High-Quality CH₃NH₃PbI₃ Thin Film Fabricated via Intramolecular Exchange for Efficient Planar Heterojunction Perovskite Solar Cells

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Abstract

The high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film with excellent coverage and uniformity was prepared using an intramolecular exchange technology via a low-temperature, two-step sequential deposition process. The $\text{PbI}_2(\text{DMSO})$ complex was synthesized at room temperature without any additives and was deposited, then the $\text{CH}_3\text{NH}_3\text{I}$ solution was deposited subsequently. The further controllable thermal annealing process resulted in the complete formation of flat and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with large-size grains and (110) preferred crystallographic orientation. The perovskite solar cells (PSCs) with a very simple inverted planar heterojunction structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al and without other buffer layers, *e.g.*, C_{60} , LiF, BCP, *etc.*, were fabricated, resulting in a power conversion efficiency (*PCE*) as high as 14.26%. The results suggest that the low-temperature, two-step sequential deposition process with intramolecular exchange technology provides a good route to fabricate high-quality perovskite thin film and efficient PSCs, which would match with large-scale, high-output roll-to-roll (R2R) printing/coating techniques.

Keywords: planar heterojunction; perovskite solar cells; intramolecular exchange; $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film; $\text{PbI}_2(\text{DMSO})$

1. Introduction

Since organic/inorganic hybrid perovskite materials with a formula $\text{CH}_3\text{NH}_3\text{PbX}_3$ (MAPbX_3 , $\text{X}=\text{Br}, \text{I}$) were first used in solar cell [1], organometallic halide perovskites solar cells (PSCs) have attracted particular attention attributed to the excellent absorption coefficient, high carrier mobility, appropriate direct band gap and long carrier diffusion length [2-9], as well as the compatibility of roll-to-roll (R2R) printing process [10, 11]. Especially, the power conversion efficiency (*PCE*) of PSCs has been improved dramatically [12-15] and reached to over 20% [16]. The PSCs usually have two typical architectures, *i.e.*, mesoporous structure and planar heterojunction (PHJ) structure. In mesoporous structure, a mesoporous scaffold, for example, TiO_2 , should be sintered at a temperature as high as over 450 °C, which is normally not suitable to fabricate flexible PSC devices and does not match with the low-cost, large-scale R2R printing process. While PHJ-PSCs with a simple P-i-N structure could be fabricated by a low-temperature, solution process, in which the intrinsic perovskite layer is sandwiched between hole transport layer (HTL) and electron transport layer (ETL). However, a buffer layer, such as C_{60} , LiF and BCP, fabricated by vacuum deposition, is normally inserted between the ETL and the cathode in PHJ-PSCs for improving the performance of PSCs [17-18], which complicates the fabrication process and especially is disadvantageous to R2R printing process.

It is well known that the quality of perovskite thin film plays a key role on the performance of PSC devices, and several advanced deposition methodologies have been used to fabricate perovskite thin films, including one-step solution deposition [19-21], two-step sequential solution deposition [14] and vacuum vapor deposition [8]. Although one-step solution deposition is a simple and low-cost process, the deposited inhomogeneous perovskite thin film normally needs further controllable solvent or thermal treatments for obtaining efficient PSC devices [22-25]. Two-step sequential deposition has been widely used in mesoscopic structural PSCs and superior

