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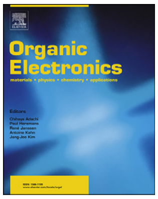

Efficiency enhancement of polymer solar cells via zwitterion doping in PEDOT:PSS hole transport layer

Zhiqiang Zhao [a], Xiang Chen [a], Qing Liu [a], Qiliang Wu [a], Jun Zhu [b], Songyuan Dai [b], Shangfeng Yang [a, *]

[a] *Hefei National Laboratory for Physical Sciences at Microscale, Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences, Department of Materials Science and Engineering, Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China (USTC), Hefei 230026, China*

[b] *Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, China*

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ABSTRACT

Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was doped by a novel zwitterion, 3-(N-morpholino)-2-hydroxypropanesulfonic acid (MOPSO), leading to a dramatic improvement of its conductivity and consequently efficiency enhancement in polymer solar cells (PSCs) based on PEDOT:PSS hole transport layer (HTL) and versatile photoactive systems. Under the optimized MOPSO doping concentration of 20 mmol l^{-1}, the conductivity of PEDOT:PSS film increased by about two orders of magnitude, and this is interpreted by the weakening of the Coulombic attractions between PEDOT and PSS components induced by MOPSO. MOPSO doped PEDOT:PSS was applied as HTL of bulk heterojunction (BHJ) PSC devices based on different photoactive layers including poly(3-hexylthiophene-2,5-diyl) (P3HT)/[6,6]-phenyl C61-butyric acid methyl ester ($PC_{61}BM$), poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT)/[6,6]-phenyl C71-butyric acid methyl ester ($PCDTBT:PC_{71}BM$) and thieno[3,4-b]-thiophene/benzodithiophene (PTB7):$PC_{71}BM$, leading to the best power conversion efficiency (PCE) of 3.62%, 7.03% and 7.56%, respectively, which are obviously enhanced relative to those of the corresponding reference devices based on pristine PEDOT:PSS HTL. The efficiency enhancement upon MOPSO doping is found to result from the increase of short-circuit current density (J_{sc}), which is attributed to the increase of the photoabsorption of the photoactive layer and the improved conductivity of PEDOT:PSS HTL.

1. Introduction

During the past two decades, polymer Solar cells have been attracting increasing attention as an emerging and promising renewable energy source, and showing advantageous potential in low-cost manufacturing, flexible and easy roll-to-roll fabrication [1–9]. Recently power conversion efficiency (PCE) of single-junction PSCs exceeding 10% has been reported, attributing to the complicated synthesis of novel conjugated polymer donors and fullerene acceptors and/or interface engineering [10–12]. In particular, optimization of the device structure especially the interfaces between donor(acceptor)/electrodes has been extensively studied recently and revealed to be a practical and facile route toward further enhancement of PCE, because such interfaces play an important role on efficient charge transport and extraction for PSC device [3,7,13–18]. For a typical bulk heterojunction (BHJ) structure of PSC device comprising an interpenetrating donor/acceptor network, the energy level offsets between donor(acceptor) and electrodes generally result in pronounced potential loss and consequently the limited performance of BHJ-PSC devices. Thus, interfacial layers or buffer layers are usually introduced between the active layer and electrodes so as to lower such energy level offsets and improve the interfaces between donor(acceptor)/electrodes by means of promoting charge collection and extraction via inducing interfacial charge redistribution, geometry modifications and/or chemical reactions [3,7,15,19–23].

Hole transport layer (HTL) introduced between the active layer and anode is crucial for selectively transporting holes and blocking electrons [7,21,23]. Up to now versatile HTL materials have been reported, including poly(3,4-ethylene dioxythiophene):poly(styrene

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* Corresponding author.
E-mail address: sfyang@ustc.edu.cn (S. Yang).

