RAPID COMMUNICATION

Doped hole transport layer for efficiency enhancement in planar heterojunction organolead trihalide perovskite solar cells

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KEYWORDS
Organolead trihalide perovskite; Photovoltaic; Hole transport layer; Doping

Abstract
We demonstrated the efficiency of a solution-processed planar heterojunction organometallic trihalide perovskite solar cell can be increased to 17.5% through doping the hole transporting layer for reducing the resistivity. Doped Poly(triaryl amine) (PTAA) by 2,3,5,6-Tetrafluoro-7,7,8,8-Tetracyanoquinodimethane (F4-TCNQ) reduced device series resistance by three-folds, increasing the device fill factor to 74%, open circuit voltage to 1.09 V without sacrificing the short circuit current. This study reveals that the high resistivity of currently broadly applied polymer hole transport layer limits the device efficiency, and points a new direction to improve the device efficiency.

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Introduction
In the past five years, organometallic trihalide perovskite (OTP) solar cells have been attracting tremendous interest because of their unique properties for photovoltaic applications, such as strong absorption in the visible spectrum [1], long and balanced carrier diffusion length [2-5], solution processability and insensitivity to defect formation [6,7]. Recently, a number of endeavors have been directed to developing charge transport materials to further increase the efficiency of OTP photovoltaic devices [8-12]. While a lot of new hole transport materials (HTMs) have been synthesized and applied in the inverted structure OTP devices where HTMs were spun directly on top of the perovskite films [8,9,11], most of these HTMs are difficult to be applied in regular structure planar heterojunction (PHJ) OTP devices with the hole transport layer (HTL) underneath the perovskite layer. This is because the general solvents used for the OTP, such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), have too good solubility and can wash off most commonly used small molecular HTMs, such as 2,2’,7,7’-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9’-spirobifluorene (Spiro-OMeTAD). Therefore, although solution processed regular structure PHJ OTP solar cells have shown higher fill factor (FF) of over than 80% and great promise to

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achieve higher power conversion efficiency (PCE), most of these PHJ OTP devices still adopted Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) as HTL [13-15]. However, the low work function of PEDOT:PSS caused a relatively small open circuit voltage ($V_{OC}$) of around 0.90 V in these PHJ devices, compared to the typical $V_{OC}$ of ~1.05 V in the inverted structure OTP devices.[14,16-18] Recently, polymer HTMs have been studied because of its sustainability to DMF wash, for example, poly(N, N′-bis(4-butylphenyl)-N, N′-bis (phenyl)benzidine) (poly-TPD), was introduced into PHJ perovskite devices with device $V_{OC}$ greatly increased to 1.10 V. [19,20] Meanwhile, we found that another polymer HTM, Poly (triaryl amine) (PTAA), also showed great capability to increase device $V_{OC}$ and survive the DMF wash. However, the PCE of these polymer HTLs based OTP devices was still around 15% [19,20]. Compared with the best reported efficiency of PEDOT: PSS based perovskite devices, the higher $V_{OC}$ of polymer HTL based OPT devices was obtained at the expense of a smaller fill factor (FF) [13,14,16]. We speculate that the higher resistivity of these polymer HTMs than PEDOT:PSS may hinder charge extraction efficiency which reduces FF of these devices. Here, we report highly efficient solution-processed PHJ perovskite solar cells using 2,3,5,6-Tetra-ethylpyridine) Polystyrene sulfonate (PEDOT:PSS) as HTL[13,14] and non-wetting to DMF that PbI2 precursor was hardly spun the PTAA solution because the bare PTAA (m-tolyl)amino]triphenylamine (m-MTDATA) was mixed in the PTAA solution under a spin speed of 4000 RPM. For the device fabrication, small amount ($\sim$0.01 wt%) of F4-TCNQ were dissolved in toluene and mixed by desired F4-TCNQ and PCBM ratios ranging from 0.01 wt% to 10 wt%. The mixture of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13]. The PTAA and F4-TCNQ/PTAA ratios ranging from 0.01 wt% to 10 wt%. The mixture of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13]. The PTAA and F4-TCNQ/PTAA ratios ranging from 0.01 wt% to 10 wt%. The mixture of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13].

