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A Simple Method to Enhance Performance of Inverted Planar Perovskite Solar Cells by Using PEDOT:PSS Doped with DMSO as Hole Transport Layer

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Abstract: In this work, the photovoltaic properties of inverted planar perovskite solar cells are promoted *via* a simple method by adding Dimethyl sulfoxide (DMSO) into Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) hole transport layer. Compared to the control device based on pristine PEDOT:PSS, the device with DMSO doping shows different enhancement in short circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE), respectively. The J_{sc} is increased from 21.29 mA/cm² to 22.15 mA/cm², the FF is increased from 76.35% to 80.09%, and the PCE is increased from 16.02% to 17.01%, showing 4%, 5% and 6% enhancement, respectively. A combination of characterizations has been utilized to systematically investigated the effect of DMSO doping on properties of PEDOT:PSS and perovskite film. It can be found that the incorporation of DMSO leads to a moderate phase separation of PEDOT:PSS, which causes the PEDOT component to form a better conductive channels, enhancing the conductivity and hole transport ability of PEDOT:PSS. The steady-state photoluminescence spectra exhibit significant fluorescence quenching, indicating promoted hole extraction ability of PEDOT:PSS after doping with DMSO. Thus, a more efficient hole transfer between the perovskite active layer and the anode is achieved, which contributes to the high fill factor above 80%. So that an effective and easy approach to improve the photovoltaic performance of inverted planar perovskite solar cells or organic solar cells is provided.

Key words: hole transport layer; conductivity; perovskite solar cell; photovoltaic performance

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优化反式平面钙钛矿太阳电池性能的简便方法—— 利用 PEDOT:PSS 与 DMSO 共混空穴传输层

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摘要: 优化界面接触、增强界面处载流子传输对于提高钙钛矿电池性能具有重要意义。本研究将适量二甲基亚砜 (DMSO) 添加到聚(3,4-乙炔二氧噻吩)-聚(苯乙烯磺酸盐) (PEDOT:PSS) 空穴传输层中, 改善了空穴传输层的导电性和空穴传输特性, 有效提高了反式平面钙钛矿太阳能电池光伏性能。短路电流 (J_{sc}) 从 21.29 mA/cm² 提高到 22.15 mA/cm², 填充因子 (FF) 从 76.35% 提高到 80.09%, 转换效率 (PCE) 从 16.02% 提高到 17.01%。薄膜与器件性能综合测试结果表明, DMSO 的掺入使 PEDOT:PSS 发生适度相分离, 形成更好的

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PEDOT导电通道,增强了 PEDOT:PSS 的导电特性。稳态光致发光光谱呈现出显著的荧光猝灭效应,也表明掺杂 DMSO 后 PEDOT:PSS 的空穴提取能力得到提高,钙钛矿活性层与阳极之间的空穴传输更加顺畅,有助于实现高达 80% 以上的填充因子。本研究为改善反式平面钙钛矿太阳能电池或有机太阳能电池光伏性能提供了一种高效、简便的方法,具有很好的现实意义。

关 键 词: 空穴传输层; 电导率; 钙钛矿太阳能电池; 光伏性能

1 Introduction

Optimizing interface contact and promoting carrier transport at the interface are particularly important for improving the photovoltaic performance and stability of perovskite solar cells^[1-4]. Poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) is the most commonly used hole transport material in organic photovoltaic cells and inverted planar perovskite cells^[5-13]. It is usually sandwiched between indium tin oxide (ITO)-coated glass and perovskite or organic active layer, not only regulating the ITO surface function, but also extracting the holes to facilitate the transport and collection of photo-generated charges^[14-16]. However, the recombination of photo-generated charges at PEDOT:PSS anode interface is one of the reasons for decreasing the efficiency of solar cells^[17-19]. The morphology, surface roughness and uneven conductivity from inside to outside of PEDOT:PSS film also affect the hole transport process.

