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Impact of Halide Additives on Green Antisolvent and High-Humidity Processed Perovskite Solar Cells

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Abstract: Organometal halide perovskites have recently gained remarkable interest as a light absorber for photovoltaic technology. However, the majority of efficient perovskite solar cells (PSCs) are fabricated in the glovebox. From the mass production perspective, it is vital to improve the quality of ambient-processed perovskite, as well as to reduce health risks, costs, and complexity of fabrication. This study investigates the effect of using green antisolvent ethyl acetate with various halide additives on the performance of ambient-processed planar PSCs by a one-step deposition method, under a high relative humidity (RH) of 50-60%. Differences in microstructures, crystallinity, surface chemistry and optoelectronic properties for the green antisolvent and ambient-processed perovskite films with the addition of PbCl₂, PbBr₂, and MAI are observed, compared to the pristine film. Ambient-processed perovskite films with PbCl₂ addition remarkably improves the PCE of the pristine device by 17.3% and achieves a fill factor up to 76.3%. Addition of PbCl₂ also enhances the stability of the devices and retains 81% of their initial PCEs after storage in ambient air for 28 days. These findings provide a strategy of using halide additives and green antisolvent for the fabrication of high-quality perovskite films under high relative humidity without the need of glovebox.

Keywords: green antisolvent; ambient-processed; planar perovskite solar cells; halide additives; long-term stability

1. Introduction

Organometal halide perovskites with an ABX_3 crystal structure have attracted great attention in the photovoltaic (PV) field, ascribed to their superb optoelectronic properties such as high absorption coefficients, long carrier diffusion length, high carrier mobilities, and low exciton binding energy [1–5]. Within only a decade of research, the power conversion efficiencies (PCE) of perovskite solar cells (PSCs) have rapidly increased from 3.8% to 25.2% [6]. Despite the rapid development of this emerging PV technology, PSCs are known to be sensitive to moisture and oxygen in both fabrication and operation processes [1,7]. Therefore, in most cases, highly efficient laboratory-scale PSCs are mainly fabricated in a nitrogen-filled glovebox or controlled atmosphere [8]. In order to reduce the costs and complexity of fabrication for the industrialization of PSCs, there is a need to develop facile methods for the fabrication of high-quality perovskite films in ambient air [1,9].

The influence of the environmental humidity during the formation of the perovskite film is still under debate [1,10,11]. At the early stage of the PSCs research, it was believed that N_2 -filled glovebox with a low level of moisture and oxygen has to be used in order to fabricate efficient PSCs due to the loss of the organic cation in the perovskite under the ambient condition [1,7]. Later on, some studies suggested that a controlled relative humidity (RH) of around 20-35% can improve the crystallinity of the perovskite films, resulting in an increase of the device PCE [11–13]. However, several studies suggested that the moisture in ambient air can be detrimental to the device PCE when the $RH > 40\%$ [14]. For instance, Yang *et al.* fabricated $CH_3NH_3PbI_xCl_{3-x}$ based PSCs in a glove box or with a controlled RH of 15-20% achieved the device PCE of 11.32% or 10.71%, respectively [15]. However, the device PCE dropped to only 4.07% or 0.53% when the perovskite films were fabricated under a RH of 40-50% or 60-70%, due to poor coverage of the perovskite films on the substrate. Li *et al.* obtained similar results, and they found that the device PCE was significantly reduced when the $RH > 40\%$ for both one-step and two-step deposition processes [16].

To date, several strategies have been established to fabricate the highly efficient PSCs in ambient air under different RH. Su *et al.* employed hot air blowing to spray-coating the $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ for ambient-processed PSCs at RH <30% and achieved a PCE of 13.5% [17]. Liu *et al.* used 4-*tert*-butylpyridine (tBP) as the additive to form a hydrophobic layer on the surface of perovskite film to improve the PCE of ambient-processed PSCs by a two-step process and achieved the PCE of 12.62% and 10.88% at RH of 40-50% and 50-60% [18]. Tai *et al.* used $\text{Pb}(\text{SCN})_2$ as the lead precursor to fabricate $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ film by a two-step process and achieved a device PCE of 15.12% for the mesoscopic PSCs fabricated at RH>70% [19]. Guo *et al.* also used a two-step process to deposit $\text{CH}_3\text{NH}_3\text{PbI}_3$ with ZnO as the electron transport layer and archives a PCE of 14.25% at 50% RH [20]. Cheng *et al.* demonstrated a preheating technique of the substrate and PbI_2 solution with a two-step process and achieved a device PCE up to 18.11% [10]. However, they found that it was challenging to prepare the high-quality perovskite film by a one-step process due to the uncontrollable and rapid crystallization process of the film in ambient air [10].