photovoltaic performance could be produced [26]. Thus it was acted as an efficient low-cost route to fabricate PHJ-PSC devices [14, 27, 28]. The lower performance may result from the formation of poorer thin film and the incomplete surface coverage of perovskite layer [25, 29]. For improving the quality of perovskite layer and accelerating the complete conversion, the intramolecular exchange technology was developed [16]. The strongly coordinative solvent dimethyl sulfoxide (DMSO) was used to prepare PbI_2 solution and form $\text{PbI}_2(\text{DMSO})$ complex precursor, resulting in an amorphous featured precursor PbI_2 thin film. It could efficiently generate uniform perovskite crystals with a full conversion and yield highly reproducible performances with certified *PCEs* exceeding 20% for formamidinium lead iodide (FAPbI_3) based mesoporous structural PSCs. Furthermore, the intramolecular exchange between $\text{PbI}_2(\text{DMSO})$ and FAI was used to fabricated FAPbI_3 thin film via two-step sequential deposition for structuring PHJ-PSCs with TiO_2 blocking layer and a *PCE* as high as 17.6% was achieved [30]. In addition, a series $\text{PbI}_2(\text{DMSO})_x$ ($0 \leq x \leq 1.86$) complexes were controllably fabricated via intramolecular exchange between DMSO and $\text{CH}_3\text{NH}_3\text{I}$, resulting in dense and ultraflat perovskite thin film [31]. The strong coordination effect between DMSO and PbI_2 would prevent PbI_2 thin film from crystallizing, and the intramolecular exchange enable $\text{PbI}_2(\text{DMSO})_x$ complex to successfully convert into perovskite.

Normally mesoscopic layer or several buffers were used to achieve highly efficient PSCs using intramolecular exchange process [16, 30, 31]. Herein, a two-step sequential solution deposition with intramolecular exchange process at the low temperature was used to fabricate PHJ-PSCs with a very simple inverted structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3)/PCBM/Al, in which there was not mesoscopic scaffold or other more buffer layers, *e.g.*, C_{60} , LiF, BCP, *etc.* The low-temperature intramolecular exchange between $\text{CH}_3\text{NH}_3\text{I}$ and $\text{PbI}_2(\text{DMSO})$ solid precursor resulted in the formation of large-size grain, dense and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film, as well as a high *PCE* over 14%. The low-temperature, two-step sequential solution deposition with intramolecular exchange, matching with

large-scale R2R printing process, showed great potential application to fabricate large-area, efficient PHJ-PSCs.

2. Experiment

The $\text{PbI}_2(\text{DMSO})_2$ solide complex was synthesized at room temperature (25 °C) via a solution process [32]. A 3 g PbI_2 powder (Zhengpin, shanghai) was dissolved in 9 ml DMSO and a pale yellow solution was formed. The transparent colorless $\text{PbI}_2(\text{DMSO})_2$ crystals could be formed after 72 hrs, which was totally different from toluene induced process [16]. The $\text{PbI}_2(\text{DMSO})_2$ was annealed at 60 °C for 24 hrs in a vacuum oven and resulted in the formation of the $\text{PbI}_2(\text{DMSO})$. The $\text{PbI}_2(\text{DMSO})$ and PbI_2 were dissolved in anhydrous N,N-dimethylformamide (DMF, J&K Seal) with a concentration of 620 mg/ml and 462 mg/ml, respectively. The fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, Polymer Light Technology Corp., Xi'an) was dissolved in anhydrous chlorobenzene (CB, J&K Seal) at a concentration of 16 mg/ml. The above three solutions were stirred vigorously at 60 °C for 12 hrs. The $\text{CH}_3\text{NH}_3\text{I}$ (Polymer Light Technology Corp., Xi'an) was dissolved in anhydrous isopropanol at a concentration of 45 mg/ml and was stirred at 45 °C for 12 hrs. The preparation of all the solutions was carried out in glove box and the raw materials were used as received without further purification.

The PHJ-PSCs were fabricated with a inverted structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al (Fig. 1a). The patterned ITO substrate was cleaned with sonication in acetone, detergents, deionized water and IPA for 20 min, respectively. Then it was dried using N_2 flow and treated with UV-ozone for 15 min. The PEDOT:PSS (Baytron, PVP AI 4083) as the HTL was coated on the ITO by spin-coating at 3000 rpm for 30 s and then was annealed at 150 °C for 15 min to form an about 40 nm layer. The $\text{PbI}_2(\text{DMSO})$ complex solution was spin-coated onto the PEDOT:PSS-coated ITO substrate at a speed of 3000 rpm for 30 s, resulting in the formation of semi-transparent faint yellow $\text{PbI}_2(\text{DMSO})$ thin film. Then, the $\text{CH}_3\text{NH}_3\text{I}$ solution was dropped onto $\text{PbI}_2(\text{DMSO})$ thin film quickly after the spinning for 3s at a

