Investigation of buffer layer modified by doping glycerol for polymer photovoltaic devices

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1. Introduction
Organic photovoltaic devices (OPVs) have attracted considerable attention due to their potential for flexible, lightweight, and low-cost application of solar energy conversion. Bulk heterojunction organic photovoltaic devices (OPVs) have recently been intensively investigated with a view to increasing their efficiency.[1-4] One of the most studied systems is regioregular-poly(3-hexylthiophene-2,5-diyi) (P3HT) blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The power conversion efficiency observed from P3HT:PCBM solar cells reaches 3%-5% in different institutions.[5-8] Another studied system is surface treatment of electrode including oxidation, the addition of a self-assembled layer,[9,10] or poly(styrene-sulfonate) (PSS) layer insertion[11] that can lower or raise the work functions of cathodes and anodes, or enhance the cohesion, and thus lower the interfacial series resistance (Rs). In practice, a low series resistance (Rs) is required simultaneously for an ideal photovoltaic device.

2. Experiments
The inset of Fig. 1 schematically depicts the device configuration and the molecule structures we used in this work. The entire structure is described as glass/indium-tin-oxide (ITO)/PEDOT:PPS (+glycerol)/P3HT:PCBM/aluminum (Al). For modification of PEDOT:PPS film, glycerol was doped into PEDOT:PPS layer. The active area of the device is 1 mm². Calcium (Ca) (60nm) and Aluminum (Al) (150 nm) were thermally deposited onto the surface of the P3HT:PPS film inside a vacuum chamber (1x10⁻⁸ Torr) as the device cathode. All the procedure are implemented inside a nitrogen-filled glove box except for coating the PEDOT:PPS layer. The active area of the device is 1 mm².

3. Results and discussion
Figure 2 shows the J-V characteristics curves of the polymer photovoltaic devices with different-concentration modified buffer layer. The most optimum concentration was 30 mg/ml. The short-circuit current density (Jsc) of the reference device was 8.43 mA/cm² and the open-circuit voltage (Voc) was 0.6 V; the fill factor (FF) was 0.67. According to formula η = (IscVocFF)/Pin, the value of power conversion efficiency (PCE) (η) calculated from the obtained data was equal to 3.37 %.[15] Compared with the device made from neat PEDOT:PPS, incorporation of glycerol into PEDOT:PPS buffer layer led to improvement of PCE. The most optimum concentration was 30 mg/ml; the PCE and Jsc were 4.27 % and 10.46 mA/cm², respectively, on this concentration. However, the variation of FF was not conspicuous while doping glycerol into PEDOT:PSS has been reported,[13] we reported more sufficient and detail issues to demonstrate the improvement of PEDOT:PPS film quality and performance of OPVs. We discussed the interface between PEDOT:PPS film and P3HT:PCBM active layer by using atomic force microscopy (AFM) measurement.

Fig. 1 Device structure and molecule structures we used in this work

![Device structure and molecule structures](image-url)
PEDOT:PSS with different concentration.

One may wonder why the performance increased conspicuously while PEDOT:PSS buffer layer was modified by glycerol. First of all, we conferred the effect of the conductivity of glycerol-PEDOT:PSS film on the device performance. Fig. 3 shows the conductivity of the devices with different glycerol-concentration modification. From this figure, it was found that the conductivity of PEDOT:PSS film increases with the increase of the concentration of glycerol doped into PEDOT:PSS. However, with the increase of the concentration, we also found that the morphologies of PEDOT:PSS films have become rough. The rougher morphologies would influence the growth quality of P3HT:PCBM active layer and the leakage current of the devices.

Fig. 4 presents the J-V characteristics curves of the devices with different glycerol-concentration modification under the dark. At the negative bias and the linear regime of forward, as shown in Fig. 3, where the current is limited by shunt (parallel) resistance ($R_{sh}$) due to the leakage current, the current gradually increased with doping concentration. The increasing current with doping concentration further supports that the excess glycerol caused that the device leakage current. This is reason why the electric performance was not relatively improved with the increase of the concentration.

Fig. 5 shows the electric hysteresis curves of the devices with different glycerol-concentration modification. After measuring the black curve from -2 to 2 V, the red curve was measured from 2 to -2V continuously. The red and black curves will be over-lapped together on the ideal device. If these curves were not over-lapped together, it presented that there were many defects in the device which can catch the carriers transmit through the device. The caught carriers would form the space charges that hinder the transmission of the carriers generated in P3HT:PCBM active layer. From this figure, we can find that glycerol can improve the defects of PEDOT:PSS film.

4. Conclusion

The modification of the PEDOT:PSS film by doping glycerol indeed enhances the conductivity of the film, and then improves the performance of OPVs. The best power conversion efficiency value we obtained was 4.27% after modifying PEDOT:PSS film. Nevertheless, with the increase of concentration, the quality of the PEDOT:PSS morphologies became rougher. The effect would influence the device leakage current. This is reason why the electric performance was not relatively improved with the increase of the concentration. We also found that the defects of PEDOT:PSS film were improved by doping glycerol into PEDOT:PSS. For fabricating high power-conversion-efficiency polymer photovoltaic devices, this is an excellent method that doping polyalcohols into PEDOT:PSS to improve the conductivity of the film. At the same time, glycerol will be a good candidate for polymer photovoltaic device.

Reference