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Flexible Perovskite Solar Modules with Functional Layers
Fully Vacuum Deposited

Ting Lei, Feihong Li, Xinyi Zhu, Hua Dong,* Zhiwen Niu, Siwei Ye, Wu Zhao, Jun Xi, Bo Jiao, Liming Ding,* and Zhaoxin Wu*

Large-area homogeneous and uniform perovskite films are key to the mass production of perovskite solar cells, especially the flexible ones. Different from the solution-processed preparation, herein an all-evaporation technique is developed for both perovskite films and the hole-transporting layer in the modules. With the two-step strategy of active-layer design, homogeneous large-area perovskite films are prepared via evaporation of first PbI2 and then CH3NH3I. An 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ)-doped 4,4',4'-tris(N-aphthalene-2-yl)-N-phenylamino)triphenylamine (2T-NATA) hybrid hole-transporting layer is deposited on the indium-tin-oxide electrode via coevaporation. A power conversion efficiency (PCE) beyond 13% is achieved with the as-prepared flexible perovskite solar module (active area of 16.0 cm²), which exhibits both higher stability and higher efficiency than the conventional solution-processed module using poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as the hole-transporting material. This novel strategy of all-evaporation functional layers provides a feasible way for the industrialization of flexible perovskite solar cells.

1. Introduction

Flexible solar cells based on plastic substrates have become the focus of the international photovoltaic community[1] because of their characteristics of thinness, light weight, and flexibility and they can be used for portable power in consumer electronics as well as military and aviation applications. Due to the superb characteristics of organic–inorganic perovskite semiconductors, including the large absorption coefficient, wide absorption spectrum, and long carrier diffusion lengths,[2] the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased from 3.8% to 25.2% in the last decade.[3] In particular, flexible PSCs built on plastic substrates have attracted much attention because perovskite films can be prepared at low temperature.[4]

There are various techniques for preparing perovskite films. The most dominant technique for efficient devices is spin coating,[5] however, it is not suitable for large-area films. Several methods, such as spray coating,[6] slot die,[7] inkjet printing, and blading,[8] were developed to manufacture large-area films via one- or two-step processes. Nevertheless, the preparation of homogeneous, large-area perovskite films remains a big challenge. Adopting vacuum thermal deposition, which is a mature and successful technology, particularly for the mass production of organic light-emitting diodes, is regarded as a promising solution. This technology readily helps to prepare uniform and large-area films, and its low-temperature character is compatible with the fabrication of lightweight, flexible perovskite modules, which is rarely reported with solution-based methods.[9] Evaporation deposition technologies, such as dual-source coevaporation, single-source flash technology, and chemical vapor deposition (CVD), were developed by Snaith’s group, Bolink’s group, and Qi’s group, respectively.[10] Unfortunately, the aforementioned techniques have their limitations, such as difficulty in monitoring methylamine iodine (MAI) in vacuum deposition as well as the easy decomposition of MAI in the coevaporation method, and difficulty in obtaining uniform films in large areas in the single-source flash evaporation method.
Therefore, the shortcomings of these technologies have become bottlenecks for the further development of perovskite evaporation technology in mass production.

Traditionally, poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate) (PEDOT:PSS), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), and NiO$_x$ are widely used for inverted PSCs.$^{[4a,b]}$ However, PEDOT:PSS can easily interact with water and oxygen in the air due to its hydrophilicity and acidity, thus causing damage to the active layer and corroding indium doped tin oxide (ITO) glass, and eventually becoming detrimental to the efficiency and long-term stability of the device. PTAA is expensive and not compatible with the vacuum method. The preparation of NiO$_x$ films requires a high temperature for sufficient hydrolysis and crystallization. Therefore, the exploration of hole-transporting materials (HTMs) and related deposition technologies is also important for stable and highly efficient PSCs.