spin speed of 5000 rpm and spin-coating for 40 s. The resulted thin film were placed on heater table, among which about 10 μ l toluene solution was dropped, covered by glass dish and annealed at 100 °C for 90 min. The PCBM layer was spin-coated subsequently at a speed of 3000 rpm for 30s, and finally a 100 nm Al counter electrode was thermally deposited at a pressure of $\sim 4\times 10^{-6}$ mbar. The active area of PSCs is 0.09 cm². The fabrication process of PbI₂-based PHJ-PSCs was similar to that of PbI₂(DMSO)-based PHJ-PSCs.

X-ray diffraction (XRD, Bruker D8) with Cu K α radiation ($\lambda = 1.5406$ Å) was performed at a scan speed of 0.02°/min from 10° to 60° with a mode a theta-2theta to analyze the crystal structure of perovskite thin film and intermediate phase thin film. Scanning electron microscope (SEM) was used to observe the morphology of thin films. The ultraviolet-visible spectrophotometer (UV-vis, Puxi, T9, China) was used to assess the absorption properties of CH₃NH₃PbI₃ thin film. Photocurrent-voltage (*J-V*) curves of PHJ-PSCs were measured using a solar simulator (91160s, Newport, AM 1.5G) with a digital Source Meter (Keithley 2420) and a light intensity of 100 mW/cm² calibrated by using Si-reference cell. The scanning direction was located from +1.5 V to -1.5 V at a scanning speed of 0.3 V/s if without special illustration. Incident photon-to-electron conversion efficiency (*IPCE*) spectra of PHJ-PSCs devices were measured using the quantum efficiency measurement system (Saifan, Beijing). Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Electron Scientific Instruments, U.S.A) was employed to analyze the molecular structure for DMSO (liquid phase) and MAPbI₃ (powder, scratched from MAPbI₃ film) between the range of 4000 cm⁻¹ and 600 cm⁻¹.

3. Results and discussions

The PHJ-PSCs with a structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PC₆₁BM/Al were fabricated and are shown in Fig.1a. The energy levels of functional layers in PHJ-PSCs are shown in Fig. 1b, in which the values were achieved from refs [24,33, 34].

Fig. 1. (a) Schematic of PHJ-PSCs with a structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al, and (b) the diagram of energy levels.

One of the crucial factors in determining the performance of PSCs is the quality of perovskite absorber layer, *e.g.*, surface roughness, coverage, crystallinity. Fig. 2 shows the formation process of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film via intramolecular exchange approach. The $\text{PbI}_2(\text{DMSO})$ solution was first deposited and the thin film was formed accordingly. Then the $\text{CH}_3\text{NH}_3\text{I}$ solution was deposited subsequently. In the first step, the dense $\text{PbI}_2(\text{DMSO})$ thin film builds a skeleton in an orderly manner via molecular self-assembly [30]. The DMSO is coordinated with Pb^{2+} (inset in Fig. 2) and it would exchange with $\text{CH}_3\text{NH}_3\text{I}$ in the second step because the $\text{CH}_3\text{NH}_3\text{I}$ have stronger affinity toward PbI_2 . Finally, the further annealing process accelerated the formation of crystalline and uniform perovskite thin film. The deposited $\text{PbI}_2(\text{DMSO})$ thin film built a mesoporous-like structure, in which the DMSO molecules replace the mesoporous temporarily and exist in the bulk phase of $\text{PbI}_2(\text{DMSO})$ thin film. The subsequent deposited $\text{CH}_3\text{NH}_3\text{I}$ molecules can diffuse into $\text{PbI}_2(\text{DMSO})$ thin film from the surface due to the strong interaction with PbI_2 , resulting in the exchange with the DMSO molecules and complete reaction with PbI_2 [16].

Fig. 2. Schematic of the formation procedure of perovskite thin film via intramolecular exchange.