PEDOT:PSS is an aqueous solution of polymer, mainly composed of conductive PEDOT and non-conductive PSS. High conductivity PEDOT:PSS aqueous solutions such as PH 1 000 or PH 500 are commonly used as transparent electrodes. PEDOT:PSS 4083 is often utilized as the hole transport layer (HTL) in organic light-emitting diodes, organic solar cells (OPVs), field effect transistors (OFETs), photodetectors and so on^[20-24]. Although PEDOT:PSS 4083 has high transparency, low viscosity, and good film formation, it also has some disadvantages such as acidity, hygroscopic nature, lower work function than the ionization potential of perovskite, poor electron blocking capability^[25] and relatively low conductivity (generally about 10^{-4} S/cm)^[26]. Moreover, PEDOT and PSS are prone to agglomera-

tion after film formation, and non-conductive PSS is easily enriched in film surface. It makes the PEDOT:PSS film have uneven conductivity from inside to outside and affects the charge transport and extraction in inverted devices. Therefore, modifying the PEDOT:PSS HTL *via* optimizing the micro-morphology or making its conductivity more uniform, is an important way to mitigate these drawbacks of PEDOT:PSS and to improve the performance of the solar cells.

For the inverted planar perovskite solar cells-based on PEDOT:PSS HTL, improving the hole transport ability of PEDOT:PSS layer is critical. Gu *et al.* applied a self-assembled monolayer (C3-SAM) to modify PEDOT:PSS, which improved the contact between the PEDOT:PSS HTL and the perovskite layer, optimized the separation and transport of hole carriers, leading to an improvement in device performance^[27]. Huang *et al.* reported that PEDOT:PSS doped with PEO (polyethylene oxide) was proved to be an effective hole-extracting layer due to its high electrical conductivity and extremely smooth surface, and could improve the efficiency of planar heterojunction perovskite hybrid solar cells^[28]. Therefore, it is necessary to improve the electrical conductivity of PEDOT:PSS layer to increase the effective transmission path of holes, thus improving the photovoltaic performance of devices. Dimethyl sulfoxide (DMSO) is well known as a strong polar solvent. Its distinctive advantages such as superior dipole moment and relatively high boiling point can lead to form strong dipole-dipole or dipole-charge interactions between PEDOT:PSS and DMSO^[29]. Liu *et al.* employed the two-dimensional MXene, $\text{Mo}_{1.33}\text{C}$ -assisted PEDOT:PSS as an efficient HTL to construct high-efficiency polymer solar cells and enhanced the device performance^[30]. Huang *et al.*

treated PEDOT:PSS with a high concentration of DMSO (10%) and obtained a P-I-N type perovskite cell with a power conversion efficiency of 16.7%. Although the short-circuit current and power conversion efficiency were improved, the filling factor was reduced.

In our work, DMSO was added into PEDOT:PSS 4083 solution. The concentration of DMSO is only 1%. It was found that the conductivity of PEDOT:PSS films continued to increase with the increase of DMSO addition, but the film forming performance of PEDOT:PSS on ITO substrate deteriorated significantly due to the deterioration of wettability of PEDOT:PSS, which was extremely detrimental to the subsequent formation of perovskite films. The introduction of 1% DMSO influences the microstructure of PEDOT:PSS through causing moderate phase separation. This facilitated the formation of better conductive channels and increased the conductivity of PEDOT:PSS by 2 orders of magnitude, thus promoting the hole transport ability of PEDOT:PSS HTL and short circuit current. Furthermore, the DMSO molecule existed in PEDOT:PSS film has a stronger coordination ability with Pb^{2+} from lead halide. This affects the crystallization of perovskite *via* a strong interaction between DMSO and Pb^{2+} , making a positive effect on the morphology of upper perovskite active layer, as similarly reported in previous literature^[26]. The perovskite film based on the PEDOT:PSS with DMSO doping exhibits larger and more uniform grain sizes, beneficial for reducing film defects and enhancing charge transport. Thus, a more efficient hole transfer between the perovskite active layer and the anode is achieved, which contributes to the high fill factor above 80%. The simultaneous improvement of the above two aspects (short-circuit current and fill factor) improves the performance of inverted planar perovskite cells based on PEDOT:PSS HTL, delivering a higher power conversion efficiency of 17.01%.

2 Experiments

2.1 Materials

All raw materials were purchased, and more

detailed purchasing information is provided in supplementary material. The preparation of perovskite precursor solutions can be easily found in our previous report^[1,4,31]. PEDOT:PSS 4083 aqueous solution was added with 1% DMSO and stirred evenly at room temperature to prepare the HTL.