One-step deposition of the perovskite film, as a simple and straightforward method, has the potential to be developed for future roll-to-roll and cost-effective fabrication of PSCs, in conjunction with the use of antisolvent bath [14,21,22]. The use of appropriate antisolvent plays a vital role in controlling the morphology during the crystallization of the perovskite films in ambient air [9,22]. Several studies have utilized different types of antisolvents with the one-step deposition process to fabricate efficient PSCs in ambient air. Gedamu *et al.* used a mixed solvent-antisolvent with 75% chlorobenzene (CL) and 25% ethanol to fabricate $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ based PSCs and achieved a PCE of 14.0% at 40% RH [23]. Yang *et al.* added methanol into diethyl ether (DE) as the antisolvent to treat perovskite film and achieves a PCE of 16.4% at 50% RH [24]. Sveinbjörnsson *et al.* used CL as the antisolvent to fabricate $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ for mesoscopic PSCs and achieved a PCE up to 18.8% at 50% RH [25]. Recently, Troughton *et al.* used ethyl acetate (EA) as antisolvent to treat the $\text{CH}_3\text{NH}_3\text{PbI}_3$

film and achieved an optimized PCE of 14.5% and 15.0% for inverted and mesoscopic PSCs at 75% RH [9]. They found that EA is able to absorb a significant volume of moisture in comparison to antisolvents such as toluene, thus may protect the perovskite intermediate phase MAI-PbI₂-DMSO during the spin-coating process from airborne moisture [9].

A critical issue that needs to be addressed is the potential risk of using these antisolvents on humans and environment since they are volatile during the deposition process, especially for the ambient or scalable fabrication process [26]. CL or toluene (TL) are antisolvents with a low threshold limit value (TLV), which are potentially harmful to humans and environment for ambient and mass production [27]. Compared to CL and TL, DE is considered to be safer to use due to its much higher TLV [27]. However, there is still potential health risks to human for heavy and long-term exposure to DE [27]. EA is recognized as a green antisolvent with a high TLV, which is less hazardous and less flammable than DE [28]. Therefore, EA can be a promising green antisolvent for future ambient and scalable production of PSCs.

To date, several studies have used the chloride or bromide salts as the halide additives or lead precursors to improve the PCE and stability of the PSCs, with the majority of the studies carried out in the inert environment [4,29–31]. However, the impact of these halide additives on the nucleation of the perovskite films with the use of EA as the antisolvent in ambient conditions is not well understood. Herein, we systematically investigate the impact of PbCl₂, PbBr₂, and MAI as additives on the one-step deposited perovskite films with EA as antisolvent, under a high RH of 50-60%. We carry out a series of characterizations to understand the effect of these halide additives on the microstructure, crystallinity, surface chemistry, optoelectronic properties, PV performance, and long-term stability of the ambient-processed perovskite films and devices. We observe that the addition of PbCl₂ enlarges the grain size, enhances the crystallinity and passivate the grain boundaries by the formation of PbI₂. In complete planar PSCs, devices with PbCl₂ addition achieve a champion PCE of 16.20%, in comparison to the standard CH₃NH₃PbI₃ with a champion PCE of 13.81%. In addition, devices with PbCl₂ retain

81% of their initial PCEs after storage in air for 28 days. The addition of PbBr_2 also enlarges the grain size of perovskite crystals and gives the least hysteresis behavior of the PSCs. The addition of excess MAI in this study shows a negative impact on the PV performance of the ambient-processed PSCs.

2. Result and discussion

Fig. 1 Schematic representation of the one-step spin-coating process of perovskite film with ethyl acetate as the antisolvent in ambient air with a humidity meter showing a relative humidity of 55.6%.

Apart from the thermal evaporation of gold electrodes, all fabrication processes are carried out in ambient conditions under RH of 50-60%. The deposition of the perovskite films is presented in **Fig. 1**. We prepare a compact TiO_2 layer on top of an indium tin oxide (ITO) coated glass and then preheat the substrates to 70 °C before deposition of the perovskite film. A standard stoichiometric precursor with the molar ratio of PbI_2 : MAI=1: 1 is used to form the pristine perovskite film. We then add ethyl acetate dropwise during the spin-coating process of the perovskite precursor and eventually anneal the substrate at 120 °C to evaporate the residual solvent and form a crystalline perovskite film. The detailed fabrication process is explained in the **Experimental Section**. To introduce the additives, we add PbCl_2 , PbBr_2 or MAI to the perovskite precursor to investigate their impact through a series of characterizations.

