Efficient and Non-hysteresis CH₃NH₃PbI₃/PCBM Planar Heterojunction Solar Cells

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ABSTRACT

Highly efficient and non-hysteresis organic/perovskite planar heterojunction solar cells was fabricated by low-temperature, solution-processed method with a structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Al. The high-quality perovskite thin film was obtained using a solvent-induced-fast-crystallization deposition involving spin-coating the CH₃NH₃PbI₃ solution followed by top-dropping chlorobenzene with an accurate control to induce the crystallization, which results in highly crystalline, pinhole-free, and smooth perovskite thin film. Furthermore, it was found that the molar ratio of CH₃NH₃I to PbI₂ greatly influence the properties of CH₃NH₃PbI₃ film and the device performance. The equimolar or excess PbI₂ was facile to form a flat CH₃NH₃PbI₃ film and produced relatively uniform perovskite crystals. Perovskite solar cells (PSCs) with high-quality CH₃NH₃PbI₃ thin film showed good performance and excellent repeatability. The power conversion efficiency (*PCE*) up to 13.49 % was achieved, which is one of the highest *PCEs* obtained for low-temperature, solution-processed planar perovskite solar cells based on the structure ITO/PEDOT:PSS/CH₃NH₃PbI₃/PC₆₁BM/Al. More importantly, PSCs fabricated using this method didn't show obvious hysteresis under different scan direction and speed.

Keywords: planar heterojunction; low temperature; perovskite solar cells; hysteresis

1. Introduction

Low-temperature and solution-processed solar cells have attracted more and more attention in recent years since they are compatible with flexible substrate for large-scale, high-throughput, and low-cost roll-to-roll (R2R) printing manufacturing [1-3]. Recently, organolead halide perovskites have arisen as excellent earth abundant photovoltaic materials and show many advantages including small bandgap, strong absorption, long carrier diffusion length, high carrier mobility, and so on [4-7]. It was reported that the certified power conversion efficiency (*PCE*) of perovskite solar cells (PSCs) is over 20 % [8]. There are several device architectures and deposition techniques used for fabricating highly efficient PSCs [7, 9-17]. Typically, perovskite materials are deposited on mesoporous metal oxide scaffold such as TiO₂ [7, 14], Al₂O₃ [12], ZrO₂ [9]. Then a hole transport layer (HTL) is deposited subsequently, which is normally one of organic semiconductor materials, for example, spiro-MeOTAD [5, 8, 11, 12, 18, 19], poly-triarylamine (PTAA) [14], P3HT [20-22]. However, the mesoporous scaffold layer has to be sintered at high temperature (usually above 450°C) [8, 14, 19]. The high-temperature sintering is a potential obstacle for the further development and commercialization of PSCs, especially in flexible large-scale R2R production process [5, 8]. It is particularly critical to explore the possibilities of preparing high-performance PSCs with a simple structure under low temperature.

Templating from organic photovoltaics (OPVs), planar heterojunction (PHJ) structure fabricated at low temperature was introduced into PSCs [1, 10, 23-25]. Planar architecture potentially provides enhanced flexibility for device optimization, multijunction construction, and the investigation of device physics, but it requires tremendous effort to fabricate high-quality perovskite thin film [10, 16, 26]. The solution-processed fabrication is highly recommended to prepare PHJ PSCs due to its low cost and high output as compared with vacuum evaporation. However, it is very difficult to control the formation of perovskite thin film with good coverage and without pinholes, which are important to the device performance [27]. The

low-temperature, solution-processed PHJ PSCs was first reported by Jeng *et. al.* in 2013, in which the *PCE* is as low as 3.9% [10]. They pointed out that it is a great challenge to form a thick and uniform perovskite thin film. Then, a relatively higher *PCE* of 9.22% was achieved based on the structure of ITO/PEDOT:PSS/Perovskite/PCBM/C₆₀/BCP/Al by optimizing the precursor ratio and utilizing multilayer modification [28]. However, the *PCEs* are still relatively lower than commonly high-temperature processed PSCs.

The anomalous hysteresis is another issue for both high-temperature mesoporous and low-temperature processed PHJ PSCs [8, 14, 29-31]. Snaith *et. al.* pointed out that the defects states including interface states or interstitial defects (iodide or methylammonium) and ferroelectric properties are the possible reasons for producing the hysteresis [29, 31]. Huang *et. al.* utilized multilayer modification in PSCs with the structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/C₆₀/BCP/Al and significantly eliminated the anomalous hysteresis [28].