2.2 Device Fabrication

Under the condition of 3 000 r/min, PEDOT:PSS with or without DMSO was coated onto the cleaned ITO substrates that had been ultrasonically cleaned by detergent and deionized water in sequence. After drying at 120 °C for 20 min in the air, the mixed lead precursor solution preheated at 90 °C on a hot plate was spin-coated at 6 000 r/min onto the ITO/PEDOT:PSS substrates. It should be noted that the substrate was placed in a spin coater with heating function, and the substrate remains heated at 40 °C during the entire spin coating process. Then the MAI precursor solution containing 0.05% 1,6-Diaminohexane Dihydrochloride (1,6-DD) additive and PCBM:BCP blend solution were spin-coated on the substrates in sequence to obtain perovskite active layer and ETL layer, specific process details had been reported in our previous articles^[1,4,31]. Finally, the Ag cathode with an area of 0.1 cm² was deposited by vacuum thermal evaporation. Each cell area was 0.1 cm², determined by the shadow mask utilized. Then the planar perovskite solar cells with inverted structure of ITO/PEDOT:PSS (without or and with DMSO)/perovskite/PCBM:BCP/Ag were obtained. All processes were performed in the air except for the Ag cathode and the perovskite preparation process which were performed in an argon-filled glove box.

2.3 Characterizations

The perovskite crystal structure was characterized by X-ray diffraction (XRD, Rigaku D/MAX 2500). Ultraviolet-visible spectroscopy (UV-Vis) was performed to characterize the absorption properties of the perovskite active layer with a Jasco-4000 spectrophotometer. AlphaStep D-100 Stylus Profiler (KLA-Tencor) was employed to measure the film thickness. The field emission scanning electron microscope (SEM, Hitachi SU-8010), atomic force

microscope (AFM, Bruker INNOVA SPM) and conduction atomic force microscope (C-AFM) were carried out to study the surface morphology and conductivity of the final perovskite film. In order to explore the defect passivation and non-radiative recombination, a fluorescence spectrometer (Jobin Yvon FluoroLog-3) was used to record the steady-state photoluminescence spectra (PL) of the film. All devices were not encapsulated and were stored under dark conditions in the air. While the current density-voltage (J - V) characteristic test of the devices was carried out in a glove box filled with argon. The J - V test was performed by a programmed Keithley 2400 sourcemeter under illumination of a Newport Oriol 150 W solar simulator (AM 1.5 G, $100 \text{ mW} \cdot \text{cm}^{-2}$), the light intensity of which was calibrated with a solar reference cell (SRC-1000-TC-QZ, VLSI standards, Inc.).

3 Results and Discussion

3.1 Influence of DMSO Doping on Morphology and Conductivity of PEDOT:PSS Film

To investigate the effect of DMSO doping on the film conductivity, PEDOT:PSS thin films of micron thickness based on pristine PEDOT:PSS and DMSO-doping were prepared *via* drop coating method. The value of film conductivity (σ) can be calculated according to Equation (1):

$$\sigma = \frac{1}{\rho} = \frac{1}{R \cdot t}, \quad (1)$$

wherein ρ is resistivity, R is square resistance obtained by using the ohmmeter test of the multimeter, and t is the film thickness measured by step profiler. Tab. 1 summarizes the conductivity of different PEDOT:PSS film samples. It is obvious that the conductivity of PEDOT:PSS film is increased by 2 orders of magnitude after doping DMSO. It means that the incorporation of DMSO facilitates the formation of better conductive channels. Actually, previous literatures^[26,32] have reported this. DMSO is conducive to the rearrangement of PEDOT components, with the PEDOT chain extending from a coil-shaped structure to a linear structure, to form a more uniform conductive paths. Thus, the hole transport

ability of PEDOT:PSS 4083 film is enhanced.

Tab. 1 Conductivity of the pristine PEDOT:PSS film and the DMSO-doped PEDOT:PSS film

PEDOT:PSS 4083 film sample	Resistance/ ($\Omega \cdot \square^{-1}$)	Conductivity/ ($\text{S} \cdot \text{cm}^{-1}$)
Pristine	3.24×10^7	3.09×10^{-4}
Doped with DMSO	2.66×10^5	3.76×10^{-2}

