Improved Efficiency of Perovskite Solar Cells with Low-Temperature-Processed Carbon by Introduction of a Doping-Free Polymeric Hole Conductor

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1. Introduction

Perovskite solar cells (PSCs) have increased tremendously in power conversion efficiencies (PCEs) during the short period of their existence, from 3.8% in 2009 to 25.5% currently.1-2 PSCs are based on lead halide perovskite semiconductors, which have attracted much attention due to their outstanding optoelectronic properties, such as high absorption coefficient with a direct bandgap, which is tunable by modification of their composition,3 long carrier diffusion length,4 high carrier mobility,5 and their versatile fabrication methods, including simple solution processes.6,7 PSCs can rival with commercial monocrystalline silicon solar cells. Despite the high efficiency of PSCs, the use of hazardous solvents in preparation and the presence of the toxic element lead increase environmental concerns. To minimized adverse effects, green solvent processing8,9 and encapsulation techniques to avoid lead leakage10 should be applied. However, long-term stability issues still remain, limiting so far the practical commercialization of PSC technology.11

In the conventional n-i-p device structure of PSCs, the metal back contact, Au (gold) or Ag (silver), give limited stability due to chemical migration of the metals and reaction with the perovskite.12-14 Furthermore, these metals are expensive and need a high-vacuum deposition technique, which makes it costly and energy intensive. As an alternative, a variety of carbon materials, such as carbon black, graphite, graphene, and carbon nanotubes, are suited as contact materials in PSCs.15,16 These carbon materials possess a work function of about 5.0 eV and allow for PSC fabrication at low temperature (<120 °C).17 In addition, carbon electrodes (CEs) offer advantages such as low cost and vacuum-free preparation, as well as giving superior stability, by acting as a moisture barrier and by suppressing ion migration.18-20

There are two types of C-PSCs. Type I C-PSCs have a mesoscopic n-i-p architecture and are typically prepared by screen printing porous layers of TiO2, insulator (ZrO2, Al2O3), and carbon, which are heated at a high temperature (≈450 °C) and subsequently infiltrated with a perovskite precursor solution. Initial reports from 2013 yielded devices with a PCEs of 6.6%,21 which improved to 17.0-17.5% in recent years.22,23 In type II C-PSCs, the CE is deposited on the top of the perovskite layer.
This deposition can be done by inkjet printing, screen printing or doctor blading, or by hot pressing of a free-standing CE film at low temperature (<120 °C). Type II C-PSCs were first reported in 2014, yielding a device performance of 9% and over 2000 h storage stability.

Addition of a hole-selective layer between perovskite and CE improves the performance of type II C-PSCs. Copper phthalocyanine (CuPc) was successfully applied as hole transport material (HTM) in C-PSCs, yielding up to 17.8% efficiency. Similarly, copper (I) thiocyanate (CuSCN) was recently used as HTM in C-PSCs, giving PCEs up to 15.5%. By application of a press transfer carbon film onto a 2.2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobi- fluorene (spiro-OMeTAD)-coated perovskite, the PCE values of up to 19.4% were achieved due to increased hole conductivity and mobility and improved energy-level matching.

Recently, P3HT with four different molecular weights (Mw) and regioregularities (RRs) synthesis (19 kDa/95%, 194 kDa/100%, 223 kDa/79%, and 338 kDa/76%, respectively) were investigated as HTMs in PSCs. Polymers with the highest Mw and lowest RR polymer increased the PCE to 17.6%, maintaining over 85% of its original efficiency at 85 °C (RH: ~70%) for over 1000 h. To date, the highest efficiency obtained in PSCs with P3HT as HTMs of 24.6% was achieved by incorporation of gallium(III) acetylatonate Ga(acac)3 into P3HT as HTMs, leading to effective interfacial passivation and superior stability for 2000 h at room temperature (RH: 85%).

In this work, we report on the use of a suitable carbon paste in PSCs, deposited either directly on the MAPbI3 perovskite film or on an intermediate undoped P3HT layer. The doctor-bladed carbon films were annealed at low temperature in ambient air. MAPbI3/P3HT/carbon devices yielded efficiencies exceeding 15% and displayed excellent stability under dry storage and maintained 70% of its performance after 900 h at 82 °C in air.