**Experimental section**

**Device fabrication and characterization**

The methods of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13]. The PTAA and F4-TCNQ/PTAA ratios ranging from 0.01 wt% to 10 wt%. The mixture of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13]. The PTAA and F4-TCNQ/PTAA ratios ranging from 0.01 wt% to 10 wt%. The mixture of cleaning ITO glass, methylammonium iodide (MAI) synthesis can be found elsewhere [13].

**Result and discussion**

Figure 1a shows the structure of the devices in this study. The perovskite films were made by interdiffusion method, in which PbI2 and MAI were sequentially spun onto the substrates, followed by a thermal annealing driven diffusion process [14]. It was discovered by us the surface of MAPbI3 can decompose during the thermal annealing process even though the annealing temperature was as low as 110 C. MAI was found to evaporate from the film surface, leaving Pb2+ rich surface, as revealed by the composition sensitive scanning probe microscopy technique [24]. Our density function theory calculation showed that the Pb2+ clusters cause deep electron and hole traps on the perovskite surface [24].
Double-layer fullerenes were used as electron transport layer, which can effectively passivate the charge traps on top of the perovskite film surface generated by the surface decomposition during thermal annealing [14,16,24]. High concentration of perovskite precursors was used in this study for stronger absorption. In addition, solvent annealing was applied in this study for larger grain size [16]. Details about device fabrication and measurements could be found in the experimental section. Figure 1b shows the cross-section scanning electron microscopy (SEM) of perovskite films on doped PTAA substrates. It is noted that the grain size of perovskite on PTAA substrates is much larger than that on PEDOT:PSS substrates. [14,25] The non-wetting surface of PTAA is beneficial for grain growth because of lower nucleus density and less dragging force [26]. The larger grain size of several micrometers observed on the PTAA substrates are of importance in suppressing grain boundary traps to obtain better device efficiency. Figure 1c and d shows the SEM images of perovskite on non-doped PTAA and 1 wt% F4-TCNQ doped PTAA film, respectively. The morphology did not exhibit noticeable difference before and after doping, excluding the influence of dopant on perovskite morphology.

Figure 2a shows the current density-voltage (J-V) curves of devices with different F4-TCNQ doping concentration in the HTLs. The thickness of the HTL was kept unchanged by using a same solution concentration and spin rate. The changed doping level was found to have a significant impact on device performance, especially FF. As shown in the Figure 2b, the devices with 20 nm non-doped PTAA layer exhibited a low FF of 65%. After doping the PTAA layer by 1 wt% F4-TCNQ, the device FF was increased to 74%. Further increasing doping level to 10 wt% deteriorated device PCE by reducing FF to 64%. The device with 1 wt% F4-TCNQ doped PTAA showed the highest efficiency with a JSC of 21.6 mA/cm², a VOC of 1.09 V, a FF of 74% and PCE of 17.5% under 1 sun illumination. Corresponding data can be found in Table 1. Figure 2c-d shows the external quantum efficiency (EQE), steady photocurrent output and stabilized PCE of the device with 1 wt% F4-TCNQ dopant in the HTL. The calculated JSC of 21.0 mA/cm² from EQE is in good agreement with that from J-V measurement. And the steady photocurrent measured at the maximum power point (0.85 V) is the same with that measured from J-V scanning, excluding the existence of obvious photocurrent hysteresis in our PHJ devices. The stabilized efficiency is 17.5%, confirming the accuracy of our device characterization. The absence of photocurrent hysteresis can be explained by the large grain grown on PTAA, and the application of double fullerene layer on the devices, which effectively reduce charge trap density at grain boundaries and film surface [13,27].