AFM and C-AFM measurements were performed to further prove the improvement of charge transport property of PEDOT:PSS film through characterizing the changes in morphology and conductivity before and after doping DMSO. Fig. 1 shows the C-AFM top-view ((a), (d)), C-AFM phase ((b), (e)) and AFM phase ((c), (f)) images of the PEDOT:PSS sample without and with DMSO. All samples are nanometer thickness thin films and prepared according to the device fabrication process. From the C-AFM top-view images, it can be found that surface roughness of the PEDOT:PSS film doped with DMSO is higher than that of pristine sample. In C-AFM phase images, the bright features are attributed to the well conductive PEDOT component, while the dark features correspond to the non-conductive PSS component. In contrast, the PEDOT:PSS film based on DMSO doping shows more relatively concentrated bright areas and has a higher potential value. DMSO is a low-volatile substance due to its relatively high boiling point ($189 \text{ }^\circ\text{C}$) and low saturated vapor pressure (0.76 kPa , $60 \text{ }^\circ\text{C}$). PEDOT:PSS film is dried for only 20 min at $120 \text{ }^\circ\text{C}$. So it can be concluded that DMSO exists in the dried PEDOT:PSS film, participates in the PEDOT:PSS film formation process and affects the performance of PEDOT:PSS film, which is reflected in the increase of film roughness and the enhancement of electrical conductivity, as shown by AFM and C-AFM phase images. It indicates that the doping DMSO causes the phase separation between PEDOT and PSS. The moderate phase separation results in a formation of a better PEDOT conductive channels and promotes the conductivity of PEDOT:PSS film, which is beneficial to enhance hole transport property.

In addition, the effect of adding more DMSO on

the conductivity and film formation of PEDOT: PSS HTL was also investigated. It was found that the conductivity of the PEDOT: PSS films continued to increase when the amount of DMSO was increased to 3% , albeit to a limited extent (shown in Tab. S1). But at the same time, the film forming property of PEDOT: PSS solution on ITO substrate was significantly deteriorated. According to the contact angle test results (shown in Fig. S1) , the contact angle of the PEDOT: PSS solution on the ITO substrate in-

creased significantly with the addition of DMSO changing from 1% to 3% , indicating that the wettability of PEDOT: PSS to ITO substrate became worse. It is speculated that due to the increase in the amount of DMSO, the degree of phase separation between PEDOT and PSS is aggravated, and PEDOT: PSS is seriously agglomerated, which is extremely unfavorable for PEDOT: PSS film formation. Therefore, the following mainly discusses the effect of 1% DMSO on the performance of perovskite cells.

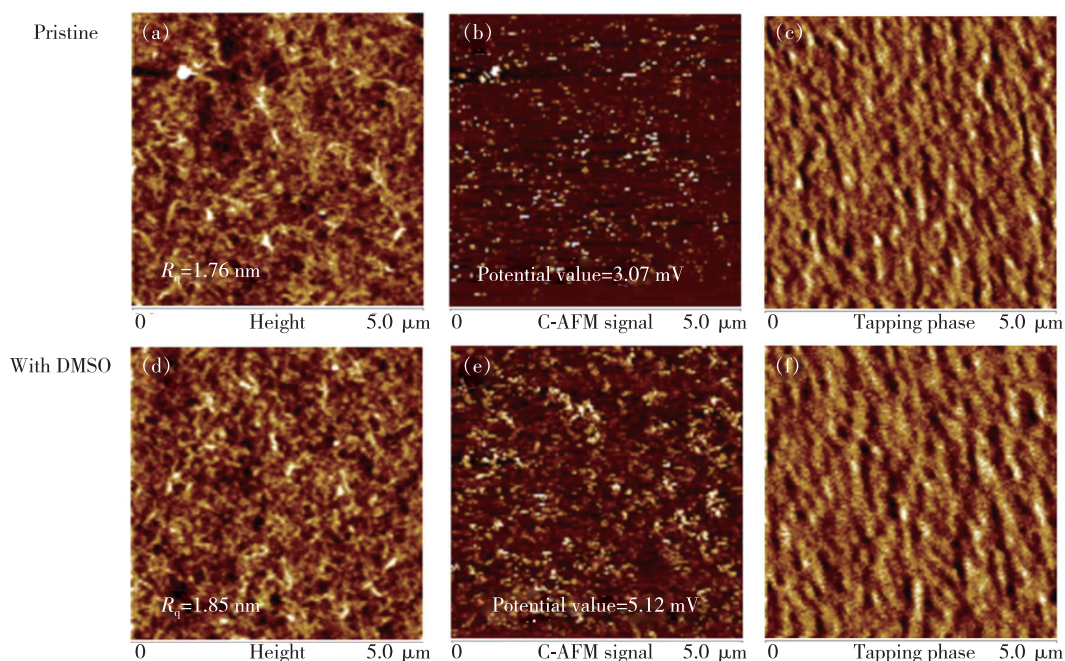


Fig. 1 C-AFM top-view ((a), (d)), C-AFM phase ((b), (e)) and AFM phase ((c), (f)) images for pristine PEDOT: PSS and PEDOT: PSS doped with DMSO films.