We first perform scanning electron microscopy (SEM) with in-lens detector to understand the impact of adding PbCl_2 , PbBr_2 or MAI upon the microstructures of the perovskite films. In **Fig.**

2 and S1, the images show the surface microstructure of pristine perovskite film in comparison to the films with different additives. The pristine film shows an average grain size of $0.10 \mu\text{m}^2$ with the largest grain size up to $0.42 \mu\text{m}^2$, calculated based on **Fig. S1a** with the average size of 80 grains, as shown in **Fig. S2a**. The addition of excess MAI shows no significant change to the film morphology and gives an average grain size of $0.11 \mu\text{m}^2$ (**Fig S1b and S2b**). The addition of both PbCl_2 and PbBr_2 significantly increases the average grain size to 0.26 (**Fig S1c and S2c**) and $0.17 \mu\text{m}^2$ (**Fig S1d and S2d**), with the largest grain size up to 1.06 and $0.50 \mu\text{m}^2$.

Fig. 2. SEM (50 KX magnification) images of the perovskite films (a) pristine, (b) excess MAI, (c) with PbCl_2 and (d) with PbBr_2 . (scale bar = 400 nm)

All ambient-processed films at RH of 50-60% appear to be dense and uniform without obvious pinholes. These film morphologies are quite different compared to some previous studies on processing the $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ or $\text{CH}_3\text{NH}_3\text{PbI}_3$ in ambient air at high RH [32,33]. Gao *et al.* observed the morphologies of $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films changed from dense to the island- or rod-shaped when they were deposited in ambient air at RH of 70% by a one-step process. The low coverage of the perovskite films brought a detrimental impact on the

device's performance [32]. Wang *et al.* found that annealing $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ in ambient air at RH >50% induced large gaps between the perovskite grains and gave a PCE of 9.2% compared to the dense perovskite film annealed in a vacuum with a PCE of 12.98% [33]. Therefore, perovskite film with a denser and more uniform morphology may contribute to better photovoltaic performance according to the previous studies [32,33].

We note that the large perovskite grains are surrounded by some smaller and brighter grains for the film with PbCl_2 . These smaller grains may be ascribed to PbI_2 or PbI_2 -rich grains due to their larger bandgap and reduced conductivity, resulting in more charging of the electrons and brightness in the image [34]. However, this is not found in the film with PbBr_2 . The increase of the grain size by adding PbCl_2 may be attributed to two reasons: (1) the accumulation of negatively charged Cl^- at the grain boundaries and surface reduces the surface tension of the grain, thereby promoting the coalescence of the small grains [31]. (2) the formation of the MAPbCl_3 intermediate phase acts as a template to improve the growth orientation and grain structure of the perovskite crystals [35].

We carry out X-ray diffraction (XRD) measurement to investigate the effect of different additives on the chemical composition and crystallinity of the ambient-processed perovskite, as presented in **Fig. 3 and S3**. The film with PbCl_2 additive shows the PbI_2 diffraction peak at 12.7° , which may indicate that the brighter grains observed in **Fig. 2c** are PbI_2 or PbI_2 -rich grains [34]. It has been pointed out that the existence of the PbI_2 phase at the grain boundaries and interfaces could passivate the perovskite film, resulting in the reduction of the carrier recombination [31,34]. We also observe the PbI_2 peak in the pristine film. Both films with the addition of PbBr_2 and excess MAI, however, only show the pure perovskite crystals oriented at (110), (220) and (310) planes. The addition of PbCl_2 or PbBr_2 causes a shift of (110) planes towards higher 2θ (**Fig. 3a**), indicating the incorporation of the Cl^- and Br^- into the perovskite lattice, causing the shrinkage of the lattice due to the smaller ionic radii of the Cl^- and Br^- than I^- [31,36]. It is noted that the peak intensity of (110) planes for the perovskite film with PbCl_2

is three times higher than other films. We then calculate the crystal sizes of the pristine perovskite film and the films with the addition of PbCl_2 , PbBr_2 , and MAI by Scherrer equation, as shown in **Table S1**. Perovskite films with the addition of PbCl_2 and PbBr_2 exhibit the increase of the crystal size compared to that of the pristine film. This is in agreement with the SEM (**Fig. 2**) observation that the films with the addition of PbCl_2 and PbBr_2 show the larger grain size than the pristine film. These results indicate that the addition of PbCl_2 effectively improves the crystallinity, enlarges the grain size and promotes a preferred growth orientation at the (110) planes.

Fig. 3. XRD pattern of a pristine perovskite film and the perovskite films with the addition of PbCl_2 , PbBr_2 , and excess MAI in the 2θ range of (a) $13.4\text{--}14.6^\circ$, (b) $10\text{--}50^\circ$ and (c) $27.8\text{--}29.0^\circ$.

