

Efficiency Improvement of Polymeric Bulk-Heterojunction Solar Cells Using PEDOT:PSS Buffer Layers Doped with Alcohol Derivatives

Do Yoon Kim¹, Moon Jong Han¹, Kwang-dong Seong¹, Ju-Hyung Kim², and Soonmin Seo^{1,2}

¹ College of BioNano Technology, Gachon University, Gyeonggi 461-701, Republic of Korea.

Phone: +82-31-750-8754 E-mail: kimdy0423@gc.gachon.ac.kr

² BioNano Sensor Research Center, Gachon University, Gyeonggi, 461-701, Republic of Korea.

Abstract

We demonstrated that the use of modified PEDOT:PSS buffer layers with alcohol derivatives between an anode and photoactive layer improved the performance of polymeric bulk-heterojunction solar cells. The polymeric solar cells containing the modified PEDOT:PSS layers show significant improvement in power conversion efficiency by up to ~ 59% when compared to the cell containing the pristine PEDOT:PSS layer. Changes in surface roughness and arrangement of PEDOT and PSS corresponding to the dopant-concentration could explain the behaviors of the polymeric bulk-heterojunction solar cells with the modified PEDOT:PSS layers.

1. Introduction

Organic photovoltaics (OPVs) are receiving much attention due to their advantages of low cost, light weight, solution-based process and mechanical flexibility compared to silicon-based devices. However, because of the relatively lower efficiency of OPVs than silicon-based solar cells, efforts to develop novel molecular designs and device-fabrication methods have been made to improve the performances of OPVs, which is still an ongoing issue.

OPV devices normally have multilayer structures and require proper selections of components, which are essential to improving performance. One of the OPV structures that has recently attracted attention is the bulk-heterojunction (BHJ) structure. To achieve efficient BHJ solar cells, a mixture of poly(3-hexylthiophene-2,5-diyl) (P3HT) and C₆₁-butyric acid methyl ester (PCBM) has been widely used for the photoactive layer, and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a promising material for the buffer layer between the anode and the photoactive layer. Although it has been known that the conductivity of PEDOT:PSS increases over two orders of magnitude after doping with polyalcohols, only a few attempts have been made to apply this modified buffer to OPV devices [1-4].

In this study, four different kinds of alcohol derivatives (i.e., glycerol, erythritol, xylitol, and mannitol) were doped into PEDOT:PSS at different concentrations to investigate their effects on the efficiency of polymeric BHJ solar cells. With P3HT and PCBM in chlorobenzene as the photoactive layer, the power conversion efficiency (PCE) of polymeric BHJ solar cell with the pristine PEDOT:PSS layer was 2.52% as the reference device. All devices with

the modified PEDOT:PSS layers performed better than the reference device.

2. Experimental

The polymeric BHJ solar cells in this work were fabricated on glass substrates coated with indium-tin-oxide (ITO). The ITO-coated glasses were cleaned by sonication in trichloroethylene, acetone, and isopropyl alcohol and subsequently subjected to ultraviolet ozone treatment. Modified PEDOT:PSS layers were individually spin-coated onto these ITO-coated glass substrates. To modify the PEDOT:PSS, glycerol, erythritol, xylitol, and mannitol were doped into PEDOT:PSS, respectively. These dopants have three, four, five, and six hydroxyl functional groups in normal alkane hydrocarbon backbones, respectively. The concentration of each dopant was varied (i.e., 2, 4, 6, 8, and 10 wt-%) to further evaluate the effects of modification, and non-doped pristine PEDOT:PSS was also prepared for comparison. After thermal annealing, the photoactive layer was spin-coated onto each sample in an argon-filled glove box. The photoactive solution consisted of a mixture of 1 wt-% P3HT and 0.8 wt-% PCBM in chlorobenzene. An aluminum layer was then deposited onto the photoactive layer of each sample by thermal evaporation in a vacuum chamber to complete the device structure. The device samples were finally annealed at 150 °C in an argon-filled glove box. The current density-voltage (*J*-*V*) characteristics of each device sample were measured under air mass (AM) 1.5 illumination (100 mW/cm²). The modified PEDOT:PSS films were analyzed with atomic force microscope (AFM), and the conductivities of the films were also measured.

3. Results and discussion

The *J*-*V* characteristics of the device samples are shown in Fig. 1. All the devices containing the modified PEDOT:PSS layers showed a higher PCE with an increase of short circuit current (*J*_{sc}) when compared to the device containing the pristine PEDOT:PSS layer. The devices modified with four different alcohol derivatives showed a similar tendency in device properties. The PCE and *J*_{sc} of each device increased as the dopant-concentration was increased up to a certain level (6 ~ 8 wt-%); however, these values decreased if the dopant-concentration exceeded this threshold level. These results indicate that the performance of the device was significantly improved as a result of modifying the PEDOT:PSS layer.