2. Results and Discussion

Three different n–i–p solar cell device structures were used in this study, schematically depicted in Figure 1a: carbon-contact PSCs with and without P3HT polymer hole conductor and PSCs with P3HT and a gold contact. Unless stated otherwise, the P3HT was undoped. The perovskite used was MAPbI3, prepared using a standard one-step method with antisolvent treatment. Cross-sectional SEM images of ITO/SnO2/MAPbI3/P3HT/carbon device are shown in Figure S1a, Supporting Information. The overview image is dominated by the carbon layer with a thickness of about 25 μm. Large graphite flakes are clearly visible. From higher-magnification images, the MAPbI3 absorber layer (thickness 350 nm) and P3HT layer (30 nm) can be clearly discerned, while a very thin SnO2 layer (~20 nm) can just be seen. A cross section of ITO/SnO2/MAPbI3/P3HT/Au device is shown in Figure S1b, Supporting Information. The basic characterization of the perovskite films is shown in Figure S2, Supporting Information.

The current–voltage (J–V) characteristics irradiation of champion devices, recorded under 100 mW cm−2 AM1.5 G, are illustrated in Figure 1b, while the corresponding average and maximum solar cell performance values are listed in Table 1. When the carbon contact is deposited directly on top of the perovskite film, a decent solar cell performance is obtained, with a PCE of 12.76% for the champion device, an open-circuit voltage (VOC) of 0.86 V, a short-circuit photocurrent density (JSC) of 23.25 mA cm−2, and a FF of 0.64. Addition of a P3HT hole conductor layer in between the perovskite and the carbon layer leads to a significantly improved solar cell performance. The champion device yielded a PCE of 15.74%, a VOC of 0.94 V, a JSC of 23.22 mA cm−2, and a FF of 0.72. The addition of a P3HT layer specifically improved the FF and the VOC, which is ascribed to improved extraction of the holes from the perovskite film at the perovskite/carbon contact when the intermediate P3HT layer is added. It must be noted that higher VOC values over 1 V are found in state-of-the-art devices using MAPbI3. For comparison, also PSC devices using gold contacts on the top of the P3HT were prepared. Interestingly, MAPbI3/P3HT/Au devices attained...
lower performance than MAPbI3/P3HT/carbon devices and even MAPbI3/carbon devices, with the best PCE of only 11.65%, Voc of 0.83 V, Jsc of 23.13 mA cm\(^{-2}\), and a FF of 0.60.

Incident photon-to-current conversion efficiency (IPCE) spectra of the investigated devices are shown in Figure 1c. Consistent with the results from the J–V curve characterization, the MAPbI3/P3HT/carbon device showed the highest IPCE with a broad peak of about 85% in the wavelength range from 450 to 650 nm. While the IPCE spectrum of MAPbI3/carbon device was similar, but slightly lower, the IPCE of MAPbI3/P3HT/Au was much lower and its spectrum flatter. In the red part of the spectrum, 650–800 nm, not all light is absorbed by the perovskite layer in a single pass. Reflection of the light by the Au contact back to the perovskite improves the IPCE in the red region for the MAPbI3/P3HT/Au device. The Jsc values obtained from the integration of the IPCE with respect of the solar spectrum are 18.32 mA cm\(^{-2}\) (MAPbI3/P3HT/carbon), 17.36 mA cm\(^{-2}\) (MAPbI3/carbon), and 12.36 mA cm\(^{-2}\) (MAPbI3/P3HT/Au), lower than the values measured in the solar simulator. We ascribe this to the very low monochromatic light intensity used in the IPCE without bias light, yielding photocurrents of only a few microamperes. Under such conditions, shunt current losses through pinholes in the P3HT may occur for the gold-coated devices.