To investigate the surface chemistry of the perovskite with different additives, we performed X-ray photoelectron spectroscopy (XPS), as presented in **Fig. 4 and Table S2**. We observe that all the major Pb $4f_{7/2}$ peaks (denoted as Pb–I) are located at binding energies (BEs) of 138.6 ± 0.1 eV, in agreement with the values for $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite in the literature [7,37]. Additional minor Pb $4f_{7/2}$ peaks (denoted as Pb–Pb) can be seen at 136.8 ± 0.1 eV, indicating the presence of metallic lead (Pb^0) at the surface [7,38]. The I/Pb value reveals the synchronous reduction of iodine and nitrogen relative to lead according to the standard stoichiometric values

(3.0, respectively). Both the pristine (2.6 ± 0.1) and with the PbCl_2 (2.7 ± 0.1) films show lower I/Pb values than the film with PbBr_2 (2.8 ± 0.1) and excess MAI (2.9 ± 0.1), suggesting that more PbI_2 may exist on the surface of the film with PbCl_2 and the pristine film. This finding further confirms the existence of PbI_2 at the surface of the film with added PbCl_2 and the pristine film, which is in good agreement with the results from the SEM and XRD characterizations.

Fig. 4. (a) XPS spectra of a pristine perovskite film and the film with the addition of PbCl_2 , PbBr_2 and excess MAI. Ratios of (b) $\text{Pb}^0/\text{Pb}^{2+}$, (c) I/Pb, and (d) N/Pb for various films

determined by XPS. Note only Pb^{2+} is considered for the Pb in (c) and (d). To investigate the impact of different additives on the photovoltaic performance of the perovskite, we assembled planar perovskite solar cells with an architecture of ITO-glass/ TiO_2 /perovskite/spiro-OMeTAD/Au. Previous studies have recognized that planar PSCs are more vulnerable to moisture during the perovskite deposition process than the mesoscopic PSCs [12,14]. This is because the use of mesoporous TiO_2 helps to hold the perovskite in place

during the spin-coating process and with thicker perovskite film to reduce the chance of short circuit [12,14]. Therefore, it is more challenging to fabricate efficient planar PSCs in ambient air under high RH. **Fig. S4** shows an image of the actual devices after assembly. In **Fig. 5** and **S5**, we present the typical current density voltage (J - V) curves for the ambient-processed devices. The addition of PbCl_2 achieves an average PCE of the PSCs to 15.21% and a champion device PCE of 16.20%. The measured device PCE is relatively steady under the different scanning rates, as shown in **Fig. S6**. On the other hand, the pristine PSCs show an average short-circuit current (J_{sc}) of 18.53 mA cm^{-2} , an average open-circuit voltage (V_{oc}) of 1019.5 mV, an average fill factor (FF) of 71.7%, yielding an average PCE of 13.53% with a champion device PCE of 13.81%. We notice that the improvement of the PCEs by PbCl_2 additive is contributed from enhanced J_{sc} and FF.

Fig. 5. Current density–voltage (J - V) curves for the devices based on the pristine film and the films with the addition of PbCl_2 , PbBr_2 , and excess MAI measured from reverse scan (RS) under simulated AM1.5 sunlight measured at ambient air under RH of 50-60%.

Fig. 6. Photovoltaic parameters distribution of (a) PCE, (b) FF, (c) J_{sc} and (d) V_{oc} for the ambient-processed devices with the pristine film and the films with excess MAI, PbCl₂ and PbBr₂.

The distribution and a summary of the photovoltaic parameters based on the films with different additives are shown in **Fig. 6** and **Table S3**. The enhanced device performance with PbCl₂ additive can be mainly attributed to two reasons: (1) the improved crystallinity of the perovskite with the enlarged grain size; (2) the passivation of the grain boundaries and surfaces by the existence of PbI₂ [39]. On the other hand, addition of PbBr₂ to the films slightly reduces the photovoltaic performance, mainly due to the lower average J_{sc} of 17.94 mA cm⁻². Although addition of PbBr₂ also enlarges the grain size of the perovskite film, it seems that the formation of PbI₂ to passivate the film plays an important role in improving the device PCEs. Nonetheless, the device with PbBr₂ additive does exhibit the lowest hysteresis index (HI) of 33.83% based on the equation (1) [40]:

$$HI = \frac{PCE_{RS} - PCE_{FS}}{PCE_{RS}} \times 100\% \quad (1)$$

Where PCE_{RS} is the PCE measured in the reverse direction, and PCE_{FS} is the PCE measured in the forward direction. It has been pointed out that partial replacement of Γ^- by Br^- could increase the Γ^- migration activation energy due to the local structural distortion induced by the Br^- substitution, resulting in a decreased hysteresis behavior [5]. Excess MAI in the current study leads to the reduction of the photovoltaic performance mainly due to the lower average FF of 67.8% and average V_{oc} of 992.4 mV. Nevertheless, according to other studies, it is found that the addition of a different amount of $PbBr_2$ [41] and MAI [42,43] can enhance the device PCE. A summary of the photovoltaic performance of several recent ambient-processed PSCs compared that in the current work is given in **Table S4**.