The FF enhancement can be explained by the series resistance reduction of the PTAA HTL caused by F4-TCNQ doping. To verify this, the series resistance of devices with different F4-TCNQ doping concentrations was derived by the slope of J-V curves. As shown in Figure 3, doping the PTAA film by 1 wt% F4-TCNQ reduced the device series resistance...
from 9.07 Ω cm² for non-doped PTAA to 6.07 Ω cm². Further increasing F4-TCNQ doping level to 10 wt% increased the device series resistance to 9.77 Ω cm², most likely caused by the increased aggregation of F4-TCNQ [28–31]. The series resistance derived from the J-V curve slope can be an indirect evidence for the doping effect because it represents the series resistance of the whole device rather than the PTAA films. To confirm the doping effect of F4-TCNQ, we further conducted four-probe measurements on the PTAA films with different doping levels. Details about four probe measurement can be found in the experimental section and our previous publication [21]. It should be noted that 200 nm PTAA film, which is much thicker than the PTAA layer in devices, was used to reduce noise in the four-probe measurement. To estimate the series resistance of the PTAA in real devices, the series resistance got from four-probe method was divided by a factor by assuming the series resistance has a linear relationship with the PTAA thickness. As shown in Figure 3, the resistivity variation measured by four-probe method follows the same trend with that derived from J-V curves, confirming F4-TCNQ doping can change the PTAA resistivity. It is noted that the resistance measured by a four-probe method is slightly larger than the resistance measured by J-V slope. One possible reason is the four-probe method measures the resistivity of film in lateral direction and the resistivity of PTAA film in the lateral and vertical directions can be different. Another possible reason is the electric field in J-V measurement is much larger than

<table>
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<th>Doping ratio (wt%)</th>
<th>JSC (mA/cm²)</th>
<th>VOC (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Rs (Ω cm²)</th>
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that in the four-probe measurement. In addition, the thickness of PTAA layer in devices was thin and may barely cover the whole substrate.

Now that we have demonstrated the doping effect of F4-TCNQ in changing the resistivity of the PTAA layer, the influence of resistance on device efficiency needs to be clarified. Here, we applied the equivalent circuit and simulation method in inorganic solar cell to calculate FFs. Details about the calculation can be found in the experimental section. The two curves in Figure 2b are the device FFs derived and J–V measured. The calculated FF variation is in good agreement with the measured data, indicating series resistance variation is the primary reason for the FF change in our devices. The calculation also implies the importance of reducing series resistance for further device PCE enhancement. The up limit of FF was calculated from Eq. (4) in the experimental section to be 89%, which provides a large potential for efficiency enhancement and great promise to boost PCE exceeding 20%. Since F4-TCNQ can only change the resistivity by several times, better dopants are expected in the future study to further reducing the resistivity and increasing FF.

Another merit for F4-TCNQ doping is that the reduced HTL resistance should make the device efficiency less dependent on HTL thickness. To demonstrate it, we compared the devices with doped or non-doped PTAA HTLs with different HTL thicknesses from 20 nm to 70 nm. Figure 4a–b shows the J–V curves of devices with and without F4-TCNQ doping, respectively. Without doping, the device J–V curve gradually showed s-kink when the HTL thickness increased to 70 nm. On the other hand, the devices with 1 wt% F4-TCNQ doped PTAA HTLs have PCE almost insensitive to PTAA film thickness. Figure 4c summarizes the series resistance of the devices with non-doped and doped PTAA of different thicknesses. For the devices containing 20 nm HTL, 1 wt% F4-TCNQ doping reduced the series resistance from 8.8 Ω cm² to 6.2 Ω cm². Lower series resistance was observed in the doped device, especially when the HTL is thick. The resistivity of the device with 70 nm HTL was reduced three times from 26.6 Ω cm² to 9.33 Ω cm² after doping with 1 wt % F4-TCNQ. The insensitivity of device PCE on HTL thickness is benefit for device reproducibility and especially attractive for large-area device fabrication.

Conclusion

In conclusion, we reported the increased device FF and enhanced device PCE of OTP solar cells using a doped polymer hole transport layer. By optimizing doping level, a high device PCE of 17.5% was achieved. This study emphasized the advantages of doping hole transport layer on the PCE of OTP solar cells and pointed out a direction of further increasing the efficiency of OTP PHJ solar cells to above 20% by exploring better dopants.

Uncited reference

[23]
Acknowledgments

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References