The XRD pattern of $\text{PbI}_2(\text{DMSO})$ powder is shown in Fig.3a, which is consistent with the reported results [16, 31]. It obviously indicates that the DMSO molecules were intercalated in PbI_2 bulk phase. The main diffraction peaks in XRD pattern of deposited $\text{PbI}_2(\text{DMSO})$ thin film on ITO/PEDOT:PSS substrate is similar to that of $\text{PbI}_2(\text{DMSO})$ powder (Fig. 3b), of which the intensity and position of peaks are consistent. The XRD pattern of PbI_2 thin film was shown in Fig. 3c as well. As shown in Fig. 3b and c, the (001) peaks of $\text{PbI}_2(\text{DMSO})$ and PbI_2 thin film were located at the 2θ of 10.3° and 12.7° , respectively, corresponding to the d distances of 0.858 nm and 0.696 nm, respectively. The intercalation of DMSO molecules into PbI_2 resulted in an obvious increase of d distance along the crystal c -axis. The SEM images showed that pin-hole free and dense $\text{PbI}_2(\text{DMSO})$ thin film with good surface coverage could be obtained (Fig.3d). In contrast, the surface coverage of PbI_2 thin film was dramatically decreased (Fig.3e).

Fig. 3 (a-c) XRD patterns of $\text{PbI}_2(\text{DMSO})$ powders, $\text{PbI}_2(\text{DMSO})$ thin film and PbI_2 thin film, respectively. (d-e) SEM surface images of $\text{PbI}_2(\text{DMSO})$ and PbI_2 thin films. The two SEM images have the same scale bar.

Fig. 4a shows the XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films on ITO/PEDOT:PSS substrate resulted from PbI_2 and $\text{PbI}_2(\text{DMSO})$ at the different annealing temperature. A set of diffraction peaks associated with tetragonal perovskite crystals exhibited at 14.08° , 28.4° , 31.82° , 40.66° and 43.0° , which could be assigned to the reflections of (110), (220), (312), (224) and (314) lattice plane, respectively [35-37]. The stronger intensity of diffraction peaks (110) and (220) planes indicated the growth of

perovskite crystals with the preferential orientation [8,38], and the sharp diffraction peaks suggested the formation of well-crystallized perovskite thin film. Furthermore, there were not diffraction peaks coming from $\text{PbI}_2(\text{DMSO})$ or $\text{CH}_3\text{NH}_3\text{I}$ except for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ diffraction peaks, which proved that the $\text{CH}_3\text{NH}_3\text{I}$ could completely react with $\text{PbI}_2(\text{DMSO})$ and there was not $\text{CH}_3\text{NH}_3\text{I}$ or $\text{PbI}_2(\text{DMSO})$ left. In contrast, the XRD pattern showed an obvious diffraction peak of PbI_2 at 12.66° for $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film fabricated with PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ directly (without intramolecular exchange) by two steps, which indicated the $\text{CH}_3\text{NH}_3\text{I}$ solution didn't completely diffuse into the pre-deposited PbI_2 layer to fully convert to $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Furthermore, the phase conversion at the different annealing temperature was followed by XRD as well (Fig. 4a). With increasing the annealing temperature, the intensity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal diffraction peaks was enhanced dramatically, resulting from the large increase in crystallinity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. The reaction between $\text{CH}_3\text{NH}_3\text{I}$ and $\text{PbI}_2(\text{DMSO})$ could be completed within a short time even without annealing process, and the thin film color turned to dark brown instantly after depositing $\text{CH}_3\text{NH}_3\text{I}$ solution, which resulted in the immediate formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase. As shown in Fig.4a, the XRD pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$ without annealing process was identical to that of the annealed $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films except for the difference in the peak intensity. Unlike the perovskite thin film derived from the $\text{PbI}_2(\text{DMSO})$, the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase derived the PbI_2 required an interdiffusion process via the annealing step at a suitable temperature [14], of which some PbI_2 left and could not react with $\text{CH}_3\text{NH}_3\text{I}$.