To further understand why adding $PbCl_2$, $PbBr_2$ or excess MAI leads to differences in the photovoltaic performance of the devices; we perform ultraviolet-visible (UV-Vis) absorption spectroscopy and photoluminescence (PL) spectroscopy as shown in **Fig. 7a and b**. The addition of $PbCl_2$ leads to an increase in the absorption over the wavelength range from 400-500 nm, possibly due to the enhanced crystallinity and enlarged grain size, in good agreement with the higher J_{sc} of the PSCs. A stronger PL intensity in the film with the $PbCl_2$ additive further confirms the passivation of the grain boundaries and surfaces by PbI_2 , which effectively reduces the nonradiative recombination in the film, resulting in improved photovoltaic performance [31]. The film with $PbBr_2$ additive and excess MAI exhibits reduced light absorption and PL intensity, inconsistent with the decreased photovoltaic performance of the PCE measurement.

Fig. 7. Characterization of the pristine film and the films with excess MAI, PbCl_2 and PbBr_2 . (a) absorbance measured by UV-Vis spectroscopy, (b) steady-state PL spectra. (C) transmission measured by UV-Vis spectroscopy. (d) an image of actual ambient-processed perovskite film with PbCl_2 .

The optical bandgaps of the different films are presented in **Fig. S7**, Both the pristine film and the film with PbCl_2 additive have a bandgap of 1.58 eV. The film with excess MAI has a bandgap of 1.57 eV. The film with PbBr_2 exhibits a slightly larger bandgap of 1.60 eV, in agreement with the observation of a lower J_{sc} relative to the other PSCs [4]. However, the addition of PbBr_2 shows no improvement in V_{oc} for the devices in this study. This finding could be explained by a redshift (10 nm) from the PL peak, which possibly indicates the formation of deeper traps upon addition of PbBr_2 [44]. The average visible transmissions (AVT) [45,46] calculated from the data in **Fig. 7c** between 370-740 nm are 11.48%, 13.04%, 11.06%, and 12.30% for the pristine film and the films with the addition of excess MAI, PbCl_2 and PbBr_2 ,

respectively. **Fig. 7d** shows an image of the actual perovskite layer with addition PbCl_2 , with a thickness of around 230 nm measured from the cross-sectional SEM image shown in **Fig. S8**. The pristine film and the films with the addition of excess MAI and PbBr_2 also shows a similar thickness, as shown in **Fig. S8**.

Having understood the improvement of photovoltaic performance by adding PbCl_2 to the ambient-processed perovskite films, we further investigate their long-term stability by storing the devices without encapsulation in ambient air under RH of 50-60%. **Fig. 8a** shows the PCEs as a function of aging time for the pristine devices and the devices with PbCl_2 additive. The devices with PbCl_2 additive retain 81% of their average initial PCEs of 15.42% and yield an average final PCEs of 12.50% after aging in ambient air for 28 days. The pristine devices show retention of 71% of their average initial PCEs of 13.70% and yield an average final PCEs of 9.74%. We observe an increasing amount of degradation product PbI_2 in the pristine film compared to the film with PbCl_2 additive, evidenced by a stronger XRD peak intensity at 12.7° in the pristine film compared to the film with PbCl_2 additive (**Fig. 8b**) after aging in the ambient air for 14 days. The formation of more pinholes (red circles) also observed in the pristine films (**Fig. 8c**), compared to the film with added PbCl_2 (**Fig. 8d**), after storage in air for 28 days further confirming better ambient stability for the film with the PbCl_2 additive. **Fig. S9** shows the digital images for the perovskite film with the addition of PbCl_2 and the pristine film before and after storage in ambient air under RH of 50-60% for 30 days. It is noted that the perovskite film with the addition of PbCl_2 shows less degradation than the pristine film. We find that better long-term stability of the devices with PbCl_2 additive than the pristine film is mainly due to a smaller decrease of FF, as shown in **Fig. S10 and S11**. This result is possibly due to a higher uniformity and fewer pinholes of the perovskite film with the PbCl_2 additive than the pristine one, which caused less nonradiative recombination and a more efficient charge transport at the interface [47]. Thermal stability for the device based on different additives has been studied by

comparing their PCE before and after heating on a hotplate at 85 °C for 1 h, as shown in **Fig. S12**. It is noted that the devices based on the films with the addition of PbBr_2 and PbCl_2 showed less reduction on the PCE due to the thermal degradation than that of the films with excess MAI.