Herein, we used a low-temperature, solution-processed method combining with a solvent treatment technique, *i.e.*, solvent-induced-fast-crystallization deposition (SIFCD), to form a very continuous and flat CH₃NH₃PbI₃ layer on ITO/PEDOT:PSS substrate, and further fabricate perovskite/fullerence PHJ solar cells. The morphological, absorbance and crystallographic properties of perovskite thin film as well as PSCs performance were studied in detail. It was found the morphology of perovskite films and the size of perovskite crystals are sensitive to the precursor composition, and a 1:1 precursor stoichiometry could lead to the best performance. Using a simple structural PHJ PSCs based on ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Al, a *PCE* as high as 13.49 % was achieved, which is one of the highest *PCEs* based on this device structure [1, 10]. More interestingly, the performance of these simple structural PSCs showed good repeatability and no obvious hysteresis, which have great potential application in commercial R2R production.

2. Experimental section

2.1 Materials

Organolead halide perovskite precursor solution was made with mixing methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, 99 %, Jingge, Wuhan) and lead iodide (PbI_2 , 99 %, Zhengpin, Shanghai) in N,N-Dimethylformamide (DMF, J&KSeal) with various molar ratios ($\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$) at 1:0.6, 1:0.8, 1:1, 1:1.2. The precursor solution was vigorously stirred over night at 60°C , and was filtered with a $0.22\ \mu\text{m}$ PVDF filter before the deposition. Fullerene derivative [6, 6]-phenyl C61-butyric acid methyl ester (PCBM) was purchased from American Dye Source, and was dissolved in anhydrous chlorobenzene (CB, J&KSeal). All materials were used directly without any purification.

2.2 Device fabrication

Fig. 1 shows the structure of PSCs. The patterned indium tin oxide (ITO) coated glass was used as the substrate, which was ultrasonically cleaned in acetone, detergents, distilled water and isopropyl alcohol for 15 min respectively, then dried by hot air and treated by UV-ozone for 15 min. The PEDOT: PSS layer (Baytron, PVP AI 4083) with a thickness of about 50 nm was spin-coated at 3000 rpm onto the patterned ITO substrate and dried on hot plate at 150°C for 15 min. The deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was performed in a glove box (both H_2O and $\text{O}_2 < 1.0\ \text{ppm}$) and the SIFCD method was used to produce high-quality film, in which a poor solvent was introduced to induce the formation of perovskite thin film [14, 26]. The scheme of perovskite films prepared by the SIFCD method is shown in Fig. S1a. Firstly, $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution ($50\ \mu\text{L}$) was first dropped onto a PEDOT:PSS coated ITO substrate, of which the size is $1.5\ \text{cm} \times 1.5\ \text{cm}$. The substrate was then spun at 4000 rpm. When the precursor roll out, anhydrous CB solvent ($50\ \mu\text{L}$), as a poor solvent, was quickly dropped onto the center of the substrate (The detailed speed-time profile for spin coating process with CB drop-casting was shown in Fig. S1b). The color of just deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was changed from transparent to light brown. The thickness of perovskite film was controlled using the concentration of precursor solution. The total precursor concentration was varied from 450 mg/ml to 650 mg/ml

with an interval of 50 mg/ml, correspondingly to form 210 nm to 370 nm perovskite films with a similar interval of about 40 nm. The samples were subsequently treated at 100 °C for 10 min. After cooling to room temperature, PCBM solution was spin-coated onto the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer with different thicknesses. Finally, a bar-like defined Al electrode (100 nm) by mask was deposited on top of PCBM film by thermal evaporation under the vacuum of $\sim 4 \times 10^{-6}$ mbar, resulting in an active area of 0.09 cm^2 .

Fig. 1. The schematic of PSC structure.

