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NH₄Br-Assisted Two-Step-Processing Rich Guanidinium Perovskite Films for Extremely Stable Carbon-Based Perovskite Solar Cells in Ambient Air

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Abstract

The substitution of portion of methylammonium (MA) for guanidinium (GA) has been verified to be able to enhance the stability of the MA-based devices. However, high dose GA cation will introduce localized distortions to the perovskite lattice structure and destroy the microstructure of the perovskite films, impairing the stability and reproducibility of perovskite solar cells (PSCs) eventually. In this work, for the first time, we adopt the NH₄Br-assisted all-atmospheric two-step process to fabricate GA rich (20%) perovskite films. The NH₄Br induces formation of the intermediate phase NH₄PbI₃ and alleviates the disorder of the octahedron caused by the big GA. Consequently the modified perovskite film shows increased tolerance for the roughness fluctuation
and reduced risk of forming voids and pinholes. The fabricated compact rich GA perovskite films behave extremely well in photovoltaic performance when assembling as carbon-based perovskite solar cells (C-PSCs), delivering a high power conversion efficiency (PCE) of 16.19% and stability against moisture and sunlight. Especially, the unencapsulated devices in ambient air sustain 95.1%, 91.8%, and 95.7% of their initial PCEs after 2400 h of storage, after 1000 h of 65 °C heat environment and after 800 h of sunlight illumination, respectively.
1. Introduction

Perovskite solar cells (PSCs) have become an attractive thin-film photovoltaic (PV) technology in the last ten years [1], with power conversion efficiency (PCE) nowadays over 25% for single-junction devices [2, 3]. Despite the impressive evolution, the instability of PSCs remains a major obstacle in the way of commercialization [4]. Various technological approaches have been proposed to address the instability issues, among which carbon-based perovskite solar cells (C-PSCs) without expensive hole transport materials and metal counter electrodes are prominently stable device structure for commercial applications, owing to their suppressed ion migration [5, 6], excellent stability [7], low cost [8], moderate efficiency [9] and simple manufacturing process [10]. Initial C-PSCs showed a complicated mesoporous-structured construction such as TiO$_2$/ZrO$_2$/C [7], and these devices have gained a highest PCE of 17.47% so far [11]. However, it requires a high temperature annealing procedure (> 400 °C) to remove the template between the space layer and carbon layer [7], which will undoubtedly increase energy consumption and restrict large-scale production on a flexible or plastic substrate. The low-temperature processed paintable C-PSCs is explored for flexible applications [12], and its PCE boosted from 10.2% in 2014 to 16.25% in 2020 [12-15]. Note that although the paintable C-PSCs are stable in device structure, the stability issue is only partially solved, which has limited its commercial application [16]. In a typical SnO$_2$/perovskite/C-PSC, the device stability is largely determined by the perovskite layer. Thus, it is challenging to design and prepare a highly stable perovskite light-absorbing film [17].

It is well known that the prototype perovskite i.e. MAPbI$_3$ itself suffers serious degradation upon exposure to moisture [18-21] and/or light owing to the fragile methylammonium cation (MA = CH$_3$NH$_3$)$_+$ [22, 23]. Various approaches have been proposed to improve the stability of the perovskite layer [24-30]. Remarkably, compositional engineering contains substituting or replacing the “A” site cation [31, 32] or “X” site anion [33] in the APbX$_3$ (X is one of or a mixed of I, Cl or Br) perovskite lattice has been demonstrated to be effective to obtain stable perovskite films. Substituting a portion of “A” site cation i.e. MA (217 pm) with large-sized...
cations such as formamidinium cation \((\text{FA} = (\text{NH}_2)_2\text{CH}^+)(253 \text{ pm})\) [34] and guanidinium cation \((\text{GA} = \text{NH}_6\text{N}_3^+)(278 \text{ pm})\) [35, 36] enables the adjustment of the tolerance factor of \(\text{APbX}_3\) perovskite lattice and hence improves its intrinsic stability [36]. GA with the two amine groups can form stronger H-X bond with the Pb-X framework, consequently leading to more stable \(\text{APbX}_3\) lattice [37-40] so as to demonstrate excellent durability upon environmental moisture and oxygen. Note that the reported GA-incorporated perovskite only involves low dose GA from 5% to 10 mol %, because high dose GA cation would introduce localized distortions to the \(\text{APbX}_3\) lattice structure, and thus destroy the microstructure of the perovskite films and eventually impair the stability and reproducibility of PSCs [38]. Theoretically speaking, incorporation of high dose GA (15% - 20 mol %) will be optimal for the photoelectric properties of the perovskite films and devices [41]. It was reported that the crystalline lattice distortions arising from high-dose GA substitution can be validly alleviated by adjusting the “X” site anion [42]. Replacing I by the electrically more negative \(\text{Br}^-\) can increase the H-X bonding strength to enhance the stability of the \(\text{APbX}_3\) framework; meanwhile \(\text{Br}^-\) with a smaller volume can spare more room for the large dose of GA [32, 43]. Besides, introduction of \(\text{NH}_4^+\) in the perovskite crystallization was suggested to enhance the stability of the perovskite film, since \(\text{NH}_4^+\) could occupy the crystalline lattice center of the \(\text{PbI}_6^-\) octahedral framework, effectively retarding the direct formation of \(\text{APbX}_3\) perovskite [44, 45]. Moreover, the perovskite surface morphology would be further optimized in the low-temperature annealing process by the release of ammonia [46].