In this work, we developed an all-vacuum strategy for the preparation of both the perovskite films and transporting layers. To achieve homogeneous large-area perovskite films, a two-step flash-evaporation method was applied, in which the PbI$_2$ thin films were evaporated at first and then the MAI thin films. With a postannealing process, we realized a “solid–solid” reaction for the perovskite active layer in a way different from the “solid–vapor” reaction in the CVD method.$^{[9b]}$ This perovskite fabrication process is simple and “careless” as it does not require the careful control of the MAI conversion rates that is required in the CVD method.$^{[9b]}$ In addition, a hybrid HTM, consisting of small organic molecules 4,4',4''-tris(N-aphthalene-2-yl)-N-phenylamino)triphenylamine (2T-NATA) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), was introduced via a coevaporation process. The hybrid HTM (h-HTM) can accurately regulate the film thickness and component proportion, thus achieving a uniform film with extremely high purity and minimal material loss. For small-size devices, the best PCE of the device based on an h-HTM is 19.23% compared with 14.79% of the PEDOT:PSS-based device. For flexible perovskite solar modules with an active area of 16.0 cm$^2$, our strategy has reached a best PCE exceeding 13%. We believe that the developed “all-evaporation strategy” provides a feasible way for the industrialization of flexible PSCs.

2. Results and Discussion

In our work, the inverted planar solar cell devices were manufactured with the structure of ITO/2T-NATA/perovskite/C$_{60}$/bathocuproine (BCP)/Ag (Figure 1a), where all functional layers were prepared via an evaporation process. Especially, different to the conventional solution-processable polymeric HTM, a small organic molecular material 2T-NATA was used as an efficient HTM due to its remarkable characteristics, including the low glass transition temperature, high light transmittance, and excellent conductivity. Figure 1b shows the energy-level diagram of the PSC measured by ultraviolet photoelectron spectroscopy (UPS). In particular, the highest-occupied molecular orbital (HOMO) level of 2T-NATA (UPS spectra shown in Figure S1, Supporting Information), $-5.11$ eV, exhibits a better alignment with the valence-band edge of the perovskite than PEDOT:PSS ($-5.0$ eV). Thus, we can expect a higher efficiency of extracting holes and block electrons at the perovskite/HTM interface. The cross-section scanning electron microscopy (SEM) image of the 2T-NATA-based device (Figure 1c) clearly shows the

![Figure 1](https://www.advancedsciencenews.com/)

**Figure 1.** a) Illustration of the inverted PSC structure. b) Energy level diagram of the PSCs using PEDOT:PSS and 2T-NATA as HTMs. c) Cross-sectional SEM image of the PSC with the structure: ITO/HTM/perovskite/C$_{60}$/BCP/Ag. d) The chemical structures of 2T-NATA, F4-TCNQ, and PEDOT:PSS.
layered structure, where the thickness of the MAPbI₃ layer is assessed around 400 nm. In addition, F4-TCNQ was doped into the 2T-NATA for higher conductivity of the HTM. The chemical structures of the involved HTMs, F4-TCNQ, 2T-NATA, and PEDOT:PSS, are shown in Figure 1d.

Vacuum evaporation has advantages of producing uniform films and controllable film thickness. Figure 2 displays the physical vapor deposition (PVD) process to prepare HTM and the active layer for the designed PSCs. Here, the h-HTM was prepared by coevaporating 2T-NATA and F4-TCNQ in a series of evaporation rate (ER) ratios. Perovskite films of all PSCs were fabricated by a flash-evaporation method. A film of PbI₂ was first deposited on the HTM layer, and then MAI was deposited to the former layer with a subsequent annealing process (the detailed process can be found in the Experimental Section).