Fig. 8. (a) Long-term PCEs performance for the PSCs with pristine film and the film with addition of PbCl_2 after storage in ambient air under RH of 50-60% for 28 days. (b) XRD pattern of pristine film and the film with addition of PbCl_2 after storage in ambient air under RH of 50-60% for 14 days. SEM (80 KX Magnification) images of perovskite film (c) pristine, (d) with PbCl_2 addition after storage in ambient air with the relative humidity at 50-60% for 28 days. (scale bar = 400 nm)

3. Conclusion

In summary, we report the impact of adding PbCl_2 , PbBr_2 , and excess MAI in the perovskite precursors on the microstructure, chemical composition, crystallinity, optical properties, photovoltaic performance, and ambient stability with EA as antisolvent for ambient-processed

perovskite films. Adding PbCl_2 into the pristine perovskite films, leads to ambient-processed films with enlarged grain size with PbI_2 located on the grain boundaries and surfaces, enhanced crystallinity, improved light absorption, and reduced nonradiative recombination. These effects induced by PbCl_2 addition lead to a significant improvement in the device PCE up to 16.20% compared to a PCE of 13.81% for the pristine film. Device with PbCl_2 addition also shows enhanced long-term stability performance with a retention of 81% of their initial PCE for the planar PSCs, after storage in ambient air for 28 days. The addition of PbBr_2 reduces the hysteresis of the devices but gives no improvement in the PCE, possibly due to the formation of deeper trap states. The addition of excess MAI in this study shows negative effect on the device performance. Nevertheless, it is worth further investigating the effect of adding different ratios of the additives on the ambient-processed perovskite and PSCs. Our findings on the effect of halide additives for the fabrication of planar PSCs with green antisolvent in ambient air potentially contribute to the ambient and mass production of PSCs.

4. Experimental Section

Materials: Methylammonium Iodide (MAI, 98%), spiro-MeOTAD (99.5%), pre-patterned 8-pixel ITO glass ($20\Omega/\text{sq}$) were purchased from Ossila. Lead iodide (PbI_2 , 99.9985%) was purchased from Alfa Aesar. Lead chloride (PbCl_2 , 99.999%), lead bromide (PbBr_2 , 99.999%), ethyl acetate (99.8%), dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), 4-tert-Butylpyridine (tBP, 98%), acetonitrile (99.8%), bis(trifluoromethane)sulfonimide lithium salt (99.95%, LiTFSI), chlorobenzene (99.9%), titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol), 1-Butanol (99.8%) and Hellmanex III detergent were purchased from Sigma-Aldrich.

Perovskite precursor preparation: We prepared the pristine perovskite precursor by firstly dissolving 1.1 M PbI_2 (506 mg) in a mixed solvent of 0.8 ml DMF and 0.15 ml DMSO and stirring at 70 °C for 20 mins. The PbI_2 precursor solution was then cooled for 10 mins.

Subsequently, 1.1 M MAI (175 mg) was added to the PbI_2 precursor and stirred for 20 mins to complete the preparation. To prepare the perovskite precursor with PbCl_2 , 1 M PbI_2 (460 mg) and 0.1 M PbCl_2 (28 mg) was added to the solvent and the same process described above for the preparation of pristine precursor, before adding the MAI, was followed. 1.2 M MAI (190 mg) was then added to the precursor and stirred for 20 mins to complete the preparation. To prepare the perovskite precursor with PbBr_2 , the PbCl_2 (28 mg) was replaced by 0.1 M PbBr_2 (37 mg) and the rest of the process followed the preparation of the perovskite precursor with PbCl_2 . To prepare the perovskite precursor with excess MAI, an additional 0.1 M MAI (16 mg) was added to the PbI_2 solution and, the procedure for preparation of pristine perovskite precursor was followed as described above. The preparation of these precursors were based on the modification of the previous studies [9,48,49].