In this work, we prepare thick GA rich perovskite films characteristics of smooth and dense surface using a two-step procedure. The \(\text{NH}_4\text{Br}\) induces formation of the intermediate phase \(\text{NH}_4\text{PbI}_3\) and alleviates the disorder of the octahedron caused by the big GA. As a result, the tolerance for the perovskite roughness fluctuation is increased and the risk of appearing voids and pinholes in the perovskite films is reduced. The fabricated C-PSCs device with a configuration of ITO/SnO\(_2\)/perovskite/C deliver the highest PCE of 16.19% for the unencapsulated rich GA devices under an ambient-air condition. Furthermore, the \(\text{NH}_4\text{Br}\)-modified devices in ambient air exhibit extremely excellent stability against \(\text{O}_2\) and/or \(\text{H}_2\text{O}\), heat and sunlight, sustaining 95.1%, 91.8% and 95.7% of their initial PCEs after 2400 h of storage, after 1000 h of 65 °C heat environment and 800 h of sunlight illumination, respectively.

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2. Result and Discussion

We adopt the two-step spin-coating process in an atmospheric environment to fabricate MA-GA perovskite films (Figure 1a) [47]. In process I, different amount of GAI (10 %, 15%, 20% and 25 mol %) was added to the MAI solution to promote the optoelectronic performance and stability. It is found that GA can significantly improve the perovskite crystallinity (Figure S1, Supporting Information) and sunlight absorption (Figure S2, Supporting Information). Herein, we selected the MA0.80GA0.20PbI3 (MAGA) perovskite for further optimization because of its excellent crystallinity, light absorption and photoelectric performance (Figure S3, Supporting Information) [38]. However, large amount of GA (20 mol %) induces obvious lattice distortion (Figure S1, Supporting Information) and rough surface with pin holes in the perovskite films (Figure S4, Supporting Information). The reason is that GA with large radius induce slower precipitation of A-position cations [38]. Note that in such a typical spin-coating process, the Pb-X framework precipitated first, and then A cation will occupy the lattice center of the PbI6 octahedra. Thus, the large different precipitation inconsistency in the time dimension between PbX2 and AX introduces the formation of A-site defects when the solvent is evaporated. To balance the precipitation period of inorganic PbX2 and organic AX, we introduced NH4+ with a small ionic radius (~ 161 pm) to the PbI2 precursor in the first step to mediate the perovskite crystallization process (process II). NH4+ first occupied the center of the Pb-X framework, forming NH4PbX3 transient phase, which can alleviate the PbI2 precipitation, and hence facilitate the growth of high-quality perovskite crystalline as evidenced by the scanning electron microscopy (SEM) image (Figure 1b&c). Furthermore, the small cation NH4+ can occupy the A-site of APbX3 framework and alleviate the disorder of the octahedron caused by the big GA [46]. Compared with other ions in perovskite precursor solutions, the amounts of Br− and NH4+ were very low, thus, the transient phase was mainly the NH4PbI3 phase (Figure 1d). Subsequently, MA and GA substitute NH4+ in the NH4PbI3 phase to form MA-GA perovskite, and NH4+ converse to NH3 gas in the annealing of 130 °C. The release of NH3 gas will be beneficial for alleviating the passivation of the perovskite surface so as to form smooth and even films [46].

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Figure 1. a) The crystallization processes of MAGA perovskite without (process I) and with NH$_4$Br (process II). Surface SEM images of b) MAGA and c) NH$_4$Br-modified MAGA films, the scale bar: 1 μm. d) XRD patterns of MAGA films in process I and process II. e) The TGA curves of the intermediate phase and different perovskites.