High transmittance of the HTM in the range of 300–850 nm favors efficient light harvesting of the perovskite layer. For the PEDOT:PSS and h-HTM (with different ER ratios of F4-TCNQ:2T-NATA 0.10:1, 0.15:1, 0.20:1, 0.25:1, and 0.30:1) films, Figure 3a (see Figure S2, Supporting Information, for details) shows that the optical transparency of the ITO deposited by the h-HTM film with ER ratio 0.20:1 is higher than that of the PEDOT:PSS-film-deposited ITO, and slightly lower than that of the bare ITO in the range of 400–850 nm with slightly reduced compared with the bare ITO. Figure 3b and Figure 3c, Supporting Information, show the electrical conductivity of h-HTMs with different ER ratios and PEDOT:PSS in the vertical direction, measured with the device whose structure is sketched in the inset. The hole conductivity of the h-HTM films is obviously higher than that of the PEDOT:PSS-film in the vertical direction, revealing the better charge-transporting property of the h-HTM. This may be attributed to the strong electron acceptor property of F4-TCNQ and the interaction between the dipoles of F4-TCNQ⁻ and 2T-NATA⁺. In addition, there is a lower HOMO level (−5.11 eV) for the F4-TCNQ-doped (0.20:1) than the undoped 2T-NATA (−5.06 eV), which also leads to a more rapid hole extraction (Figure S1, Supporting Information). This lowering of the HOMO level is in agreement with earlier reports. From the SEM images of the h-HTM and PEDOT:PSS films (Figure S4, Supporting Information), we can see that both the vapor-deposited h-HTM and spin-coated PEDOT:PSS on ITO are quite dense and without pinholes, indicating that both contribute to a nearly complete coverage on the ITO. The trend of steady-state photoluminescence (PL) spectra in Figure 3c (see Figure S5, Supporting Information, for details) suggests that the PL intensity obviously decreases with an increasing ER ratio. When the ER ratio is 0.20:1, the PL intensity reaches its minimum, which is ascribed to the increased conductivity of the hole transport layer. The higher PL intensity for perovskite films with a higher ER ratio (>0.20:1) may be associated with the aggregation of F4-TCNQ (Figure S6, Supporting Information), which will deteriorate the interface contact with 2T-NATA. As the proportion of F4-TCNQ increases, the conductivity of the hole-transporting layer increases, indicating that this ER ratio helps to extract holes most efficiently.

The relative roughness of the perovskite layers on the h-HTM and PEDOT:PSS was measured by an atomic force microscope (AFM) (Figure S7, Supporting Information). The (root mean square) results are 7.5 and 10.6 nm, respectively. The smooth perovskite films in both cases are beneficial to the proper interfacial contact between the perovskite layer and the functional layers, thus promoting the carrier-transfer efficiency. X-ray diffraction (XRD) measurements were conducted to investigate the crystallinity of the perovskite films on the different HTMs. The XRD spectra (Figure 3d and Figure S8, Supporting Information) show the (110) peak of the perovskite at 14.08°. The full width at half maximum (FWHM) of PEDOT:PSS-based and h-HTM-based perovskite films are 0.202° and 0.173°, respectively. The similar XRD intensity and FWHM of both PEDOT:PSS-based and h-HTM-based perovskite films indicate that their similar crystallinity. Perovskite films grown on different HTMs (Figure 3e,f) demonstrate similar morphologies without obvious pinholes. From the grain size distribution spectra (Figure S9, Supporting Information), the perovskite grains based on both PEDOT:PSS and h-HTM exhibit similar size distribution and average grain size. All these results show a similar quality of perovskite films prepared on PEDOT:PSS and h-HTM.