Device fabrication: The pre-patterned ITO-coated glass was washed sequentially with 2% Hellmanex detergent in deionized water, ethanol, deionized water and then treated with UV–ozone for 15 mins. To prepare the compact TiO_2 film, 0.1 M titanium diisopropoxide bis(acetylacetonate) dissolved in 1-butanol was first spin-coated on the ITO-coated glass at 2000 rpm for 40 s and then dried at 120 °C for 10 mins in ambient air. 0.3 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol was then spin-coated under the same conditions. The substrates were finally annealed in the furnace at 500 °C for 30 mins to complete the fabrication of compact TiO_2 . Before the deposition of the perovskite film, the substrates were exposed to UV–ozone for 15 mins and then preheated to 70 °C for 10 mins. The substrate was then quickly moved onto the spin-coater and 90 μl of the perovskite precursor was spin-coated on the substrate at 4000 rpm for 30 s. 200 μl of ethyl acetate was added dropwise to the substrate at 6-8 s after starting the spin-coating process. The substrate was finally annealed at 120 °C for 10 mins to complete the formation of the perovskite film. To prepare the hole transport material spiro-MeOTAD, 43 mg of spiro-OMeTAD was dissolved in 0.5 ml of chlorobenzene and then mixed with 10 μl of LiTFSI (520 mg in 1 ml acetonitrile) and

15 μl of tBP. The spiro-OMeTAD solution was then spin-coated on the perovskite film at 4000 rpm for 30 s. Finally, 80 nm of gold was deposited onto the substrate by thermal evaporation to complete the device fabrication. Apart from the thermal evaporation, all processes were carried out in ambient conditions with RH of 50-60%.

Characterizations: The J – V curves were measured using an Ossila push-fit test board with a Keithley 2400 source meter under simulated AM 1.5 sunlight at 100 mW cm^{-2} irradiated from an Oriel class AAA solar simulator. The light intensity was calibrated with a Newport calibrated quartz filtered Si reference cell. A measurement aperture mask with an aperture area of 2.4 mm^2 was used to define the active area of the devices. The XRD pattern of the perovskite films was measured using a PANalytical XRD2 diffractometer. The morphology and cross-section of the perovskite films were investigated using a Zeiss Ultra 55 FEG-SEM with an inlens mode. PL spectra of the perovskite films were measured using an Edinburgh Instruments FLS980 spectrophotometer. The absorbance and transmission spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2401PC). The surface chemistry of the perovskite films was examined using a Kratos Axis Ultra X-ray Photoelectron Spectroscopy (XPS) equipped with a monochromated Al $K\alpha$ X-ray source with a photon energy of 1486.7 eV. All XPS data were analyzed using CasaXPS software.

Supplementary data

The supplementary data is available free of charge on the Publications website.

Declaration of Competing Interest

The authors declare no competing financial interests.

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Supporting Information

Impact of Halide Additives on Green Antisolvent and High-Humidity Processed Perovskite Solar Cells

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Fig. S1 SEM (30 KX magnification) images for the perovskite films (a) pristine, (b) excess MAI, (c) with PbCl₂ and (d) with PbBr₂.

Fig. S2 Grain size distribution for the perovskite films (a) pristine, (b) excess MAI, (c) with PbCl_2 and (d) with PbBr_2 .

Fig. S3 XRD pattern for pristine perovskite film and the films with the addition of PbCl_2 , PbBr_2 , and excess MAI at the 2θ range of 10-18°.

Fig. S4 An image of actual ambient-processed planar PSCs with an architecture of ITO-glass/ TiO_2 /perovskite/spiro-OMeTAD/Au.

Fig. S5 Current density–voltage (J – V) curves for the devices with (a) pristine film, (b) the films with the addition of excess MAI, (c) PbCl₂ and (d) PbBr₂ measured from reverse scan (RS) and forward scan (FS) under simulated AM1.5 sunlight measured in ambient air.

Fig. S6 Current density–voltage (J – V) curves of the devices with the addition of PbCl_2 measured from reverse scan under different scanning rate.

Fig. S7 Optical bandgaps calculated from Uv-vis spectra for pristine perovskite film and the films with the addition of PbCl_2 , PbBr_2 , and excess MAI.

Fig. S8 SEM cross-section image of perovskite films (a) and (b) with PbCl_2 , (c) with PbBr_2 , (d) pristine and (e) excess MAI.

Fig.S9 Digital images of perovskite film with the addition of PbCl₂ and the pristine film before and after storage in ambient air under RH of 50-60% for 30 days.

Fig.S10 *J-V* curves for the devices based on (a) the perovskite film with the addition of PbCl₂ and (b) the pristine perovskite film after storage in ambient air under RH of 50-60% at 0, 7, 14, 21 and 28 days.

Fig. S11 Change of (a) FF, (b) V_{oc} and (c) J_{sc} versus storage time for the devices based on the pristine perovskite film and the film with the addition of PbCl₂.

Fig. S12 *J-V* curves for the devices based on the perovskite films with the addition of (a) PbBr₂, (b) PbCl₂ and (c) excess MAI before and after heating on a hotplate at 85 °C for 1 h. (d) PCE distribution for the devices based on the films with different additives before and after heating on a hotplate at 85 °C for 1 h.

