High efficiency bulk heterojunction organic solar cell by using high conductivity modified PEDOT: PSS as a buffer layer*

DENG Zhen-bo(邓振波)[1]**, **CHEN Zheng**(陈征)[1], **WU Hui**(武慧)[1], **LÜ Zhao-yue**(吕昭月)[2], **DU Hai-liang**(杜海亮)[1], **ZOU Ye**(邹业)[1], **ZHANG Guo-liang**(张国良)[1], and **ZHOU Mao-yang**(周茂杨)[1]

1. Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, China

2. Department of Physics, School of Science, East China University of Science & Technology, Shanghai 200237, China

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In this paper, bulk heterojunction solar cells with poly-(3-hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM) as an active layer and modified poly (3,4- ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) as a buffer layer are fabricated. The buffer layer is modified by adding 1% to 5% dimethyl sulfoxide (DMSO) into PEDOT: PSS solution before spin-coating. The conductivity of modified PEDOT:PSS and the performance of solar cells with modified PEDOT:PSS are measured. The highest conductivity of modified PEDOT:PSS with 4% DMSO can achieve 89.693 S/cm. The performance of organic solar cell with PEDOT:PSS modified by 4% DMSO is the best. The 4% DMSO-modified-PEDOT:PSS cell has a power conversion efficiency of 3.34% , V_{oc} of 5.7 V, J_{sc} of 14.56 mA/cm^2 and filling factor (*FF*) of 40.34%.

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Various kinds of sdar cells have been studied[1-4]. Si-based solar cells have achieved success in commercial applications[1]. However, the organic solar cells (OSCs) received more and more attention due to their potential for low-cost production and flexible device applications[2-4]. Immense amounts of experiments have been done to increase the conversion efficiency of OSCs[5,6].

Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)[7,8] was widely used in organic semiconductor devices because of its high conductivity and stability in air[9-12]. It was found that using PEDOT:PSS as an anode buffer layer to enhance photo induced carriers collection is an effective way to improve the conversion efficiency of organic solar cell[11,12]. On the other hand, the conductivity of PEDOT:PSS films can be improved significantly by adding high boiling point polar organic solvents[13-15]. It suggested that we can enhance the OSCs' performance by using modified higher conductivity buffer layer to further enhance carrier collection. In this paper, a bulk heterojunction device with poly-(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM) as an active layer and modified PEDOT:PSS as a buffer layer is fabricated. The results demonstrate that the performance can be enhanced significantly due to the increased conductivity of PEDOT:PSS by the addition of DMSO. Furthermore, an optimized modified PEDOT:PSS buffer layer is found.

First, a series of PEDOT:PSS solutions were prepared by adding dimethyl sulfoxide (DMSO) with various volume ratios (from 1% to 5%). The solution of P3HT:PCBM with the mass ratio of 1:1 and a concentration of 20 mg/ml was prepared by mixing P3HT and PCBM solutions which were prepared by dissolving each solute into chlorobenzene, respectively. Second, the bulk heterojunction devices as shown in Fig.1 were sequentially fabricated by spin-coating PEDOT: PSS (buffer layer) and P3HT: PCBM (active layer) onto cleaned ITO-coated glass substrate. Third, the devices were transferred into a vacuum drying oven for annealing at 140 °C with 20 min. Finally, aluminum cathode was deposited by vacuum thermal evaporation in vacuum chamber under a pressure of 3×10^{-3} Pa.

The conductivity characteristics of PEDOT:PSS samples were measured by four-point probe meter, the surface pro-

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** E-mail: zbdeng@bjtu.edu.cn

files of the films were characterized by atomic force microscopy (AFM), and the photoelectric conversion characteristic of the devices was measured by Keithley 2410 sourcemeter under a solar simulator with an illumination of 100 mW/cm^2.

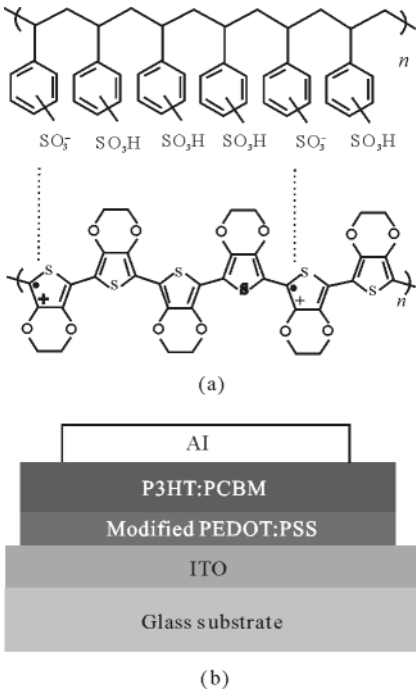

Fig.1 Schematic diagrams of (a) the molecular structure of PEDOT:PSS[10] and (b) the bulk heterojunction device with P3HT:PCBM as the active layer and modified PEDOT:PSS as the buffer layer