To investigate the performance of the PSCs using h-HTMs, we fabricated a series of inverted PSCs of the structure of ITO/h-HTM/MAPbI₃/C₆0/BCP/Ag with the same procedures except for different HTM parameters. The J–V characteristics of h-HTM-based (with ER ratios of F4-TCNQ:2T-NATA 0.10:1, 0.15:1, 0.20:1, 0.25:1, and 0.30:1) and PEDOT:PSS-based PSCs...
under a solar simulator with AM 1.5G (100 mW cm\(^{-2}\)) are shown in Figure 4a. Furthermore, the device performance parameters, including the open-circuit voltage (\(V_{oc}\)), the short-circuit current density (\(J_{sc}\)), the fill factor (FF), and the PCE, are shown in Figure S10, Supporting Information, and the statistical data are summarized in Table 1. We should note that a too thin HTM will result in direct contact between the electrode and the perovskite layer, thus inducing severe carrier recombination.\(^{[14]}\) To realize the full coverage of the h-HTM on the ITO, we evaporated the h-HTM to a thickness of 15 nm. As the ER ratio of F4-TCNQ:2T-NATA increases from 0.10:1 to 0.20:1, the average PCE is slightly improved from 13.81% to 17.45%, accompanied by the improvement of the average \(J_{sc}\) (21.65 mA cm\(^{-2}\)) and FF (0.772). This could be attributed to the increased conductivity of h-HTMs that facilitates the effective extraction of holes from perovskite films to HTMs. When the ER ratio further increases to 0.25:1 and 0.30:1, the parameters of devices decline slightly, probably because the interfacial contact may be deteriorated by the aggregation of F4-TCNQ as its proportion in the h-HTM increases.\(^{[12]}\) Compared with the best PEDOT:PSS-based PSC with a PCE of 14.79%, \(V_{oc}\) of 0.962 V, \(J_{sc}\) of 20.90 mA cm\(^{-2}\), and FF of 0.736, the best coevaporation h-HTM-based PSC with the ER ratio of 0.20:1 achieves a higher PCE of 17.85%, \(V_{oc}\) of 1.054 V, \(J_{sc}\) of 21.98 mA cm\(^{-2}\), and FF of 0.770. Figure S11, Supporting Information, shows the \(J–V\) curves of different thicknesses (15–30 nm) of the 2T-NATA-based PSC. It is found that the average PCE increases from 17.29% to 18.68% when the thickness increases from 15 to 20 nm. In this case, the outstanding device performance shows a PCE of 18.86%, \(V_{oc}\) of 1.059 V, \(J_{sc}\) of 22.38 mA cm\(^{-2}\), and FF of 0.795. The PCE decreases with the further increase of h-HTM thickness toward 30 nm. Table S1, Supporting Information,
summarizes the optical characteristics of 30 cells at different thicknesses (15, 20, 25, and 30 nm) of the h-HTMs. It is found that further increasing the thickness of h-HTM films above 20 nm degrades the performance of the device. The possible reason is that the increase in thickness leads to an increase in series resistance (R_s) and a decrease in FF.[15]

The best device based on the flash-evaporation process (ER ratio of 0.20:1, thickness of 20 nm) shows a PCE of 18.80% with a V_{oc} of 1.063 V, J_{sc} of 22.44 mA cm\(^{-2}\), and FF of 0.788 at the forward scan, and PCE of 19.23% with V_{oc} of 1.060 V, J_{sc} of 22.42 mA cm\(^{-2}\), and FF of 0.809 at the reverse scan (Figure 4b). The hysteresis of the h-HTM-based device is

Table 1. Summary of the photovoltaic characteristics based on 30 cells with the structure of ITO/h-HTM/MAPbI\(_3\)/C\(_60\)/BCP/Ag.

<table>
<thead>
<tr>
<th>ER ratios</th>
<th>V_{oc} [V]</th>
<th>J_{sc} [mA cm(^{-2})]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>0.944 ± 0.019</td>
<td>20.52 ± 0.45</td>
<td>0.735 ± 0.009</td>
<td>14.16 ± 0.63</td>
</tr>
<tr>
<td>0.10:1</td>
<td>1.014 ± 0.013</td>
<td>18.89 ± 0.62</td>
<td>0.713 ± 0.016</td>
<td>13.81 ± 0.51</td>
</tr>
<tr>
<td>0.15:1</td>
<td>1.019 ± 0.019</td>
<td>20.51 ± 0.44</td>
<td>0.717 ± 0.008</td>
<td>15.15 ± 0.38</td>
</tr>
<tr>
<td>0.20:1</td>
<td>1.048 ± 0.008</td>
<td>21.65 ± 0.39</td>
<td>0.722 ± 0.007</td>
<td>17.45 ± 0.44</td>
</tr>
<tr>
<td>0.25:1</td>
<td>1.035 ± 0.010</td>
<td>20.93 ± 0.48</td>
<td>0.768 ± 0.011</td>
<td>16.74 ± 0.50</td>
</tr>
<tr>
<td>0.30:1</td>
<td>1.020 ± 0.013</td>
<td>20.01 ± 0.65</td>
<td>0.731 ± 0.018</td>
<td>14.62 ± 0.65</td>
</tr>
</tbody>
</table>