Steady-state PL spectra measurement was carried out to make further insight into the charge transport between perovskite active layer and anode before and after adding DMSO into PEDOT: PSS. Fig. 2 shows the steady-state PL spectra of perovskite films based on PEDOT: PSS with and without DMSO. The sample structure is ITO/PEDOT: PSS (without or with DMSO)/Perovskite. PL characterization can well reflect the effect of introduction of DMSO on charge extraction ability of PEDOT: PSS hole transport layer. Obviously, compared to the sample with pure PEDOT: PSS HTL, the PL intensity of the sample based on DMSO doping is reduced, showing significant fluorescence quenching. This indicates that adding moderate DMSO into PEDOT: PSS

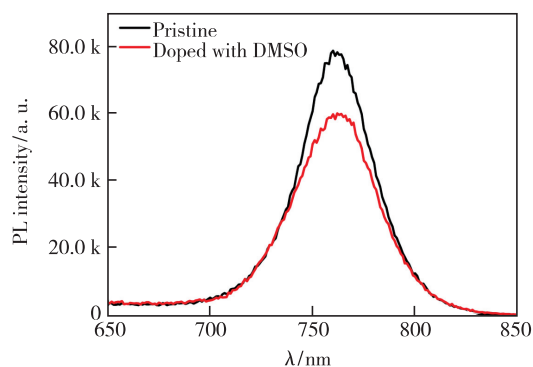


Fig. 2 Steady-state photo-luminescence (PL) spectra of the perovskite films based on pristine and DMSO-doped PEDOT: PSS

dose effectively enhances the hole extraction capacity of PEDOT: PSS materials and accelerates the hole transport between perovskite layer and anode. C-AFM

and AFM characterization have proved that the introduction of DMSO significantly increased the conductivity of the PEDOT:PSS thin film due to the formation of better conductive channels, which helps to enhance the hole transport ability and improve the photovoltaic performance of the device. The PL measurement confirms this conclusion again. So, for the planar perovskite solar cells with the inverted structure of ITO/PEDOT:PSS with DMSO/perovskite/PCBM:BCP/Ag, anode interface modification combined with cathode interface modification (reported in our previously work^[11]) can achieve the extraction balance of photo-generated charges in the device^[33], suppresses the charge accumulation and recombination at the interfaces. Thus, the short-circuit current is increased, the filling factor is up to 80%, and the power conversion efficiency of the device is also significantly improved. These will be described systematically in the next section.

3.2 Photovoltaic Performance of Devices

To investigate the influence of DMSO doping on the photovoltaic performance of solar cells, the organic solar cells based on typical P3 HT: PCBM system and perovskite solar cells were prepared. The J - V characteristics and the photovoltaic parameters

for the organic solar cells based on different PEDOT:PSS hole transport layers are shown in Fig. S2 and Tab. S2, respectively. It can be seen that after DMSO added, the device performance is improved, especially the short circuit current (J_{sc}) increased from 7.33 mA/cm² to 8.33 mA/cm² with 13% improvement, leading to the promoting the power conversion efficiency (PCE) increasing from 2.94% to 3.57%. Therefore, the increase in conductivity of the PEDOT:PSS HTL has a direct impact on the J_{sc} of device, greatly contributing to the boost in PCE of solar cells.

The perovskite solar cells based on DMSO-doped PEDOT:PSS HTL also exhibit improved performance. Tab. S3 summarizes the photovoltaic parameter values of the perovskite solar cells with pristine PEDOT:PSS and DMSO-doped PEDOT:PSS HTL. Fig. 3 displays the statistic analysis of the photovoltaic parameters shown as box charts. Obviously, compared to the devices with pristine PEDOT:PSS as HTL, there is a significant improvement in both J_{sc} and fill factor (FF) for the devices based on PEDOT:PSS doped with DMSO. The average J_{sc} and FF increase 4% and 5%, respectively. The open circuit voltage (V_{oc}) is slightly decreased. This may