2.3 Characterization

Crystallographic properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were characterized by X-ray diffraction (XRD, Rigaku D, Max 2500, Japan). Absorption properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were characterized by UV-vis spectrophotometer (UV-vis, TV-1800PC, Pgeneral). The morphology was characterized by atomic force microscopy (Agilent Technologies 5500 AFM/SPM System, USA) with tapping-mode. Current density–voltage (J – V) characteristics of PSCs were measured by digital Source Meter (Keithley, model 2420). During the measurements, the scan speed was located at 0.3 V/s and the scan direction is form +1.2 V to -1.2 V if without special description. A solar simulator (91160s, Newport, AM 1.5G) was used for PCE test. Light intensity was 100 mW/cm^2 calibrated by a standard silicon solar cell. The thickness of the perovskite and PCBM films were measured with both surface profiles (Dektak 150, Veeco, USA) and AFM.

3. Results and discussion

The precursor ratio is closely related to the quality of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer and the performance of PSCs. To achieve a high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, the precursor ratio of $\text{CH}_3\text{NH}_3\text{I}$ to PbI_2 was varied from 1:0.6 to 1:1.2 and the total precursor concentration was fixed at 450 mg/ml. Fig. 2 shows the XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with different molar ratios. The strong diffraction peaks at $2\theta = 13.98^\circ$, 28.22° , and 31.67° appear for all samples, corresponding to the (110), (220) and (310) planes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal, indicating the formation of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure [1, 13]. For the precursor ratio larger than 1:1, there are some diffraction peaks coming from the impurities. The intensity of those peaks decreased and eliminated finally at the precursor ratio of 1:1. With further decreasing the molar ratio to 1:1.2, two diffraction peaks coming from PbI_2 are observed, indicating the existence of PbI_2 crystal in $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. The unreacted materials can form the interstitial defects (iodide or methylammonium), which would influence the performance of PSCs and induce the anomalous hysteresis [29]. Therefore, the 1:1 precursor ratio is probably beneficial to achieve higher *PCE* and eliminate the anomalous hysteresis.

Fig. 2. XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with different molar ratios of $\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$.

The absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared via the SIFCD method with different molar ratios are shown in Fig 3, indicating the strong photon harvesting capability for the spectral range from 400 nm to 800 nm. It is found that the film

shows indistinct absorbance edge at the precursor ratio 1:0.6, probably resulting from the impurities in the film. For the films prepared at the precursor ratio of 1:0.8, 1:1 and 1:1.2, the obvious onsets of absorbance spectrum appear at 780 nm, showing a intrinsic bandgap of about 1.6 eV (inset of Fig. 3), which is similar to the reported value [1, 8]. Considering the similar thickness for all the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, the difference in *UV-vis* spectra should relate with the morphology and composition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films.

Fig. 3. Absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared with different molar ratios.

It is well known that a high-quality perovskite surface is necessary to prepare highly efficient PHJ PSCs [10, 16, 26]. However, $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared with conventional spin-coating technique are composed of large grains with lots of pinholes [10, 28, 32], leading to the shunting of PHJ PSCs. In our experiments, the very poor surface morphology was also observed regardless of the precursor ratio, as shown in Fig. S2. The PSC devices based on these perovskite films hardly shows photovoltaic performance. To improve the quality of perovskite films, the SIFCD technology was introduced to fabricate PHJ PSCs at low temperature for achieving highly efficient devices. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution was first spin coated onto the PEDOT:PSS/ITO layer. Then, the CB solvent, as a poor solvent, was quickly dropped

onto the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film at specified drop-point, as shown in Fig. S1. By trial and error, we found that the surface of perovskite film is strongly dependent on the drop-point. In order to find the optimum drop-point, we fixed the precursor ratio in 1:0.6 and the detailed optimization process for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is shown in Fig. S3. It can be seen that highly compact and smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was achieved when the drop-point is just 6s after starting spinning and the root-mean-square roughness (RMS) is about 12 nm. When the drop-point was located in 8s, the film becomes relative rougher and the RMS is increased to about 23 nm. If the drop-point was further delayed, the SIFCD method did not work any more. However, the drop-point cannot be further shifted to an early time since the CB solvent will wash away the perovskite film. The optimized drop-point is fixed at 6s after starting spinning. The absorbance measurements obviously showed that the intrinsic absorption peaks of perovskite films appeared for the drop-point located at 6 s and 8 s (Fig. S4), while the relative density of these absorption peaks decreased for other samples because of the scattering effect coming from the large-size perovskite crystals. Meanwhile, XRD results suggested that the intensity of diffraction peaks, *i.e.*, (110) and (220), was increased for the samples fabricated by the SIFCD method, implying that the crystallinity of perovskite thin films was improved (Fig. S5). The above discussion states that both morphology and crystallinity of perovskite thin films were improved by the SIFCD method.