Solar cell statistics of 3 × 16 devices were assessed by J–V measurements under 1 sun AM1.5G illumination and confirmed the trends observed for the champion devices, as shown in Figure 2 and Table 1. MAPbI3/carbon and MAPbI3/P3HT/Au devices exhibited an average PCE of 12.1 ± 0.4% and 10.8 ± 0.5%, respectively. MAPbI3/P3HT/Au devices display poor average performance with a very broad distribution in JSC and FF. MAPbI3/P3HT/carbon devices are highly reproducible,

### Table 1. Champion and average photovoltaic performance (16 cells) of perovskite devices with P3HT/Au contacts and carbon-based PSCs with and without P3HT layer.

| Devices            | PCE [%] | Voc [V] | Jsc [mA cm\(^{-2}\)] | FF [%] |
|--------------------|---------|---------|----------------------|--------|
|                   | Champion | Average | Champion | Average | Champion | Average | Champion | Average |
| MAPbI3/P3HT/Au     | 11.65   | 10.84 ± 0.52 | 0.83 | 0.82 ± 0.02 | 23.13 | 22.59 ± 0.91 | 60.39 | 58.4 ± 3.14 |
| MAPbI3/carbon      | 12.76   | 12.07 ± 0.41 | 0.86 | 0.86 ± 0.02 | 23.25 | 22.86 ± 0.24 | 63.8 | 61.33 ± 2.13 |
| MAPbI3/P3HT/carbon | 15.74   | 14.81 ± 0.51 | 0.94 | 0.91 ± 0.02 | 23.22 | 23.05 ± 0.17 | 72.12 | 70.28 ± 1.13 |
showing a narrower distribution in all solar cell parameters, while PCE, FF, and $V_{OC}$ are dramatically increased in comparison with the other devices, with an average PCE of 14.8 ± 0.5%.

The poor performance of MAPbI$_3$/P3HT/Au devices is due to low $V_{OC}$ and FF, which can have several possible origins: there could be pinholes in the thin P3HT layer that cause additional recombination in case of gold electrodes but not for the CEs that consist of large particles (graphite). Alternatively, the undoped P3HT layer could be too resistive, leading to increased series resistance in the solar cell and low FF. In the case of CEs, the carbon particles could penetrate into the P3HT layer (as the solvents of the carbon paste might partially dissolve the P3HT layer) and can make an intimate contact with the polymer. Evidence for this comes from the strong adherence of the carbon film on P3HT, while the Au film is easily peeled off in an adhesive tape test (see Figure S3, Supporting Information).

We also prepared standard PSC devices with the configuration MAPbI$_3$/doped spiro-OMeTAD/Au. These devices gave a decent PCE (17.0%), $V_{OC}$ (0.97 V), FF (81.9%), and $J_{SC}$ (21.74 mA cm$^{-2}$). This demonstrates the reasonably good quality of the MAPbI$_3$ films and our device preparation. In contrast, devices where doped spiro-OMeTAD were coated with carbon films gave PCE of only 9.1% at best, with a lower $V_{OC}$ (0.87 V) and FF (49.7%) and similar $J_{SC}$ (20.85 mA cm$^{-2}$). see Figure S4 and Table S1, Supporting Information. The carbon paste used in this study contains several solvents, namely 2-(2-ethoxyethoxy)ethyl acetate, 2-methylnaphthalene, and pentylenzene, which may be incompatible with spiro-OMeTAD films or its dopants.

All investigated devices displayed significant hysteresis effects in $J$–$V$ curve characterization, as shown Figure 1b or Figure S5 and Table S2–S5, Supporting Information. To qualify the hysteresis effects in $J$–$V$ curves, hysteresis indices (HI) of perovskite devices with carbon, P3HT/carbon, and P3HT/Au contacts were calculated from the forward and reverse scans for a fixed scan rate of 50 mV s$^{-1}$, using the following formula: [52]

$$HI = \frac{PCE^- - PCE^+}{PCE^- + PCE^+}$$

where + and – represent the forward and reverse $J$–$V$ scans from which PCEs are determined. The highest hysteresis was found for MAPbI$_3$/P3HT/Au devices (HI: 36%), followed by MAPbI$_3$/spiro-OMeTAD/carbon (HI: 28%), MAPbI$_3$/carbon, MAPbI$_3$/P3HT/carbon (HI both 23%), and finally MAPbI$_3$/spiro-OMeTAD/Au (HI: 19%).