The ultraviolet–visible absorption of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from $\text{PbI}_2(\text{DMSO})$ and PbI_2 at different annealing temperature was performed, as shown in Fig. 4b. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film exhibited a broad absorbance range between 350 nm and 850 nm, and the rapid increase intensity of absorbance at about 780 nm. With increasing the annealing temperature, the absorbance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from $\text{PbI}_2(\text{DMSO})$ was enhanced obviously, which is consistent to the XRD

patterns. At the annealing temperature of 100 °C, the absorbance was much stronger than that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from PbI_2 .

Fig. 4. XRD patterns and absorbance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from PbI_2 annealed at 100 °C as well as derived from $\text{PbI}_2(\text{DMSO})$ without annealing (as-deposited) and with annealing at 50 °C and 100 °C, respectively.

Furthermore, IR spectroscopic results suggested that the stretching vibration of $\text{S}=\text{O}$ appearing at 1045 cm^{-1} [39] was not detected in thermal-annealed $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$, as shown in Fig.5. The disappearance of $\text{S}=\text{O}$

stretching vibration indicated that the DMSO molecules could be effectively removed with thermal annealing, which would not influence the performance of PSCs.

Fig. 5. Fourier transform infrared spectrometer of thermal-annealed $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 100 °C derived from $\text{Pb}_2(\text{DMSO})$ and DMSO. Inset is the magnified finger-print region of S=O vibrations.

The SEM morphology images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from PbI_2 and $\text{PbI}_2(\text{DMSO})$ are exhibited in Fig. 6a and Fig. 6b, respectively. As compared with $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from PbI_2 (Fig. 6a), The continuous, dense and homogeneous morphological $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$ with better surface coverage and larger-size grains could be obtained (Fig. 6b). Inset in Fig. 6b is the cross-sectional image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$ on ITO/PEDOT:PSS substrate, which obviously shows the large-size grains. The size distribution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films is shown in Fig. 6c, in which the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$ shows the average size of about 321 nm and 495 nm in the longitudinal direction and transverse direction while the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from PbI_2 shows the average size of only about 103 nm and 159 nm,

respectively. It is attributed to pre-deposited $\text{PbI}_2(\text{DMSO})$ layer that constructs a suitable framework, in which the $\text{CH}_3\text{NH}_3\text{I}$ molecules can replace the DMSO molecules to self-assemble easily during the subsequent deposition process and result in the conversion of the dense $\text{PbI}_2(\text{DMSO})$ thin film into $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film directly without apparent change in volume [16]. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with large-size grains could decrease crystal defects and enhance carrier mobility, resulting in highly efficient PSCs [16]. Meanwhile, the large-size grains of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$ could be helpful to maintain the separation of electron-hole pairs and block the path of charge recombination [31].

Fig. 6. (a-b) SEM morphology images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from PbI_2 and $\text{PbI}_2(\text{DMSO})$, respectively. Inset in b is cross-sectional image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film deprived

from PbI₂(DMSO) on ITO/PEDOT:PSS substrate. (c) The statistical analysis of grain size distributions for CH₃NH₃PbI₃ thin films derived from PbI₂ and PbI₂(DMSO), as well as along the longitudinal direction and transverse direction, respectively.

The PHJ-PSCs with a structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PC₆₁BM/Al was fabricated using two-step sequential deposition, in which only the PCBM was used as the ETL. The performance parameters of PHJ-PSCs with two kinds of CH₃NH₃PbI₃ thin films derived from PbI₂ and PbI₂(DMSO), respectively, were shown in Table 1. The average *PCEs* of PHJ-PSCs derived from PbI₂ was only about 6.87 % (the highest one was 8.35%). While the average *PCEs* of PHJ-PSCs derived from PbI₂(DMSO) was dramatically improved to about 12.27 %, and the highest one up to 14.26 % was achieved with an open-circuit voltage (*V_{oc}*) of 0.95 V, a *J_{sc}* of 21.6 mA cm⁻² and fill factor (*FF*) of 69.5%. The typical *J-V* curve was shown in Fig. 7a. The good performance parameters were attributed to the excellent crystallinity of high-quality CH₃NH₃PbI₃ thin film, which was confirmed by XRD and SEM results above. The crystallinity of CH₃NH₃PbI₃ thin film shows very important impact on the charge generation and transport, as well as the carrier recombination [38, 40-41]. The grain boundary of perovskite thin film is the main carrier recombination site [42]. As discussed above, the grain size of CH₃NH₃PbI₃ thin film derived from PbI₂(DMSO) is about twice of that of CH₃NH₃PbI₃ thin film derived PbI₂. Thus it could effectively reduce the grain boundary, resulting in a high *J_{sc}* and *FF*. The *IPCE* spectrum (Fig. 7b) showed that the peak value exceeded 85% was obtained for CH₃NH₃PbI₃ thin film derived from PbI₂(DMSO), which is consistent with the *J_{sc}* measurements based on *J-V* curves.