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sulfonate) (PEDOT:PSS) [5,23–25], semiconducting metal oxides such as MoO_x [20,26,27], polymers and small-molecule organic materials, self-assembled monolayers and graphene oxides etc [4,28–31]. Among them, since the first application in the late 1990s with effectiveness in hole transporting [32], PEDOT:PSS has been the most widely used HTL for conventional-structure BHJ-PSCs owing to its high optical transparency in the visible light spectrum, easy aqueous solution processing and high work function (4.8–5.2 eV as usually reported) beneficial for the formation of an Ohmic contact with many common donor polymers [5,24,33]. These advantages of PEDOT:PSS enable it as an alternative transparent anode material in ITO-free PSCs as well [6,34]. However, the conductivity of the pristine PEDOT:PSS film is usually very low (<1 S cm^{-1}) because of the existence of insulating PSS moiety [23,35,36], which is unfavorable for its efficient hole transport as HTL or transparent anode material. Therefore, it is highly desirable to improve the conductivity of PEDOT:PSS in order to facilitate hole transport and consequently to enhance the device efficiency. A practical approach for conductivity improvement of PEDOT:PSS film is to dope the aqueous PEDOT:PSS solution with some small-molecule organic compounds such as polar solvents (e.g. N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), ethylene glycol (EG), diethylene glycol, D-sorbitol), ionic liquid, anionic surfactant, dimethyl sulfate etc., and inorganic salt like $CuBr_2$ [7,23–25,37–41]. The conductivity improvement of PEDOT:PSS film induced by the versatile additives was generally interpreted by the weakening of the Coulombic attractions between the hydrophobic/conductive/positively charged PEDOT and hydrophilic/insulating/negatively charged PSS components due to the preferential interactions of polar additives with individual component [7]. Besides, another approach primarily developed for application of PEDOT:PSS as a transparent anode material in ITO-free PSCs is based on a "dipping" post-treatment of the PEDOT:PSS films with polar organic compounds, zwitterion, surfactant, inorganic salts and acids etc [34–37,42,43]. Such a "dipping" treatment usually leads to conductivity improvement of PEDOT:PSS film as well, but the improvement mechanism was attributed to the removal of the PSS component from PEDOT:PSS mixture [36,42]. In particular, zwitterion as a special molecule carrying both cation and anion with their charges immobilized has been applied in "dipping" treatment of PEDOT:PSS film for ITO-free PSCs, including 1-(N,N-dimethylcarbamoyl)-4-(2-sulfoethyl)pyridinium hydroxide (DMCSP), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDMAP), and N,N-dimethyl-N-[3-(sulfooxy)propyl]-1-nonanaminium hydroxide (DNSPN). All these three zwitterions resulted in moderate conductivity improvement of PEDOT:PSS film. However, PCE of the ITO-free PSC device based on zwitterion-treated PEDOT:PSS film as anode did not follow the same trend of conductivity improvement owing to the influence of the film roughness upon zwitterion "dipping" treatment [35]. These results revealed the complicated effect of zwitterion on PEDOT:PSS film. Besides, few studies reported the applications of conjugated zwitterions as electron-collection interlayers of BHJ-PSCs, contributing to obvious PCE improvements [44,45]. Hence, the unique amphiprotic nature of zwitterion enables its versatile application in PSCs, and it is desirable to develop novel zwitterion suitable for PSCs and to understand deeply its effect on device performance.

In this paper, we introduced a novel zwitterion, 3-(N-morpholino)-2-hydroxypropanesulfonic acid (MOPSO), to dope aqueous PEDOT:PSS solution, resulting in significantly improved conductivity of PEDOT:PSS film and consequently PCE of the BHJ-PSC devices comprised of versatile active layers including poly(3-hexylthiophene-2,5-diyl) blended with [6,6]-phenyl-C61-butyric acid methyl ester (P3HT:$PC_{61}BM$), poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) blended with [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) (PCDTBT:$PC_{71}BM$) and thieno[3,4-b]-thiophene/benzodithiophene (PTB7):$PC_{71}BM$. The doping concentration of MOPSO was optimized, and the effects of MOPSO doping on the conductivity, optical property and morphology of PEDOT:PSS film as well as BHJ-PSC device performance were investigated. Finally the mechanism for the efficiency enhancement upon MOPSO doping was discussed.

