure 1). We investigated the effect of the PSS-enriched surface layer of the PEDOT:PSS film on the surface WF and hole extraction capability by using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

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tyric acid methyl ester (PCDTBT:PC_{70}BM). A layer of PEDOT:PSS of ca. 25 nm thickness was spin-coated on top of an ITO/glass substrate. After the ITO/PEDOT:PSS was thermally annealed at various temperatures in order to control the surface composition of the PSS-enriched surface, the P3HT:PCBM or PCDTBT:PC_{70}BM photoactive layer was spin-coated onto the PEDOT:PSS layer. Figure 2 a shows current density–voltage (J–V) characteristics of the devices. With increasing PEDOT:PSS annealing temperature, from 110 to 200 °C, the \( V_{oc} \) did not change while \( J_{sc} \) and the FF increased, which improved the PCE. The PCE of the device annealed at 110 °C was the lowest (2.4%) among all samples. The PCE of the OPV devices was highest (3.5%) at an annealing temperature of 200 °C.

We tried to understand the PCE enhancement by probing the surface composition and WF of the annealed PEDOT:PSS layers. X-ray photoelectron spectroscopy (XPS) was used because it can provide valuable information on the surface composition of the PEDOT:PSS films annealed at various temperatures (Figure 3). It is well-established that a PSS-rich layer results after spin-casting of PEDOT:PSS because of phase segregation, with an excess of PSS in the surface region.\(^7\)\(^–\)\(^10\) Figure 3 shows 2p core level spectra of PEDOT:PSS films annealed at 110, 150, and 200 °C. The main feature of 2p peak usually consists of a two-spin-split doublet, \( S_{2p_{1/2}} \) and \( S_{2p_{3/2}} \), with an energy splitting of 1.20 eV. The higher-binding-energy peak at ca. 169 eV is assigned to the sulfur atoms in PSS, and the lower one at ca. 164 eV is assigned to the sulfur atoms in PEDOT, based on well-established
XPS studies on PEDOT:PSS films.\textsuperscript{[7–10]} The peaks at 168.4 and 168.9 eV correspond to the PSS\textsuperscript{-} salt and PSSH, respectively.\textsuperscript{[8]} In addition, a very small peak at about ca. 167 eV was added for satisfactory fitting, which can be assigned to an intermediate state, sulfone (\(-\text{SO}_2\)).\textsuperscript{[9]} The ratios of PSS/PEDOT were calculated by using the area ratios under the two different peaks and are shown in Table 1. Surprisingly, the PSS/PEDOT ratio at the HEL surface consistently increased with increasing HEL annealing temperature. At 110 °C, the PSS/PEDOT ratio was only 3.675, but at 200 °C, the ratio was 8.397, more than double. This indicates that thermal annealing can control the concentration of the surface-enriched layer.

As the annealing temperature increased, the series resistance ($R_s$) decreased from 28.8 \(\Omega\) cm$^2$ at 110 °C to 14.8 \(\Omega\) cm$^2$ at 200 °C. The FF and $J_{sc}$ also increased in spite of increased PSS surface concentration. This can be explained in terms of increasing PEDOT:PSS conductivity\textsuperscript{[6e]} and p-doping of P3HT by the PSS surface layer.\textsuperscript{[6f]} Upon annealing, the insulating PSS chains that are not bound to PEDOT will be phase-segregated from the conducting PEDOT:PSS grains and migrate toward the film surface. This makes the annealed PEDOT:PSS more conductive,\textsuperscript{[6e]} which can decrease $R_s$. Huang et al. reported p-doping of P3HT by PSS at the PEDOT:PSS/P3HT interface upon heating.\textsuperscript{[6f]} Therefore, even if thermal annealing generates an insulating PSS layer at the film surface, some portion of PSS enriched at the surface of the annealed PEDOT:PSS film induces doping of P3HT during heating, which facilitates hole extraction via the PSS surface layer.

In an earlier work, we found that the luminous current efficiency in polymer light-emitting diodes is strongly affected by the surface WF of the films spin-cast from various PEDOT:PSS compositions.\textsuperscript{[9]} The surface WF of PEDOT:PSS films was tuned by controlling the molecular weight of PSS and the relative bulk concentration of PSS to PEDOT in PEDOT:PSS.\textsuperscript{[9]} The surface WF consistently increased as the ratio of PSS to PEDOT in the composition increased. In the present work, we demonstrate that the surface WF of single PEDOT:PSS composition can also be tuned by adjusting the thermal annealing temperature to control the degree of surface segregation of PSS. UPS measurements of the surface WF of PEDOT:PSS film show a systematic increase of the WF as the annealing temperature increased (Figure 4). The surface WF of PEDOT:PSS steadily increased as the PSS/PEDOT ratio increased and tended to saturate when the ratio was more than 8 (Figure 4). Overall, we found that the surface segregation of PSS in PEDOT:PSS layer could be controlled by various heat treatments. Not only heating temperatures, but also heating time might affect the surface segregation of PSS,\textsuperscript{[11]} although experiments with varying heating times were not conducted.