**Figure 2.** Statistics of the photovoltaic parameters for MAPbI$_3$/P3HT/Au, MAPbI$_3$/carbon, and MAPbI$_3$/P3HT carbon devices, 16 cells each, measured under 100 mW cm$^{-2}$ (AM1.5G) light intensity.
In devices that display much hysteresis in $J-V$ characterization, it is important to check the steady-state power output, by, for example, maximum power point tracking. A steady-state efficiency and current density of the HTM-free device decreased to 10.56% and 21.36 mA cm$^{-2}$ after 500 s at an applied potential (close to the maximum power point potential) of 0.64 V, see Figure 3. MAPbI$_3$/P3HT/carbon device shows a stable PCE of 15.07% and a current density of 23.0 mA cm$^{-2}$ is obtained for 500 s under 1 sun illumination at a $V_{\text{max}}$ of 0.72 V, see Figure 3. This steady-state PCE was close to that obtained from the reverse $J-V$ scan, 15.3%.

To elucidate the dominating recombination mechanism in the perovskite devices, $J_{\text{SC}}$ and $V_{\text{OC}}$ at difference light intensities from 10 to 100 mW cm$^{-2}$ were measured, see Figure 4a,b. $J_{\text{SC}}$ scales approximately linearly with light intensity, as it may be expected for good solar cells. The slope of the doubly logarithmic plot is 0.975, 0.976, and 0.977 for MAPbI$_3$/P3HT/Au, MAPbI$_3$/carbon, and MAPbI$_3$/P3HT/carbon devices. From the light intensity dependence of $V_{\text{OC}}$, the ideality factor ($n$) of the devices is derived using $V_{\text{OC}} \propto n k_B T/q \ln(I)$, where $T$ is the temperature, $k_B$ is the Boltzmann’s constant, $q$ is elementary charge, and $I$ the light intensity. In a classical approach considering only bulk recombination, radiative recombination (bimolecular recombination) should lead to an ideality factor of 1, while trap-assisted charge recombination (monomolecular recombination) gives a value of 2.$^{[53]}$ For PSCs, the interpretation is more complex: interfacial recombination and ionic charge accumulation must be considered and can lead to variation in $n$.$^{[54]}$ For the MAPbI$_3$/P3HT/Au device, an ideality factor of 2.22 is found, which is larger than that of MAPbI$_3$/P3HT/carbon (1.92) and MAPbI$_3$/carbon devices (1.55). As the bulk MAPbI$_3$ is identical in all

**Figure 3.** Maximum power point tracking under 1 sun illumination-measured MAPbI$_3$/carbon at $V_{\text{max}} = 0.64$ V and MAPbI$_3$/P3HT/carbon at $V_{\text{max}} = 0.72$ V in ambient air.

**Figure 4.** a) Current density ($J_{\text{SC}}$) and b) open-circuit voltage ($V_{\text{OC}}$) dependent as a function of light intensity ($I$) with and without P3HT/carbon and Au devices on logarithmic scale. c) Nyquist’s plots with comparison devices from EIS at an applied bias of 0.8 V in the dark. d) $V_{\text{OC}}$ decay of different structures after switching off simulated AM 1.5G (100 mW cm$^{-2}$) illumination.
devices, any changes in ideality factors must be attributed to the hole-collecting contact. For carbon-only devices, carrier selectivity will not be perfect and more recombination will take place at the perovskite/carbon interface, leading to lower $V_{OC}$. To further investigate the charge transport and recombination mechanisms, electrochemical impedance spectroscopy (EIS) was performed for MAPbI$_3$/P3HT/Au, MAPbI$_3$/carbon, and MAPbI$_3$/P3HT/carbon devices, see Figure 4c. The equivalent circuit used to fit the EIS data is shown in Figure S6, Supporting Information, and the fit parameters are shown in Table S6, Supporting Information. The fitting parameters are the series resistance $R_s$, which is the intercept at high frequencies, the recombination resistance $R_{rec}$, and the geometric capacitance $C_{geom}$. The parallel RC circuit of the latter two describes the semicircle in Figure 4c. The carbon-based devices show a larger semicircle radius than the MAPbI$_3$/P3HT/Au device. This is ascribed to a larger recombination resistance ($R_{rec}$), corresponding to a lower recombination rate and thus improved $V_{OC}$, FF, and PCE [55, 56]. The carrier lifetime ($\tau$) is calculated from the EIS data using the following equation: $	au = R_{rec} \times C_{geom}$. The higher values of $\tau$ for MAPbI$_3$/P3HT/carbon (74 $\mu$s) and MAPbI$_3$/carbon (60 $\mu$s) compared with the much lower value found for P3HT/Au (7.9 $\mu$s) show that recombination is severe in the latter types of devices, leading to low $V_{OC}$. The most likely origin is pinholes in the P3HT layer, which are detrimental in the case of evaporated gold contacts.