As shown in Fig.2(a), the conductivity of the modified PEDOT:PSS films is increased with the increase of DMSO concentration in PEDOT:PSS when the concentration of DMSO is less than 4%. And the opposite phenomenon is observed while it is more than 4%. The highest conductivity of modified PEDOT:PSS achieves 89.693 S/cm when the concentration of DMSO is 4%. However, the conductivity of pure PEDOT:PSS is 0.0884 S/cm. It must be pointed out that the concentration of DMSO in this paper means that in the PEDOT:PSS solution before spin-coating. Experiment result demonstrates that after spin-coating and annealing, there is no DMSO component observed in modified PEDOT:PSS samples.

The current density-voltage (*J-V*) curves of P3HT:PCBM-based bulk heterojunction devices with different modified PEDOT:PSS buffer layers are shown in Fig.2(b), and the detailed device characteristics are listed in Tab.1. Comparing Fig.2 (a) with (b), the open-circuit voltage (V_{oc}) is slightly decreased, but the short-circuit current density is increased significantly with the increase of DMSO concentration. And in terms of high power conversion efficiency, the solar cell with 4% DMSO modified PEDOT:PSS as a buffer layer shows the best performance among all cells, which has a power conversion efficiency of 3.34 %, V_{oc} of 5.7 V, J_{sc} of 14.56 mA/cm^2 and filling factor (*FF*) of 40.34 %.

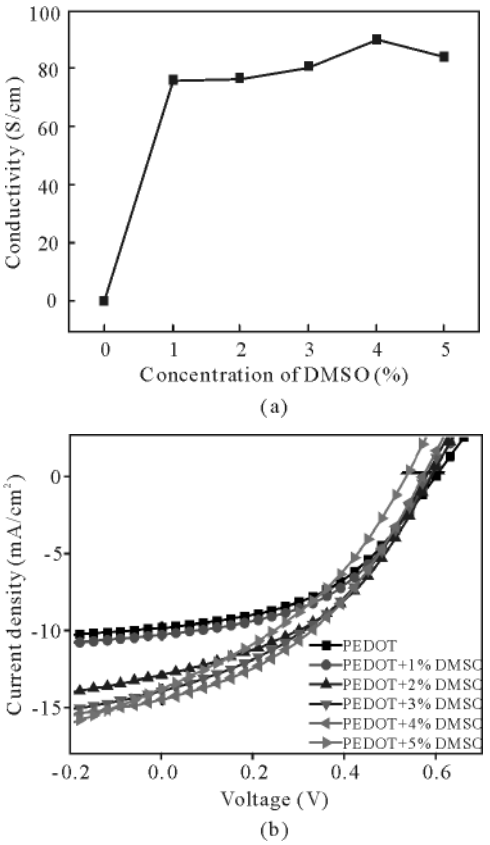

Fig.2 (a) Conductivity of buffer layer spin-coated by PEDOT:PSS solution with different concentrations of DMSO and (b) *J-V* curves of bulk heterojunction device with P3HT:PCBM as the active layer and modified PEDOT:PSS as the buffer layer

Tab.1 Characteristic parameters of the organic solar cell devices with modified buffer layer

Buffer layer deposited from	V_{OC}(V)	J_{SC} (mA/cm^2)	R_s (Ω • cm^2)	R_p (Ω • cm^2)	*FF* (%)	η (%)
Pure PEDOT:PSS solution	0.60	9.94	24.61	338.03	45.74	2.73
PEDOT:PSS+ 1% DMSO	0.59	10.41	20.53	308.22	46.90	2.88
PEDOT:PSS + 2% DMSO	0.59	12.99	18.66	142.34	42.77	3.28
PEDOT:PSS + 3% DMSO	0.58	14.01	18.57	157.67	40.10	3.26
PEDOT:PSS + 4% DMSO	0.57	14.56	18.02	166.68	40.34	3.34
PEDOT:PSS + 5% DMSO	0.53	13.85	18.16	92.30	36.87	2.71

As we all know, V_{oc} is mainly determined by the lowest unoccupied molecular orbital (LUMO) of acceptor and the

highest occupied molecular orbital (HOMO) of donor[10], so V_{oc} can not change obviously since all devices have the same active layer. On the other hand, more conductive buffer layer leads to the decrease of contact barrier at the interfaces of active layer/buffer layer and buffer layer/anode. Therefore, V_{oc} of the devices with a modified PEDOT:PSS layer is decreased slightly. The increase of current density can be explained by higher conductivity of PEDOT:PSS. Higher conductivity of PEDOT:PSS can reduce the interface contact barrier, and then improve photo induced carrier-transporting. So more carriers can be transported to anode and can be collected. Consequently, the current density is increased.