Figure 4. a) J–V curves for the devices that h-HTM prepared at different ER ratios (0.10:1, 0.15:1, 0.20:1, 0.25:1, 0.30:1). b) J–V curves with different scan directions of the h-HTM-based devices (ER ratio of 0.20:1, thickness of 20 nm). c) J–V curves of the champion devices with PEDOT:PSS and h-HTM as HTMs. d) Histograms of PCEs with different HTMs. e) EQE spectra and calculated J_{sc} of the devices based on PEDOT:PSS and h-HTM. f) The steady-state power output of the solar cells with different HTMs.
negligible, indicating that there are few defects in the MAPbI₃ thin films. With the traditional PEDOT:PSS-based PSC (PCE of 14.79%), the optimized h-HTM-based PSC (PCE of 19.23%) has significantly improved the major device performance parameters, such as the Voc from 0.962 to 1.060 V, Jsc from 20.90 to 22.42 mA cm⁻², and FF from 0.736 to 0.809 (Figure 4c). The increase in Jsc is due to the reduction in Rs and the enhancement of hole mobility. The statistical histogram of PCEs based on 25 devices fabricated with the h-HTM and PEDOT:PSS is shown in Figure 4d.

External quantum efficiency (EQE) spectra of the optimized PEDOT:PSS-based and h-HTM-based PSCs are shown in Figure 4e to analyze the charge-collection ability of investigated PSCs. The integrated photocurrents were 20.45 and 21.98 mA cm⁻², respectively, in agreement with the photocurrents shown by the J-V curves (Figure 4c). Thus, the optimized h-HTM-based device extracts holes more rapidly than the PEDOT:PSS-based device and has less charge recombination at the interface. From Figure S12, Supporting Information, the UV–vis absorption spectra of the MAPbI₃ films in both cases are similar, indicating a nearly negligible difference between their light-harvesting efficiencies. The steady-state efficiency of the optimized h-HTM-based PSC shown in Figure 4f unveils that the balanced device delivers a stabilized current density of 20.70 mA cm⁻² and a stabilized PCE of 18.63% at 0.90 V.

Electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate the carrier transport and recombination in PSCs. The inner Rs consists of the sheet resistance (Rsheet) of the electrodes, charge-transfer resistance (RCT) at the interface between the electrode and the adjacent charge-carrier layer, and RCT at the interface between the MAPbI₃ and the adjacent charge-carrier layer. Figure 5a shows a simplified model of the circuit and EIS results of the PEDOT:PSS-based device and h-HTM-based device. The spectra were measured at a bias of 0.8 V and frequencies ranging from 0.5 Hz to 4 MHz in the dark. From the figure, the RCT of the solar cell based on PEDOT:PSS and the h-HTM-based device are ~600 and 700 Ω, respectively. As the only difference between these two types of devices is the HTM, such a larger recombination resistance of the h-HTM-based device corresponds to a slower recombination rate, and thus a higher charge-collection efficiency at the interface. Time-resolved photoluminescence (TRPL) was used to measure the carrier transport in PSCs. Figure 5b shows the TRPL spectra of perovskite films based on different HTMs. The average carrier lifetime of perovskite with PEDOT:PSS is 14.5 ns, and 10.2 ns of perovskite with the h-HTM. Therefore, it is evidenced that holes can be injected from the perovskite film to the h-HTM more effectively, which is consistent with the results obtained by the steady-state PL.