Based on the optimized process, the prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with smooth and reflective surface can be clearly observed by naked eyes. The surface topography images were further measured by AFM, as shown in Fig. 4. It was found that the surface morphology and the grain size are very sensitive to the precursor ratio of $\text{CH}_3\text{NH}_3\text{I}$ to PbI_2 . As increasing the content of PbI_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$ film becomes more and more uniform and smooth. Especially, when the precursor ratio is changed from 1:0.8 to 1:1, the RMS obviously decreases from 13.40 nm to 7.33 nm for $10 \times 10 \text{ } \mu\text{m}^2$ scanning area. The RMS of surface morphology images for the precursor ratio 1:0.6 and 1:1.2 are 12.10 nm and 6.65 nm, respectively. The above statements show that the

surface can be dramatically improved when the precursor ratio decrease from 1:0.8 to 1:1. Furthermore, the coverage of all $\text{CH}_3\text{NH}_3\text{PbI}_3$ films are almost up to 100 % and no distinct pinholes can be found in them. From the enlarge AFM images (Insets in Fig 4a-d), it is obvious that the grain size decreases with increasing the content of PbI_2 . At the precursor ratio of 1:0.6 and 1:0.8, the grain size almost remains the same. The abnormally large grains with about 600 nm can be observed and some grain edges are vague. Meanwhile, many smaller grains emerge in 1:0.8 $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. As the precursor ratio decreases to less than 1:0.8, the number of abnormally large grains reduces dramatically and the grain edge can be clearly distinguished, resulting in more smooth and uniform surface (Fig. 4c and d).

Fig. 4. AFM topographic images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films fabricated with different precursor ratios of $\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$. (a) 1:0.6 (RMS = 12.10 nm), (b) 1:0.8 (RMS = 13.40 nm), (c) 1:1 (RMS = 7.33 nm), and (d) 1:1.2 (RMS = 6.65 nm).

A 50 nm thickness PCBM layer was deposited onto $\text{CH}_3\text{NH}_3\text{PbI}_3$ films to form PHJ PSCs. Fig. 5 shows the typical current density-voltage (J - V) characteristics of PSC devices with different precursor ratios under AM 1.5 one-sun illumination. The statistical performance parameters based on 10 devices are presented in Fig. 6. The PCE can be enhanced dramatically with decreasing the precursor ratio of $\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$. The PCE of PSC device with 1:1 precursor ratio reaches up to 8.60 %, which is enhanced by over 10 times as compared to the PSC device with the 1:0.6 ratio ($PCE = 0.85\%$). The improvement is mainly attributed to the increase of J_{sc} , enhancing from 1.03 mA/cm^2 to 13.99 mA/cm^2 . However, when the precursor ratio is 1:1.2, the device performance become worse, resulting in a reduced PCE of 6.98 % and a smaller J_{sc} of 10.84 mA/cm^2 . The un-reacted impurities presented in $\text{CH}_3\text{NH}_3\text{PbI}_3$ film would greatly affect the performance of PSCs. As shown in Fig. 5 and Fig. 6, the equal molar ratio (1:1) is the optimum one to achieve pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ in our work. It is different to the results reported by Huang *et al.*, of which the optimum ratio is 1:0.6 [28]. The discrepancy probably results from the different thermal annealing procedures. They used a long-term annealing time to remove the incomplete reactive $\text{CH}_3\text{NH}_3\text{I}$ and got better perovskite films. While we used a short-term annealing procedure, in which the $\text{CH}_3\text{NH}_3\text{I}$ would not decompose from $\text{CH}_3\text{NH}_3\text{PbI}$ films and results in the best precursor ratio at 1:1.