To confirm our suggestion discussed above and learn more about the relationship between the conductivity of PEDOT and the performance of OSC, the height and phase images were measured by AFM as shown in Fig.3. It can be obtained that the roughness of PEDOT is increased, which can be seen from the height image of Fig.3, and phase separation of PSS and PEDOT grain sizes is also increased with the increase of DMSO concentration in PEDOT:PSS solution, which can be seen from the phase image.

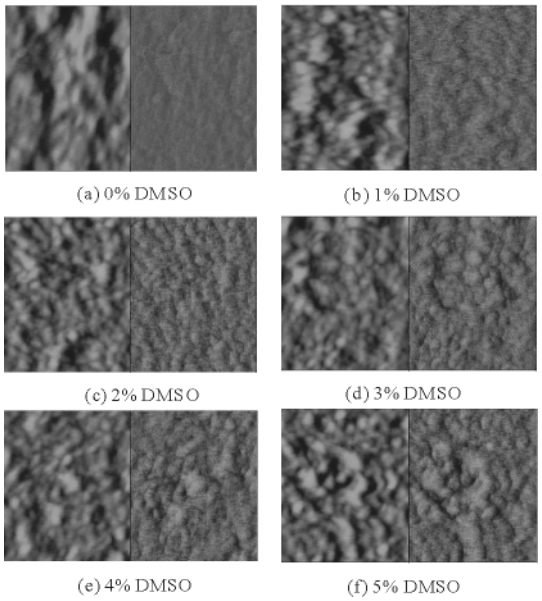

Fig.3 Height images (left) and phase images (right) of buffer layers spin-coated by PEDOT:PSS solution with 0%,1%, 2%, 3%, 4% and 5% DMSO

Based on the above experimental results and analyses, we speculate on that there are two effects of DMSO on PEDOT:PSS. One is that the decrease of insulation potential barrier between PEDOT grains reduced by phase separation of PSS enhances the probability of carrier tunneling, which can enhance the conductivity of PEDOT:PSS film, and the other is that the conductivity of PEDOT:PSS film is decreased by increasing roughness and weakening coulomb interaction between grains due to the increase of PEDOT grain size. When the concentration of DMSO is less than 4%, the effect of phase separation of PSS is dominant in two paradoxical factors, and thus both the conductivity of buffer layer and the performance of OSC are enhanced with the increase of DMSO concentration. However, if the concentration of DMSO is over 4%, the latter effect (the decrease of PEDOT:PSS conductivity) is dominant over the former effect (the increase of PEDOT:PSS conductivity). Consequently, the conductivity of PEDOT:PSS is decreased, and the performance of solar cell is deteriorated. The highest conductivity of PEDOT:PSS is 89.693 S/cm with a concentration of 4% DMSO. The best performance of solar cell is obtained with 4% DMSO modified PEDOT:PSS buffer layer, corresponding to a conversion efficiency of 3.34%, V_{oc} of 5.7 V, J_{sc} of 14.56 mA/cm^2 and filling factor of 40.34%.

Bulk heterojunction solar cells with P3HT:PCBM as an active layer and modified PEDOT:PSS as a buffer layer were fabricated. The buffer layer was modified by adding different concentrations of DMSO into PEDOT:PSS solution before spin-coating. The conductivity of modified PEDOT:PSS and performance of solar cells with modified PEDOT:PSS as a buffer layer are improved. There are two effects of DMSO on PEDOT:PSS: one is increasing the conductivity of modified PEDOT:PSS, and the other is decreasing the conductivity of modified PEDOT:PSS. When the concentration of DMSO is less than 4%, the former effect is dominant, and thus both the conductivity of PEDOT:PSS and the performance of OSC with modified PEDOT:PSS are enhanced with the increase of DMSO concentration; when the concentration of DMSO is over 4%, the latter effect is dominant, and thus the opposite phenomenon is observed. The highest conductivity of PEDOT:PSS with 4% DMSO achieves 89.693 S/cm. Based on this buffer layer, the best performance of OSC is obtained with a power conversion efficiency of 3.34%, V_{oc} of 5.7 V, J_{sc} of 14.56 mA/cm^2 and filling factor of 40.34%.

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