Open-circuit voltage decay transients of the devices display significant differences between C-PSC and the PSC with gold contact (Figure 4d). After a fast initial decay, similar for all devices, a long tail is found for devices with carbon contacts. This tail is related to ionic motion in the perovskite material. As the devices differ in the hole-selective contacts, differences must be caused by ions or ion vacancies near the positive contact. Most likely, the slow part of the $V_{OC}$ decay reflects the return of negatively charged ions or ion vacancies accumulated at carbon contacts under illumination back to the bulk of the material. The difference between C-PSC devices with and without P3HT layer may be attributed to the additional capability of P3HT to store ionic charge.

Long-term stability is one of the most critical factors for the eventual success of PSCs. Figure 5a shows the storage stability of unsealed devices under in the dark (relative humidity [RH]: 20 $\pm$ 5%; room temperature 20 $\pm$ 5 °C). All devices showed good stability under these conditions. The MAPbI$_3$/P3HT/carbon device retained 99% of its original PCE over 31 days of testing (PCE: from 14.23% to 14.05%). Similarly, results in PCE of MAPbI$_3$/P3HT/Au and hole conductor-free carbon devices were equivalent of their initial efficiency of 10.28% and 11.89%.

A thermal stress test was performed by exposing nonencapsulated devices to 82 °C in ambient air in the dark, see Figure 5b. The RH not controlled in this test of surrounding air was 50 $\pm$ 10%. The thermal stability of PSCs with gold contacts was poor compared with carbon-based PSCs. A clear improvement was found when the doped spiro-OMeTAD was replaced by doping-free P3HT. These devices remained stable for 10 days, significantly better than previously reported ITO/TiO$_2$/MAPbI$_3$/P3HT/Au devices by Conings et al., which degraded to 30% of their initial performance after 24 h at 85 °C. [57] The carbon-only device remained stable until about 200 h aging. After that, PCE dropped to 62% of its original output at 500 h, due to decrease in current and FF (see Figure S7, Supporting Information). The P3HT/carbon device exhibited a superior thermal stability, keeping 70% of its initial PCE after 900 h storage in the oven. P3HT not only resisted thermal exposure, but it also seems to provide a barrier against moisture due to its hydrophobic properties (see Figure S8, Supporting Information). It should also be noted that bare MAPbI$_3$ perovskite films are not very stable under these conditions, due to loss of MAI and formation of PbI$_2$. [57]

The observed hysteresis in $J$–$V$ curves in this study is an unwanted and problematic effect in PSCs. Several factors that possibly could affect hysteresis were therefore investigated. First, we checked the effect of the conducting glass substrates.

Figure 5. a) Storage stability of unsealed PSCs. b) Solar cell efficiency (at 1 sun condition) of carbon-based MAPbI$_3$ perovskite devices with and without P3HT and of MAPbI$_3$/P3HT/Au upon storage in the dark in a dry box (RH of 20 $\pm$ 5%) at room temperature. Thermal stability test of nonencapsulated devices in the dark at 82 °C in ambient air.
Devices prepared on fluorine-doped tin oxide (FTO, TEC15, Pilkington)-coated glass were found to give slightly lower performance compared to ITO-based devices and had similar reproducibility and hysteresis index, see solar cell statistics in Figure S9, Supporting Information. Due to its lower roughness, ITO films are probably more conformally coated with the very thin electron-selective SnO2 layer than the rougher FTO substrates. The average PCE was 13.25% for FTO/SnO2/MAPbI3/ P3HT/carbon devices and 14.84% for ITO/SnO2/MAPbI3/ P3HT/carbon devices.

Second, we studied addition of potassium chloride (KCl) to the SnO2 layer, which has been reported to reduce the defect density of perovskite layer due to the passivation effect of K+ ions.[58] Indeed, hysteresis was reduced upon KCl addition: HI was reduced from 16.7% to 7.4% (FTO device) and from 19.8% to 9.7% (ITO device), as shown in Figure S10 and S11, Supporting Information.