When the precursor ratio is tuned to 1:1.2, the evident S-shape J - V curve appears, similar to some previous reports in OPVs [33-34]. Usually, such S-shape behavior indicates a significant energy barrier for charge extraction and leads to a carrier accumulation at the interface, which increases the series resistance and decreases the FF [35]. Definitely, the S-shape J - V curve is related to the excess of PbI_2 , which influences the carrier transport and the properties of the interface between PEDOT and $\text{CH}_3\text{NH}_3\text{PbI}$ as well as $\text{CH}_3\text{NH}_3\text{PbI}$ and PCBM. The detailed reasons need to be further studied. One may notice that there is an abnormal shoulder appearing in J - V curve for the precursor ratio at 1:0.8. It is probably ascribed to abnormal morphology, in which some aggregations and ravines are formed in perovskite thin film, as shown

in Fig. 4b. However, these phenomena were not observed in other perovskite thin films.

Fig. 5. *J-V* curves of PSCs under AM1.5 simulated illumination with different precursor ratios.

Fig. 6 is the statistical performance parameters of PSCs with different precursor ratios. The change trends of statistical performance parameters are consistent with that of typical *J-V* curves in Fig. 5. At the optimized precursor ratio 1:1, PSCs show the best performance with an average *PCE* of 7.82%, a J_{sc} of 13.10 mA/cm², a V_{oc} of 0.87 V, and a *FF* of 69 %. The performance parameters show excellent reproducibility and the stability. At the precursor ratio of 1:0.6, the average *PCE*, J_{sc} and V_{oc} are 0.75 %, 1.04 mA/cm² and 1.03 V respectively; while at the precursor ratio of 1:0.8, they are 3.25 %, 4.88 mA/cm² and 0.86 V, respectively. One should notice that the *FF* shows large vibrations, in which over 20 % change for 1:0.6 ratio and over 10 % change for 1:0.8 ratio. On the other hand, it is worth to indicate that the highest *FF* of 83% and an average *FF* of 77% can be achieved in PSCs with the precursor ratio at 1:0.8. They are much higher than many reported values [1, 10, 16], which potentially provides a way for preparing PSCs with a high *FF*. The vibration of *FF* is evidently decreased when the precursor ratio at 1:1 and 1:1.2. For the precursor ratio at 1:1.2, it results in an average *PCE* of 6.07 %, J_{sc} of 9.96 mA/cm², V_{oc} of 0.92 V and *FF* 66 %. The *PCEs* are mainly dependent on the J_{sc} , and they show the similar change trends (Fig. 6a and

6b).

Fig. 6. Statistical photovoltaic parameters as the function of precursor ratio. The filled circle is the average values.

The thickness of PCBM layer is very critical for achieving high performance PSCs [25]. A thick PCBM layer will increase the series resistance of PSCs since its low conductivity, while a very thin PCBM layer will not fully cover the perovskite layer and the top electrode would directly contact to it. The thickness of PCBM was further optimized. Fig. 7a shows the typical J - V curves of PSCs at the precursor ratio 1:1 under AM1.5 simulated illumination as varying the thickness of PCBM from 10 nm to 90 nm and the perovskite film is located on 210 nm. The average performance parameters are listed in Table 1. The inset in Fig. 7a is the change trend of PCE s as the function of the PCBM thickness. A relatively higher average PCE of 9.26 % is achieved with a 30 nm PCBM layer, and the best PSCs reach up to 9.51%. Meanwhile, the V_{oc} can close to 1 V, which is higher than many reported values using this device structure [1, 36, 37]. Further reducing or increasing the thickness of PCBM, both the PCE and J_{sc} decrease accordingly. Based on this optimized thickness of PCBM, we

further optimized the thickness of perovskite layer to achieve the best light harvesting and higher performance. Fig. 7b shows the J - V curves of PSCs with different perovskite layer from 210 nm to 370 nm. The average performance parameters are listed in Table 1. From the inset of Fig. 7b and Table 1, the best PCS devices show the PCE of 13.49 %, V_{oc} of 1.03 V, FF of 61 %, and J_{sc} of 21.53 mA/cm² based on 290 nm perovskite layer under AM 1.5 G (1 sun) simulated illumination, which is one of the highest $PCEs$ for the structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Al without any other additives. The average PCE of 12.56 %, J_{sc} of 19.99 mA/cm², V_{oc} of 0.99 V and FF of 63 % could be achieved.

Fig. 7. J - V curves of typical PSCs with varying the thickness of PCBM layer (a) and perovskite

layer (b) under AM1.5 simulated illumination at the precursor ratio of 1:1 for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. Insets show the change trend of *PCEs* as the function of the PCBM and perovskite film thickness in (a) and (b), respectively. In (a), the thickness of perovskite is located at 210 nm; in (b), the thickness of PCBM is located at 30 nm.