Table S1. Crystal size for the pristine perovskite film and the films with different additives calculated by Scherrer equation

Types of Perovskite	Peak position 2θ ($^\circ$)	FWHM ($^\circ$)	Peak intensity	Crystal size (nm)
Pristine	14.10	0.318	12125	25.16
Excess MAI	14.07	0.354	16461	22.60
With PbCl₂	14.12	0.286	50005	27.98
With PbBr₂	14.12	0.291	15637	27.50

Table S2 Elemental surface stoichiometries determined from XPS measurements for the pristine perovskite film and the films with the addition of excess MAI, PbCl₂, PbBr₂

Sample ID	I/Pb	N/Pb	Pb ⁰ /Pb ²⁺
Pristine	2.6 $\pm$ 0.1	0.6 $\pm$ 0.1	22 $\pm$ 2%
Excess MAI	2.9 $\pm$ 0.1	0.9 $\pm$ 0.1	6 $\pm$ 2%
With PbCl₂	2.7 $\pm$ 0.1	0.7 $\pm$ 0.1	16 $\pm$ 2%
With PbBr₂	2.8 $\pm$ 0.1	0.8 $\pm$ 0.1	6 $\pm$ 2%

Table S3 A summary of photovoltaic parameters for planar PSCs with the pristine perovskite film and the films with addition of excess MAI, PbCl₂, PbBr₂, under RH of 50-60%.

Types of Perovskite	PCE (%)	FF (%)	J _{sc} (mA/cm ²)	V _{oc} (mV)	HI (%)
With PbCl₂ (best)	15.21 $\pm$ 0.59 (16.20)	73.9 $\pm$ 1.6 (76.3)	20.08 $\pm$ 0.40 (20.59)	1025.2 $\pm$ 34.8 (1079.9)	49.14
With PbBr₂ (best)	12.82 $\pm$ 0.46 (13.54)	70.7 $\pm$ 2.0 (73.4)	17.94 $\pm$ 0.32 (18.33)	1010.9 $\pm$ 21.2 (1057.7)	33.83
Excess MAI (best)	12.40 $\pm$ 0.53 (13.48)	67.8 $\pm$ 2.3 (70.4)	18.45 $\pm$ 0.56 (19.08)	992.4 $\pm$ 23.7 (1058.8)	58.85
Pristine (best)	13.53 $\pm$ 0.19 (13.81)	71.7 $\pm$ 1.5 (72.9)	18.53 $\pm$ 0.28 (18.91)	1019.5 $\pm$ 21.4 (1054.5)	62.85

Table S4 A summary of PCEs for recent ambient-processed PSCs in comparison to our planar PSCs

Perovskite type	Average PCE (best PCE)	Deposition method	Humidity	Reference
CH₃NH₃PbI₃ with PbCl₂	15.21 (16.20)	One-step	50-60	This work
CH₃NH₃PbI₃	12.48 (14.25)	Two-step	50	[1]
CH₃NH₃PbI₃	6.68 (8.08)	One-step	40±5	[2]
CH₃NH₃PbI₃	(14.66)	One-step	>70	[3]
CH₃NH₃PbI_{3-x}Cl_x	7.63 (9.2)	One-step	50	[4]
CH₃NH₃PbI₃	12.0 (15.0)	One-step	75	[5]
(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}	17.6 (18.8)	One-step	50	[6]
CH₃NH₃PbI₃	(10.52)	One-step	65-75	[7]
CH₃NH₃PbI₃	13.17 (14.24)	One-step	60	[8]
CH₃NH₃PbI₃	16.13 (17.24)	One-step	40	[9]
CH₃NH₃PbI_{3-x}Cl_x	(14.0)	One-step	40	[10]
CH₃NH₃PbI₃	15.6 (16.3)	One-step	60-70	[11]
CH₃NH₃PbI₃	13.7 (16.1)	One-step	30-60	[12]
CH₃NH₃PbI₃	12.21 (12.62)	Two-step	40-50	[13]
CH₃NH₃PbI₃	16.20 (18.11)	Two-step	70	[14]
CH₃NH₃PbI₃	(7.19)	Two-step	60-70	[15]
CH₃NH₃PbI₃	8.3 (8.38)	Two-step	60	[16]
CS_{0.15}FA_{0.85}PbI₃	14.21 (15.56)	Two-step	70±10	[17]
CH₃NH₃PbI₃	(12)	Electrospray	30-50	[18]
CH₃NH₃PbI_{3-x}Cl_x	11.12 (13.50)	Ultrasonic spray	30	[19]
CH₃NH₃PbI₃	12.0 (12.3)	Slot-die	60	[20]

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