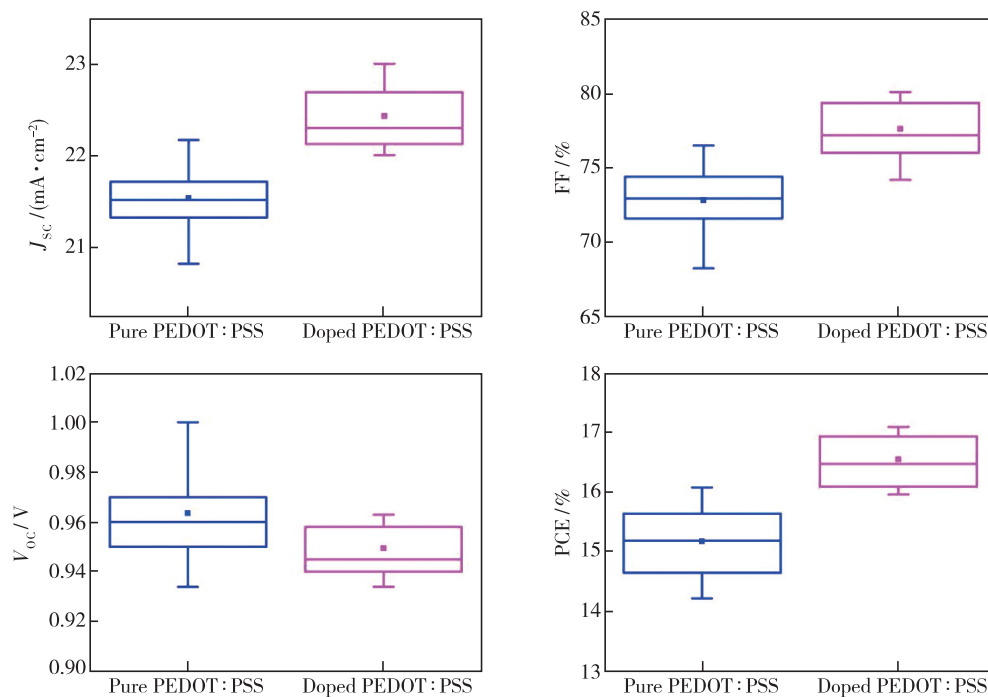


Fig. 3 Statistic analysis of the photovoltaic parameters shown as box charts for the perovskite solar cells with pristine PEDOT:PSS and DMSO-doped PEDOT:PSS HTLs

be due to the change of the microstructure of the hole transport layer, which changes the charge injection conditions and thus changes the internal electric field distribution^[32,34]. Although V_{oc} is slightly sacrificed, the J_{sc} and FF are significantly improved, so the overall PCE of the device is promoted. The champion device exhibits relatively high FF above 80% and a high PCE of 17.01%. The forward and reverse scanned J - V characteristics curves and IPCE spectra of the best devices based on PEDOT:PSS HTL without and with DMSO doping are shown in Fig. 4. Both devices show no remarkable current

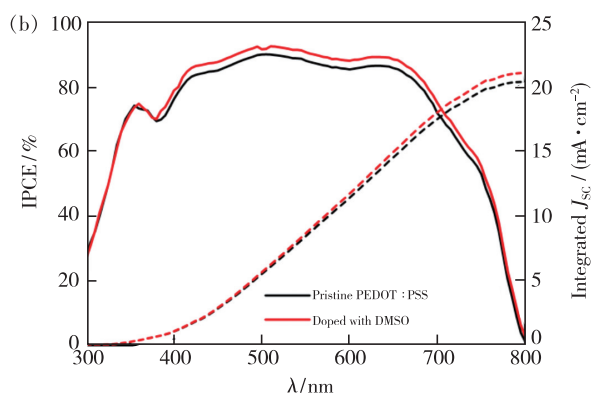
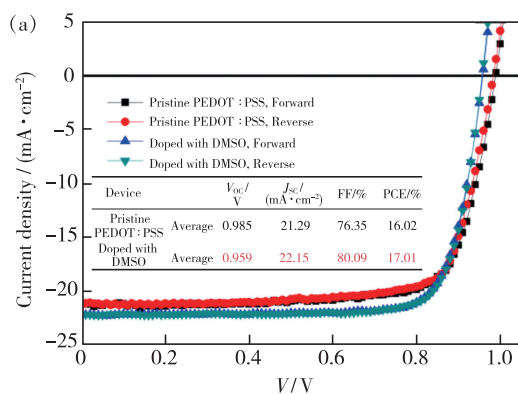


Fig. 4 Forward and reverse J - V characteristics curves(a) and IPCE spectra(b) of the best devices using PEDOT:PSS without and with DMSO doping. Both reverse and forward scan rate is $10 \text{ mV} \cdot \text{s}^{-1}$.