2. Experimental

2.1. Materials

The indium tin oxide (ITO) glass substrate with a sheet resistance of 10 Ω/sq was purchased from Shenzhen Nan Bo Group, China. PEDOT:PSS (Clevios P Al4083) was purchased from SCM Industrial Chemical Co., Ltd., for which the PEDOT:PSS concentration is 1.3% by weight and the weight ratio of PSS to PEDOT is 6:1. P3HT, PCDTBT, PTB7, $PC_{61}BM$ and $PC_{71}BM$ were bought from Luminescence Technology Corp., Solarmer Material Inc., 1-material Chemscitech Inc., Nichem Fine Technology Co. and Solenne BV., respectively. MOPSO was purchased from TCI Shanghai Co., Ltd. All chemicals were used as received without further purification.

2.2. Fabrication of BHJ-PSC devices

Our detailed fabrication procedure of the P3HT:PCBM BHJ-PSCs has been reported previously [15,22,34,46–49]. In brief, the ITO-coated glass substrate was first cleaned with detergent, then ultrasonicated in acetone and isopropanol, and subsequently dried in an oven overnight. PEDOT:PSS aqueous solution was first filtered by a 0.45 μm polyvinyl difluoride syringe filter. MOPSO was then added into the PEDOT:PSS aqueous solution with variable concentrations (10–30 mmol L^{-1}), and the MOPSO:PEDOT:PSS blend solution was ultrasonicated for 5–10 min and stored at about 4 °C in refrigerator prior to film fabrication. The pre-cleaned ITO glasses were subsequently treated by ozone-ultraviolet for 12 min. A thin film of MOPSO:PEDOT:PSS (36 ± 2 nm thick) was spin-coated onto the ITO surface at 3000 rpm for 60 s and then annealed at 120 °C for 30 min in air. Pristine (undoped) PEDOT:PSS film was also prepared under identical conditions for comparison. The P3HT:$PC_{61}BM$ (1:0.8 w/w) photoactive blend layer with a thickness of ~80 nm was prepared by spin-coating the chlorobenzene solution at 800 rpm for 60 s. Then, Titanium(IV) isopropoxide diluted by 1:200 in methanol was spin-coated on top of the photoactive layer (5000 rpm for 40 s) as electron transport layer. Finally, the device was transferred into a vacuum chamber (~10^{-5} Torr), and an Al electrode (about 80 nm thick) was thermally deposited onto the active layer through a shadow mask to define the effective active area of the devices (2×7 mm^2).

The fabrication procedures of the PCDTBT:$PC_{71}BM$ and PTB7:$PC_{71}BM$ BHJ-PSC devices follow the method we reported previously [34,41] and those reported in literature [3,50], which is slightly different to that for P3HT:PCBM devices. First, MOPSO:PEDOT:PSS films with the same thickness to those used in P3HT:PCBM devices were spin-coated onto the ITO substrate and dried in the ambient atmosphere at 120 °C for 30 min. The PCDTBT:$PC_{71}BM$ (1:4 w/w) photoactive blend layer with a thickness of ~80 nm was prepared by spin coating a blend solvent of 1,2-dichlorobenzene:chlorobenzene (3:1 v/v) solution at 2500 rpm for 60 s. The PTB7:$PC_{71}BM$ (1:1.5 w/w) photoactive blend layer with a nominal thickness of 100 nm was prepared by spin-coating a blend solvent of chlorobenzene:1,8-diiodoctane (97:3 v/v) solution at 2000 rpm for 2 min. Titanium(IV) isopropoxide diluted by 1:200 in methanol was spin-coated on top of the photoactive layer (5000 rpm for 40 s) as electron transport layer. Then, the films were