Third, we investigated the effect of interfacial modifiers such as polyvinylpyrrolidone (PVP)[59] and phenylethyl ammonium iodide (PEAI)[60] on the surface of MAPbI3 films (see Figure S12a,b, Supporting Information), but no significant effects were found. By doping the P3HT layer with Li-FTSI salt, 4-tet-butylpyridine (TBP),[45] and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), the hysteresis and performance of C-PSCs were not significantly improved either (see Figure S12b–d, Supporting Information).

The choice of conductive substrate is crucial for PSC device performance and reproducibility. In our study, devices prepared on ITO glass substrates yielded better results than those on FTO, giving about 2% (absolute) higher efficiencies. We attribute this to the higher quality of the SnO2 layers formed on the flatter surface of the ITO.

The fact that KCl addition to the SnO2 led to positive effects in the devices investigated here could be both due to the effect on the SnO2 electron-selective layer but possibly also due to effects that K+ ions can have on the MAPbI3 grain formation. In a subsequent study, to be published elsewhere, the MAPbI3 film was replaced by a mixed-ion perovskite using a two-step method. As a result, the hysteresis in the J–V curves was greatly reduced. Hence, we can draw the conclusion that the SnO2 electron-selective layer, the P3HT hole-selective layer, and the CE are not main causes of the observed hysteresis in the current study, which must therefore be attributed to the properties of the MAPbI3 film.

3. Conclusion

Low-temperature-processed C-PSCs were fabricated with the n–i–p configuration ITO/SnO2/MAPbI3/carbon and, with inclusion of a hole-selective layer, ITO/SnO2/MAPbI3/P3HT/ carbon. Insertion of an undoped P3HT layer improved Voc, FF, and PCE and a top efficiency of 15.7% was obtained. Without P3HT, an efficiency up to 12.8% was obtained, comparable with that of MAPbI3/P3HT/Au device (11.7%). Without further encapsulation, devices did not show any degradation upon dry storage for 1 month in the dark and C-PSCs with intermediate P3HT layer maintained 70% of their initial efficiency after 900 h at 82 °C in air.

C-PSCs with P3HT as hole conductor and SnO2 as electron-selective layer provide stable solar cells without the need for vacuum deposition equipment or a high-temperature process. Even with MAPbI3 perovskite as the absorber, which is known to be relatively unstable, good results were obtained, suggesting that this further improvement can be obtained using more stable and advanced perovskite compositions.

4. Experimental Section

Materials and Solar Cell Preparation: Indium tin oxide (ITO)-coated glass (12–15 Ω sq–1) was purchased from Optical Filters, England. Lead iodide (PbI2, 99.99%) was purchased from TCI (Japan). Methylammonium iodide (MAI, 99.99%) was purchased from Greatcell Solar (Australia). Tin(IV) oxide (SnO2, 15% in H2O colloidal dispersion) was obtained from Alfa Aesar. N,N-dimethylformamide (DMF, anhydrous, 99.8%), DMSO (dimethylsulfoxide, 99.8%), chlorobenzene (anhydrous, 99.8%), and poly(3-hexylthiophene-2,5-diyl) (P3HT, RR, average Mw: 50 000–100 000, prod. no. 445703) were provided by Sigma-Aldrich. Carbon paste (DN-CP01) was purchased from Dynelamo. All the materials and reagents were used as received without any further purification.

The ITO–glass substrates were etched by Zn powder with diluted hydrochloric acid (2 mol L–1) solution. After that, they were sequentially washed with detergent (2% Hellmanex water solution), deionized (DI) water, acetone, and ethanol by sonication for 30 min in each step. Afterward, air stream was treated to dry the films. Finally, all substrates were cleaned by UV–ozone treatment for 30 min before use.

SnO2 colloidal dispersion was diluted by DI water (1:4 v/v) and sonication for 15 min. After that, an electron transport layer was deposited on the ITO (24 mm × 28 mm) glass substrates at 3000 rpm for 30 s followed by annealing at 120 °C for 10 min and 150 °C for 20 min on a hotplate in ambient atmosphere.