Stability is also an important parameter of PSCs. We measured the hydrophobic angles of PEDOT:PSS and the h-HTM as shown in the inset of Figure 6a. The hydrophobic angles of the h-HTM and PEDOT:PSS are 83.37° and 13.14°, respectively, indicating the weaker ability of the h-HTM to adsorb water molecules in the air. In addition, both devices were stored at 25 °C and relative humidity (RH) of 45% for 1000 h to compare the stability. As shown in Figure 6a (normalized device efficiency chart 1000 h), after 1000 h, the h-HTM-based device still maintains ~90% of the initial PCE, whereas the PCE of the PEDOT:PSS-based device drops to ~50%. This result agrees well with the water-contact measurements. Figure 6b shows the operational stability of PSCs with different HTMs in a glovebox under 1 sun continuous illumination. After operating for 500 h, the h-HTM-based and PEDOT:PSS-based devices retain ~80% and 65% of their initial PCEs, respectively.

The laboratory-level spin-coating method is generally limited to uniform films only on small-area substrates, while for industrialization of PSCs similar to silicon-based solar panels, it is necessary to find a method of preparing large-area uniform films. Herein, using 2T-NATA and F4-TCNQ as a new h-HTM via vapor deposition, combined with a two-step flash evaporation method followed by annealing to fabricate a perovskite layer, a complete vapor-deposition process was proposed. Rigid and flexible perovskite solar modules with an active area of 16.0 cm² (8 × 2.0 cm²) were manufactured, whose J-V curves are shown in Figure 7a,b, respectively. Both the rigid and flexible modules consist of eight cells in series (Figure 7c). The best-performing rigid module shows a PCE of 15.06%, with Jsc = 2.74 mA cm⁻², Voc = 8.09 V, and FF = 0.679, while the flexible module exhibits the best PCE of 13.15% with Jsc = 2.58 mA cm⁻², Voc = 7.95 V.
and $\text{FF} = 0.641$ (Table 2). The $V_{oc}$ of each subcell of the flexible module reaches $\approx 0.99$ V under series condition. Compared with the $V_{oc}$ of h-HTM-based devices built on a small active area (1.05 V on average), we can conclude that the loss is negligible. The FF of the module, 0.641, is remarkable. In addition, the h-HTM-based flexible module shows good mechanical stability as maintaining over 80% after 1000 bending cycles (Figure S13, Supporting Information).

![Figure 6. Long-term stabilities of the PSCs based on the PEDOT:PSS and h-HTMs. a) Devices stored under ambient air (45% average RH) without encapsulation for more than 1000 h (the inset shows contact angle images of the PEDOT:PSS and the h-HTMs of optimal ratio). b) Devices placed in glovebox under 1 sun continuous illumination.](image)

![Figure 7. Perovskite solar module (eight subcells in series) made by the all-evaporation method. J–V curves and pictures of the champion h-HTM-based solar module: a) rigid module and b) flexible PSC module. c) Structure of the PSC module.](image)

Table 2. Summary of the photovoltaic characteristics for the rigid and flexible module.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid</td>
<td>8.09</td>
<td>2.74</td>
<td>0.679</td>
<td>15.06</td>
</tr>
<tr>
<td>Flexible</td>
<td>7.95</td>
<td>2.58</td>
<td>0.641</td>
<td>13.15</td>
</tr>
</tbody>
</table>
3. Conclusion

In this work, an all-evaporation method was developed to make inverted PSCs. PbI2 and MAI films were successively flash evaporated to achieve homogeneous large-area MAPbI3 films with a “solid–solid” reaction in the postannealing process. Meanwhile, a hybrid material layer consisting of small organic molecules 2T-NATA and F4-TCNQ was vapor deposited for hole transport. The fabricated PSCs demonstrate significantly enhanced performance and stability. The h-HTM-based inverted PSC offers a PCE of 19.23% (compared with the 14.79% of the PEDOT:PSS-based device). The enhancement of device performance is due to the improved conductivity of the HTM and its more efficient hole extraction. Moreover, we used this approach to make rigid and flexible perovskite solar modules with an active area of 16.0 cm2, achieving PCEs of 15.06% and 13.15%, respectively. The successful fabrication of the modules demonstrates the potential of PSCs for future industrialization.