3.3 XRD, SEM and UV-Vis

XRD, SEM and UV-Vis were carried out to investigate the effect of DMSO-doped PEDOT:PSS HTL on the crystal growth, final morphology and absorption spectrum of perovskite film, respectively. From the XRD patterns (shown in Fig. 5), PEDOT:PSS doping hardly affects the subsequent growth process of perovskite crystals, because the position and intensity of characteristic diffraction peaks of perovskite are almost unchanged. According to the SEM images (shown in Fig. 6), compared with the perovskite film based on pristine PEDOT:PSS, the sample based on doped PEDOT:PSS has no obvious difference except that the grain size is slightly increased and uniform. The grain size for perovskite films based on DMSO-doped PEDOT:PSS ranges from 150 nm to 630 nm, with an average grain size of about 360 nm. While the grain size of perovskite films grown on PEDOT:PSS substrate ranges from 90 nm to 620 nm, and the average grain size is only

hysteresis. And the integrated J_{sc} values calculated from IPCE spectra show the same trend with that obtained from the J - V curves. The significant improvement in J_{sc} proves that the incorporation of DMSO does enhance the performance of the perovskite solar cells, mainly due to the promoted hole transport ability of PEDOT:PSS, which can be attributed to the increase of the electrical conductivity of PEDOT:PSS. Combined with the performance of organic solar cells discussed above, the method of PEDOT:PSS doped with DMSO has certain universality and is applicable to both organic solar cells and perovskite solar cells.

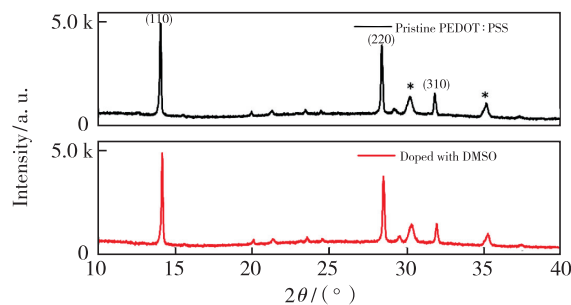


Fig. 5 XRD patterns of perovskite films based on pristine PEDOT:PSS and DMSO-doped PEDOT:PSS (The peaks marked * belongs to ITO substrate)

about 270 nm. Both the increased grain size and the improvement in uniformity for perovskite film are related to the introduction of DMSO into HTL layer. Because DMSO molecule has a stronger coordination ability with the Pb^{2+} in the lead halide, and the strong interaction effect can retard the crystallization process of perovskite, which is beneficial to an increase in the grain size and grain uniformity of the perovskite. The positive effect is similar to the impact

of DMSO on the morphology of perovskite films, reported in the previous literature^[9,35-36]. And the high-quality perovskite film is critical for efficient perovskite solar cells. UV-Vis spectra (Fig. 7) showed that the absorption of PEDOT:PSS HTL increased slightly at short wavelengths, and the absorption of the corresponding perovskite film also increased

slightly, but overall the difference was not significant. The above analysis reveals that incorporating DMSO into PEDOT:PSS has no significant influence on the crystallinity or absorption spectrum of perovskite film, but increases the perovskite grain size and grain uniformity, which is beneficial to reduce the film defects.

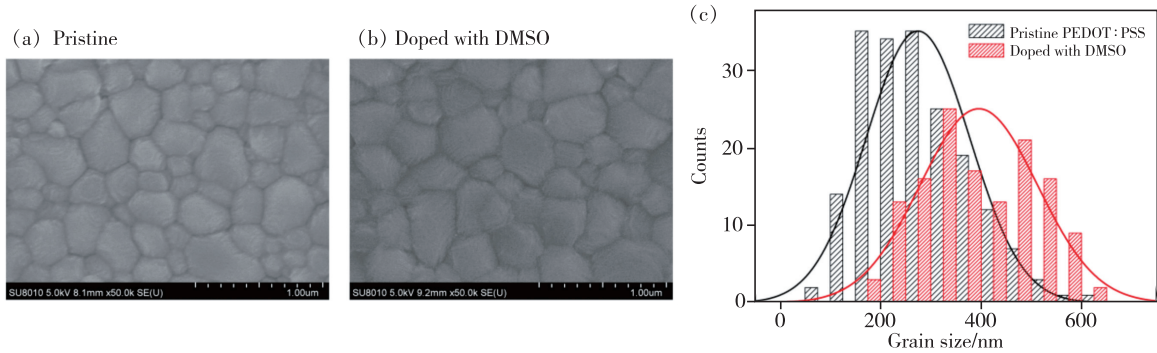


Fig. 6 Top-view SEM images ((a), (b)) and grain size distribution (c) of perovskite films based on PEDOT:PSS without and with DMSO. The grain sizes were estimated according to Nano Measurer 1.2 software.