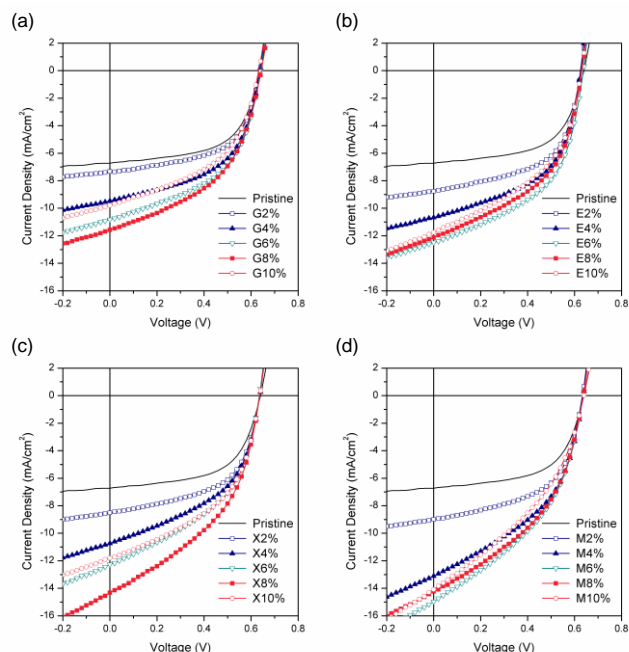


Fig. 1. J - V characteristics of polymeric solar cells containing the modified PEDOT:PSS buffer layers with (a) glycerol, (b) erythritol, (c) xylitol, and (d) mannitol. Note the highest PCE was 4.02%, which was $\sim 59\%$ higher than the PCE obtained using the device containing the pristine PEDOT:PSS layer (2.52% of PCE).

The J_{sc} significantly changed as a function of the dopant-concentration; however, the open circuit voltage (V_{oc}) remained constant (0.63 V) regardless of the modification of the PEDOT:PSS layer. The built-in-potential of the OPV is highly dependent on the difference in work-functions between the two metal electrodes, and the potential difference between the lowest unoccupied molecular orbital (LUMO) of the electron acceptor and the highest occupied molecular orbital (HOMO) of the electron donor [5, 6]. Since only the PEDOT:PSS layer was modified in this work, the constant V_{oc} was consistent with our expectation.

To further evaluate the increase in J_{sc} due to the modified PEDOT:PSS layer, the conductivities of the modified PEDOT:PSS films were measured using a simple metal-polymer-metal structure. The PEDOT:PSS layers modified with four different alcohol derivatives showed a similar tendency in conductivity. The conductivity corresponding to each dopant increased up to a saturation level as the dopant-concentration was increased. The increase in conductivity could be explained by the arrangements of PEDOT and PSS in the film. Thermal annealing of the pristine PEDOT:PSS layer leads to phase segregation of the layer, which results in an excess of PSS near the surface [3, 7, 8]. Because the surface of the PEDOT:PSS formed an interface with the metal electrode in the metal-polymer-metal structure, and since PSS showed insulating properties that were different from the PEDOT chains, which are responsible for conduction in the blend, charge-carrier injection from the metal electrode was impeded by the excess PSS at the interface. However, compared to the pristine PEDOT:PSS layer, the PEDOT:PSS layers doped with alcohol derivatives has been shown to result in a two-

to three-fold increases in the PEDOT to PSS ratios at the surfaces [1-4]. Adding dopants with polar groups into PEDOT:PSS also induces a conformational change in the PEDOT chains, which results in a higher charge-carrier mobility in the PEDOT:PSS layer [1]. Thus, the magnitude of the conductivity increase was correlated with the numbers of polar hydroxyl groups in the dopants (i.e., in the order of glycerol, erythritol, xylitol, and mannitol). In addition, doping of alcohol derivatives affects the size of the PEDOT-rich particles in the bulk PEDOT:PSS layer [2-4]. Consequently, such rearrangements of PEDOT:PSS due to the dopants enhanced not only the charge-carrier injection from the metal electrode but also the charge-carrier mobility in the bulk PEDOT:PSS film, which led to a higher conductivity.

Although the conductivities of the modified PEDOT:PSS layers increase up to saturation levels as the dopant-concentrations was increased, the J_{sc} of each complete device decreased if the dopant-concentration exceeded a certain level. This may have resulted from a change in the surface morphology of the PEDOT:PSS layer as a function of the dopant-concentration. To confirm this hypothesis, the surface roughness of each PEDOT:PSS layer was measured using AFM. For each dopant, the surface roughness of the PEDOT:PSS layer gradually increased with an increase in the dopant-concentration. These results imply that the dopants may hinder PEDOT:PSS from forming an efficient interface for charge transport with the photoactive layer at the high dopant-concentrations, and thus at the high dopant-concentrations there was a decrease in the PCE of polymeric BHJ solar cells.

4. Conclusions

In conclusion, we demonstrated that the use of modified PEDOT:PSS buffer layers by alcohol derivatives resulted in a significant increase in the PCE of polymeric BHJ solar cell, and $\sim 59\%$ increase in PCE was observed relative the pristine PEDOT:PSS layer. This enhancement of polymeric BHJ solar cell originates from an increase in J_{sc} due to the higher conductivity of the modified PEDOT:PSS layer. Rearrangements of PEDOT and PSS using the dopants could explain the behaviors of the polymeric BHJ solar cells with the modified PEDOT:PSS layers, because the arrangements of PEDOT and PSS effect not only the charge-carrier injection but also the charge-carrier mobility in the bulk PEDOT:PSS film. In addition, since the surface roughness of the PEDOT:PSS layer gradually increased with the dopant-concentration, one should be careful when modifying the PEDOT:PSS layer at a high dopant-concentration for designing the polymeric BHJ solar cells.

References

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