4. Experimental Section

Materials: MAI and PbI2 were purchased from TCI. C60, BCP, F4-TCNQ, and 2T-NATA were obtained from Nichem (Taiwan) and isopropanol (IPA, 99.5%) from Alfa Aesar.

Fabrication of Perovskite Film: First, PbI2 film was vapor deposited onto the substrate ITO at a rate of 6 nm s⁻¹ in a vacuum chamber (<3 × 10⁻⁸ Pa) with a thickness of 200 nm. MAI was flash evaporated onto a substrate to react with PbI2. The specific steps are as follows. First, the MAI was dissolved in N,N-dimethylformamide at a concentration of 3 mol L⁻¹ and then uniformly dropped on a clean molybdenum sheet (10 cm × 3.5 cm), and the molybdenum sheet was heated at 80 °C for 10 min to be used for drying. Second, a flash evaporation step was performed when the pressure of the chamber was less than 10⁻⁴ Pa. To protect the vacuum system from decomposed MAI, the valve of the molecular pump was closed to isolate the chamber from the pump and a current of 200 A was applied to the molybdenum sheet. The MAI material was evaporated onto the substrate in a very short time and then annealed at 100 °C in a nitrogen atmosphere. After 30 min, 500 µL IPA was added dropwise and dried with nitrogen to remove excess unreacted MAI.

Fabrication of PSCs: First, ITO-patterned glass substrates with a sheet resistance of ≈15 Ω square⁻¹ were cleaned with deionized water and organic solvents and then exposed to UV-ozone ambience for 5 min. Second, F4-TCNQ and 2T-NATA were coevaporated onto ITO substrate in a vacuum environment (<3 × 10⁻³ Pa) at ER ratios of 0.10:1, 0.15:1, 0.20:1, 0.25:1, and 0.30:1, respectively. The control group was mixed with PEDOT:PSS and water at a ratio of 1:3, sonicated for 2 h, then 1500 r min⁻¹ for 30 s on clean ITO glass and then annealed at 120 °C for 20 min. Then a perovskite layer was prepared. The devices were completed by successively vacuum depositing C60 (40 nm), BCP (6 nm), and an Ag cathode (120 nm) under 10⁻³ Pa. The perovskite solar module was prepared in the same way. In the fabrication of a module, the process was similar to that of small solar cells except the laser scribing patterning process. ITO patterns with nine strips were purchased from South China Xiang Science and Technology Company. A green laser of 532 nm was used to remove the BCP/C60/perovskite/HTM layers deposited by vacuum evaporation. An Ag electrode was deposited through a precisely designed mask.

Characterizations: A field emission SEM (Quanta 250, FEI Co., USA) was used to investigate the surface morphology of the h-HTM, PEDOT:PSS, and perovskite films. The crystalline structure on the ITO substrate was obtained using an X-ray diffractometer (Bruker D8 ADVANCE) with Cu Kα radiation. The absorption spectra were obtained using a UV–vis spectrophotometer (HITACHI U-3010, Japan). The TRPL spectra were recorded by 100 ps time resolution using a time-correlated single photon counting (TCSPC) system (FLS920 spectrometer) (excited by picosecond pulsed LEDs, pulse duration <850 ps, repetition rate 10 MHz). The photovoltaic performance was estimated with a AAA solar simulator (XES-3015, SAN-EI), under AM 1.5G irradiation with an intensity of 100 mW cm⁻². The J–V curve was measured using a Keithley (2602 Series Source Meter), and the scanning was performed with a 0.5 V s⁻¹ step. EQE spectra were collected in AC mode using a solar cell quantum efficiency measurement system (SolarCellScan 100, Zolix instruments. Co. Ltd). EIS of the cells were obtained using a CHI-660E over the frequency range of 0.1 Hz–100 kHz under illumination (100 mW cm⁻²). UPS characteristic were carried out by X-ray photoelectron spectroscopy (ESCALAB Xi+, Thermo Fisher Scientific).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

flexible modules, hole-transporting materials, large area, low-temperature processing, perovskite solar cells, vacuum evaporation

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