The MAPbI3 photoactive layer was deposited in a one-step method with antisolvent dripping in N2-filled glovebox. The perovskite precursor solution was prepared by dissolving 692 mg PbI2 and 239 mg MAI in a mixed solvent of 0.107 mL dimethylsulfoxide (DMSO) and 0.953 mL dimethylformamide (DMF).[45] The resulting mixture was stirred overnight at 60 °C in the dark. The transparent yellowish solution was filtered through a 0.45 μm PTFE filter syringe. Before depositing the perovskite films, the SnO2 substrates were treated by UV–ozone for 20 min to increase the wettability of perovskite solution on the films. Then, obtained films were quickly transferred into the glovebox. One-step spin coating was performed with a rotation speed of 4000 rpm for 20 s. While the spinning rotation was between 7 and 10 s, 0.15 mL of chlorobenzene antisolvent was continuously poured to remove the cosolvents and induced rapid perovskite crystalization. The resultant transparent film was then heated at 100 °C for 30 min on a hotplate to obtain a brilliant specular film.

P3HT (10 mg mL–1 in chlorobenzene) solution was shaken for 30 min at room temperature. It was spin coated onto the perovskite layer with a speed of 3000 rpm for 30 s. To improve the hole conductivity, the deposited P3HT layer was annealed at 100 °C for 10 min.[44,46] Carbon paste was coated on the perovskite or P3HT layer by manual doctor blading in ambient air (RH ≈50 ± 10%, temperature ≈20 ± 0.5 °C), followed by heating on a hotplate in air at 100 °C for 20 min.

For devices with gold contacts, 80 nm Au were thermally evaporated on the P3HT layer under high vacuum ≈3.8 × 10–9 Pa through a shadow mask (5 mm × 5 mm). Thickness and evaporation speed were adjusted using a quartz crystal by tuning 0.1 Å s–1 until 10 nm first and 0.8 Å s–1 to reach 80 nm for the final procedure.

Characterization Methods: J–V characteristics were recorded of PSCs in ambient air under 1.5 G illumination with a self-calibrating solar simulator (Wavelabs Sirius-70, class AAA, Germany). The voltage scan rate was fixed at 50 mV s–1 with 20 mV steps using a source meter (Ossila X200, UK). Reverse and forward scans were performed from +1.2 to −0.1 V and from −0.1 to +1.2 V, respectively. Solar cells were illuminated through a black metal mask with a circular aperture of 0.125 cm2 placed on the solar cell.
under ambient air, at room temperature, and without encapsulation. IPCE measurements were conducted in a system consisting of a xenon lamp and monochromator (Spectral products ASB-IE-175 and CM110) and a Labjack U6 digital acquisition device. The light intensity at each wavelength was calibrated with a certified silicon photodiode (Fraunhofer ISE) prior to characterization. EIS was performed using a potentiostat with a frequency analyzer (Autolab PGSTAT100). Measurements were carried out in the dark at an applied potential of 0.80 V. Data in the frequency range from 500 kHz and 1 Hz were fitted using FRA 4.3 software. Voc decay was recorded using a homebuilt system consisting of a white LED (Luxeon Star 1 W) and a digital acquisition board (National Instruments).

UV–vis absorption spectra were recorded on a Varian Cary 5000 spectrophotometer. Photoluminescence emission measurements were performed using a Horiba Jobin Yvon Fluorolog instrument (Model FL3-222). The measurements were performed in backscattering geometry using 30° angle of incidence from the excitation beam with respect to the surface normal. The excitation wavelength was 460 nm and the spectral resolution 4 nm. Cross-sectional scanning electron microscopy (SEM) images were taken using SEM, using a Zeiss LEO 1550 FEG instrument with in-lens and secondary electron detector operating at 3 kV. X-ray diffraction (XRD) patterns of perovskite film (≈350 nm) were measured using a Siemens D5000 θ–2θ goniometer with Cu Kα radiation (λ = 1.54051 Å) under ambient air. 0.4° Soller-slit collimator was set up with a step size of 0.1° s-1 at a scanning range of 10–60° (Bruker AXS, Karlsruhe, Germany). Water contact angle measurement was performed using an Ossila contact angle Goniometer (L2004A1).

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.

Data Availability Statement
Research data are not shared.

Keywords
hole-selective contacts, MAPbI₃, P3HT, SnO₂

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