Table 1. The average values of photovoltaic parameters obtained from *J-V* measurements for PSCs at the precursor ratio of 1:1 with different thickness of PCBM layer and perovskite layer. The best *PCEs* are shown in brackets.

Layer name	Thickness	V_{oc} (V)	J_{sc} (mA/cm ²)	<i>FF</i> (%)	<i>PCE</i> (%)
PCBM ^a	10	0.87	13.73	62	7.47 (7.53)
	30	0.99	14.17	66	9.26 (9.51)
	50	0.89	13.28	68	8.00 (8.60)
	90	0.91	10.49	64	6.15 (6.32)
Perovskite ^b	210	0.99	14.17	66	9.26 (9.51)
	250	1.03	13.52	72	9.97 (10.01)
	290	0.99	19.99	63	12.56 (13.49)
	330	1.03	16.98	62	10.81 (11.00)
	370	1.05	14.43	59	8.95 (9.12)

^a the thickness of perovskite layer is located at 210 nm; ^b the thickness of PCBM is located at 30 nm.

The abnormally hysteresis is usually observed in PSCs [8, 14, 29-31]. It probably attributes to the poor quality film and defect traps in perovskite films. Based on AFM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film prepared in this work (Fig. 4c), $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is very uniform and compact. The PSCs were further measured with different scan direction and speed. The typical *J-V* curves are shown in Fig. 8. The J_{sc} , V_{oc} and *FF* values obtained from the *J-V* curve of the reverse scan are 18.99 mAcm⁻², 0.94 V and 69 %, respectively, yielding a *PCE* of 12.33 % under standard AM 1.5 condition. As

changing the scan direction, the performance parameters are 18.07 mA/cm^2 , 0.96 V and 66% , respectively, resulting in a *PCE* of 11.39% . The *PCEs* are almost the same, and the discrepancy is smaller than 1% . In addition, *J-V* curves of PSCs measured using different scan rates are almost the same as well (Fig. 8b). In previous report, highly efficient PSCs without hysteresis were fabricated by combining interdiffusion method and PCBM/ C_{60} double fullerene layers [28]. Here we fabricated highly efficient PHJ PSCs by combining the SIFCD method and only PCBM layer for eliminating the hysteresis.

Recently, some researchers pointed out the hysteresis is attributed to the ion drift ($\text{V}_{\text{Pb}}^\bullet$ and $\text{V}_{\text{MA}}^\bullet$) nearby the electrodes. Meanwhile, this drift process is influenced by the morphology, stoichiometry and film quality of the perovskite films owing to their influence on the defect concentration [38]. Above statements means that high-quality and smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were prepared by SIFCD method, and thus a thin PCBM film can efficiently covered the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films. Meanwhile, there are few excess ions existing in the optimized $\text{CH}_3\text{NH}_3\text{PbI}_3$ film.

Fig. 8. *J-V* curves of PSCs with a structure of ITO/PEDOT:PSS/290 nm $\text{CH}_3\text{NH}_3\text{PbI}_3$ /30 nm PCBM/Al measured with (a) forward and reverse scanning directions and (b) different scanning speed under AM 1.5 G illumination.

4. Conclusion

We have successfully introduced the SIFCD method to form a flat and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ film upon the PEDOT:PSS film. The main tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$

structure diffraction peaks appeared and the impurities peaks can be eliminated by varying the precursor ratio. The pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ was achieved when the precursor ratio is at 1:1. The UV-vis spectra showed that the band gap of these $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystalline films is about 1.6 eV except for the film with 1:0.6 precursor ratio, which has no clear absorbance onset edge. The film morphology is closely related to the precursor ratio. When the ratio reached to or beyond 1:1, very smoother film is formed and the crystals become more uniform. The *PCE* of PSCs was increased with the decrease of precursor ratio $\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$. At the ratio of 1:1.2, the *PCE* was reduced since the incomplete reaction of PbI_2 existing in the film. Based on systematical optimization on the thickness of PCBM layer and $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, the *PCE* up to 13.49 % was achieved for PSCs with a simple structure ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al at a equal molar precursor ratio of 1:1. More important, these PSCs showed excellent reproducibility and also no obvious hysteresis under different scan direction or speed.

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