In addition, PEDOT:PSS layers heated at various temperatures from 110 to 220 °C were applied to PCDTBT:PC$_{70}$BM OPVs. Figure 5a shows the $J$–$V$ characteristics of these devices. With increasing PEDOT:PSS annealing temperature, from 110 to 220 °C, the $V_{oc}$ and $J_{sc}$ slightly increased (Figure 5b). Because the PSS enrichment at the PEDOT:PSS surface increased with thermal annealing temperature, the surface WF also increased with thermal annealing temperature (Figure 4). As the PEDOT:PSS WF increased at a given thermal annealing temperature, the energy level difference between the WF of PE-

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Annealing temperature & Work function & PSS/PEDOT ratio at surface & PCE \%
\hline
110 & 4.91 & 3.675 & 2.44\pm0.09 \\
120 & 4.95 & 4.065 & 2.73\pm0.06 \\
150 & 5.01 & 5.065 & 2.95\pm0.06 \\
170 & 5.04 & 8.169 & 3.13\pm0.05 \\
200 & 5.05 & 8.397 & 3.45\pm0.07 \\
\hline
\end{tabular}
\caption{The effect of thermal annealing temperature on the work function of PEDOT:PSS films, the PSS/PEDOT ratio at the film surface, and the power conversion efficiencies of P3HT:PCBM OPVs using the PEDOT:PSS films.}
\end{table}

Figure 4. Effect of PSS/PEDOT ratio at the film surface on the film WF.

Figure 5. a) Current density versus voltage, and b) $J_{sc}$ and $V_{oc}$ characteristics of PCDTBT:PC$_{70}$BM organic photovoltaic cells illuminated under 100 mW cm$^{-2}$ vs. annealing temperatures of PEDOT:PSS layer.
and the doping effect of PSS at the interface of HEL/PCDTBT; this is understood on the basis of a better alignment of HEL WF with the ionization potential of PCDTBT to increase the built-in field and on the doping effect of PSS at the interface of HEL/PCDTBT upon heating, which can compensate for the negative effect of increased concentration of insulating PSS on hole extraction in the HEL. Based on previous literature, the PSS-rich layer on the film surface was thinner than 3 nm. However, when we further increased the thickness of the PSS surface layer enriched at the film surface, the effect of increased hole extraction due to the increased built-in field across the active layer caused by increased film WF and p-doping by PSS competed with hole blocking by the thicker insulating PSS surface layer. The PCE was maximized at the PEDOT:PSS ratio of 1:3.5; this device had saturated \( V_{oc} \) and the highest \( J_{sc} \). As PSS concentration in the composition was increased above this ratio, we found a very slight gradual decrease of the \( J_{sc} \) and PCE. However, it is noted that all the OPV devices using reformulated PEDOT:PSS with higher PSS content showed higher PCEs than the control device. This indicates the importance of the surface composition to increase the surface WF and thus \( V_{oc} \) in OPVs.

**Conclusions**

We modulated the vertically segregated PSS-enriched layer at the surface of PEDOT:PSS films by adjusting the thermal annealing temperature and PSS ratio of the PEDOT:PSS composition. We showed how the surface layer affects the overall OPV device performance parameters. As the annealing temperature of the PEDOT:PSS layer increased, the PSS/PEDOT ratio at the surface increased, which also resulted in an increased surface work function and a better alignment of the hole extraction layer work function with the ionization potential of PCDTBT,
and consequently increased $V_{oc}$, $J_{sc}$, and power conversion efficiency values in organic photovoltaics that use a PCDTBT:PC$_{60}$BM photoactive layer. Furthermore, as the PSS ratio in the PEDOT:PSS compositions increased, the $V_{oc}$ increased due to the increase in surface work function and then saturated. Finally, we achieved noticeably improved power conversion efficiencies in organic photovoltaics (6.1 %). This work demonstrates that a PSS-enriched surface of the hole extraction layer is important to improve the hole extraction, the $V_{oc}$, and thus the overall power conversion efficiency of the organic photovoltaic device. These findings are widely applicable and can be used and can be improved in injection other organic electronic devices such as organic light-emitting diodes or organic transistors.

**Experimental Section**

The photovoltaic cells were fabricated on precleaned ITO/glass substrates. First, PEDOT:PSS (Baytron PH) was spin-coated to an average thickness of 25 nm. Then, the samples were annealed at 110°C for 10 min. In addition, the PSS ratio in PEDOT:PSS solution was modulated from 1:2.5 to 1:16 by adding PSS (10 min). The photovoltaic cells were fabricated on precleaned ITO/glass substrates. First, PEDOT:PSS (Baytron PH) was spin-coated to an average thickness of 25 nm. Then, the samples were annealed at 110°C for 10 min. In addition, the PSS ratio in PEDOT:PSS solution was modulated from 1:2.5 to 1:16 by adding PSS (10 min). The photovoltaic cells were fabricated on precleaned ITO/glass substrates. First, PEDOT:PSS (Baytron PH) was spin-coated to an average thickness of 25 nm. Then, the samples were annealed at 110°C for 10 min. In addition, the PSS ratio in PEDOT:PSS solution was modulated from 1:2.5 to 1:16 by adding PSS (10 min).

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