In addition, the *J-V* curves of PHJ-PSCs for CH₃NH₃PbI₃ thin film derived from PbI₂(DMSO) via intramolecular exchange measured with different scanning direction showed that there was not obvious hysteresis (Fig. 7c). The *PCE* of forward sweep was 13.50 % with a *J_{sc}* of 21.7 mA cm⁻², a *V_{oc}* of 0.94V and an *FF* of 66.2 %,

respectively; while the *PCE* of reverse sweep was 14.26 % with a J_{sc} of 21.6 mA cm^{-2} , a V_{oc} of 0.95V and an *FF* of 69.5 %, respectively. The consistent *PCEs* measured under forward and reverse sweep were originated from the formation of high-quality perovskite film with good crystallinity.

Table 1. The average photovoltaic parameters of PHJ-PSC devices for $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films derived from PbI_2 and $\text{PbI}_2(\text{DMSO})$ complexes with intramolecular exchange, respectively. The best parameters are shown in the parentheses.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	<i>FF</i> (%)	<i>PCE</i> (%)
$\text{CH}_3\text{NH}_3\text{PbI}_3$ derived from $\text{PbI}_2(\text{DMSO})$	0.96 ± 0.04 (1.02)	18.81 ± 1.63 (21.82)	67.98 ± 4.08 (73.15)	12.27 ± 1.47 (14.26)
$\text{CH}_3\text{NH}_3\text{PbI}_3$ derived from PbI_2	0.90 ± 0.05 (0.94)	12.16 ± 2.05 (16.84)	63.24 ± 4.05 (68.56)	6.87 ± 0.88 (8.35)

Fig. 7. (a-b) The typical *J-V* curves and *IPCE* spectra of PHJ-PSCs for $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film

derived from PbI_2 and $\text{PbI}_2(\text{DMSO})$, respectively. (c) The typical J - V curves of PHJ-PSCs measured under forward and reverse scanning direction for $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film derived from $\text{PbI}_2(\text{DMSO})$.

Conclusions

In summary, low-temperature, two-step sequential deposition with intramolecular exchange technology was used to fabricate high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film with excellent coverage and uniformity, in which the $\text{PbI}_2(\text{DMSO})$ complex was synthesized at room temperature and deposited accordingly, accelerating the complete formation of flat and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with depositing the $\text{CH}_3\text{NH}_3\text{I}$ solution subsequently. The PHJ-PSCs with a simple inverted structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al and without other buffer layers, *e.g.*, C_{60} , LiF, BCP, *etc.*, were fabricated, and an *PCE* up to 14.26% could be obtained, which was much higher than the *PCE* (8.35 %) of PHJ-PSCs fabricated by normal two-step sequential deposition. The $\text{PbI}_2(\text{DMSO})$ thin film could construct a suitable framework, similar to a mesoporous scaffold, and assist the $\text{CH}_3\text{NH}_3\text{I}$ to diffuse into the pre-deposited $\text{PbI}_2(\text{DMSO})$ thin film. Thus, high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with large-size $\text{CH}_3\text{NH}_3\text{PbI}_3$ grains and high crystallinity were formed, resulting in efficient PHJ-PSCs. The research provides a good route to fabricate high-quality perovskite thin film and efficient PSCs using low-temperature, two-step sequential deposition with intramolecular exchange technology, which potentially match with large-scale, high-output R2R printing/coating techniques.

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Abstract Graphic