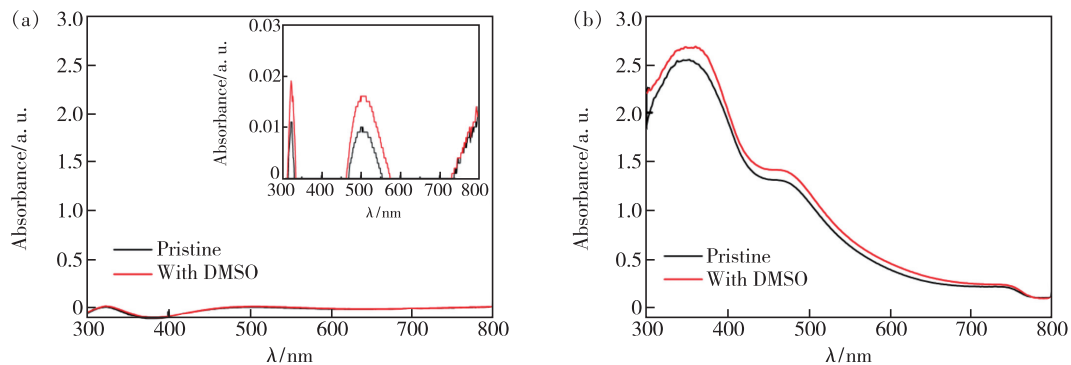


Fig. 7 (a) UV-Vis spectra for PEDOT:PSS films without and with DMSO. (b) UV-Vis spectra of perovskite films based on pristine and DMSO-doped PEDOT:PSS.

3.4 Device Stability

Since the interface is an important factor affecting the life of solar cells, the influence of adding DMSO on device stability was also inspected. All unencapsulated devices were stored in ambient air condition (Room temperature, relative humidity of 10% ~ 30%), and their performance attenuation was monitored by measuring the photovoltaic parameters periodically. The comparison of degradation characteristics of the PCE normalized to the initial values as a function of storage time is shown in Fig. S3. All devices without any encapsulation retain more than 90% of their initial efficiency after 16 days of exposure to air, implying that the introduc-

tion of DMSO had no negative effect on the device stability. It can be considered that the good stability of inverted devices is mainly attributed to the enhancement of the perovskite microstructure and the upper cathode interface modification, as we reported previously^[1,4].

4 Conclusion

In this work, the inverted planar perovskite solar cells based on PEDOT:PSS doped with 1% DMSO as HTL were fabricated. UV-Vis, AFM and C-AFM were performed to characterize the optoelectronic properties of PEDOT:PSS films without and with DMSO doping. The results show that doping

DMSO causes the phase separation between PEDOT and PSS. The moderate phase separation caused by DMSO-doping facilitates a formation of a better PEDOT conductive channels and promotes the conductivity of PEDOT: PSS film. Through doping DMSO, the sheet resistance and film conductivity of PEDOT: PSS could decrease and increase by 2 orders of magnitude, respectively. Although DMSO-doped PEDOT: PSS could not affect crystallinity or absorption spectrum of perovskite layer, the steady state PL spectra exhibit obvious fluorescence quenching, which indicates the charge extraction capacity of the PEDOT: PSS HTL layer is improved, due to more effective hole transfer between the perovskite active

layer and the anode. Therefore, compared to the control devices, the J_{sc} and FF of the devices based on PEDOT: PSS doped with DMSO are promoted by 4% and 5%, respectively, delivering a champion device with relatively high FF above 80% and high PCE of 17.01%. Furthermore, the stability test result also proves that PEDOT: PSS doped with DMSO will have no influence on the device stability. Our study provided a simple and effective way to improve the performance of inverted planar perovskite solar cells.

Supplementary Information and Response Letter are available for this paper at: <http://ejl.lightpublishing.cn/thesisDetails#10.37188/CJL.20220096>.

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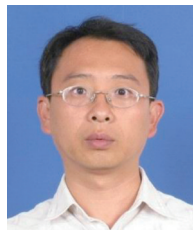
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