In order to investigate the effect of NH$_4$Br optimization on the perovskite crystallization, we examined the PbI$_2$ films without (process I) and with NH$_4^+$ (process II) after the subsequent annealing in the first step by plotting the X-ray diffraction (XRD) pattern (Figure 1d). It is found that a new peak at 9.2° appears in the NH$_4^+$ modified PbI$_2$ films, which is denoted as the NH$_4$PbI$_3$ intermediate phase (PDF card: PDF#74-0397) [45]. Then XRD tests are performed on the MAGA perovskite film prepared in process I and NH$_4$Br-motified MAGA perovskite films in process II, showing that the XRD peak intensity of NH$_4$Br-motified MAGA perovskite is stronger than that of reference MAGA one. This indicates that the addition of NH$_4$Br can facilitate the perovskite crystallization. Simultaneously, the narrowing full-width at half-
maximum (FWHM) of the (110) reflection of the films indicates the optimized crystallinity of the perovskite (Figure S5b, Supporting Information). Moreover, the positive-shift of peak is 0.4° (from 14.2° to 14.6°), indicating that the introduction of NH₄Br can effectively alleviate lattice expansion originating from the large-sized GA (Figure S5c, Supporting Information).

Additionally, thermogravimetric analysis (TGA) was carried out to examine the thermal stability of the transient phase and different perovskite. Transient phase powder samples were synthesized by simple evaporation of the solvent from NH₄I and PbI₂ with a molar ratio of 1:1 in mixed solution of N, N-dimethylformamide and dimethyl sulfoxide. Such transient phase was synthesized by the solution method and stored in an atmospheric environment, which inevitably contained water [46]. As depicted in Figure 1e, the TGA curve shows two rapid weight losses for the transient phase and only one rapid weight loss for original MA, MAGA and NH₄Br-modified MAGA samples. For the transient phase, NH₃ combined with two water molecules and firstly started to rapidly escape from the powder at 90 °C, and the loss of NH₃ combined with two water molecules might have been completed at approximately 208 °C, corresponding to the weight loss of 11.12 wt.% in the transient phase. The lower onset of the weight loss temperature of the transient phase suggests that it can easily transform into the gaseous phase. Then, the HI started to be eliminated, and the weight loss might have finished at approximately 410°C, corresponding to the weight loss of 31.10 wt.% in the transient phase. Thus, the phase transformation based on the formation of NH₄PbI₃ after adding the low-dose NH₄Br and the consumption of the transient phase via organic cation exchange has been verified via the aforementioned experimental data including XRD and TGA [44]. The MAGA sample begins to lose weight at ~ 162 °C, while the MAPbI₃ loses weight at ~120 °C, indicating the thermal stability of MAGA better than that of MAPbI₃. Furthermore, the TGA curve profile of the NH₄Br-modified MAGA sample lies upon that of MAGA sample, implying the stability of the NH₄Br-modified MAGA sample is the best among the three samples.

To deeply understand the crystallization mechanisms, we carried out some additional measurements of the PbI₂ and NH₄Br-assisted PbI₂ films including SEM, AFM and KPFM images (Figure 2). According to the SEM images (Figure 2a&b), the PbI₂ film without doping exhibits a typical compact and smooth microstructure, while the NH₄Br-PbI₂ film presents slightly looser and rougher surface. The AFM images show that the surface roughness of PbI₂

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and NH₄Br-PbI₂ films are 41.5 ± 5.30 nm and 58.5 ± 6.54 nm, respectively (Figure 2c, d). Obviously, the NH₄Br-PbI₂ film possessed larger surface roughness than the original PbI₂ film. The surface potential of PbI₂ without and with NH₄Br (Figure 2e, f) have also been observed by KPFM measurement. According to the KPFM images, the NH₄Br-PbI₂ film shows lower surface potential (-432.5 mV) than the reference PbI₂ (-166.8 mV), probably attributed to the interaction between PbI₂ and NH₄Br [44]. Particularly, the rougher surface structure and more electronegative surface potential of modified NH₄Br-PbI₂ may promote the infiltration of cationic MAGA solution in the modified PbI₂ film beneficial to better crystallinity of the NH₄Br-modified MAGA perovskite.

**Figure 2.** Surface morphology of SEM images of a) PbI₂ and b) NH₄Br-addicted PbI₂, c-d) AFM and e-f) KPFM images of PbI₂ and NH₄Br-addicted PbI₂, the scale bar: 200 nm.

The AFM height images were also performed to obtain the surface architecture information of the perovskites. An appropriate range (1 μm × 1 μm) of surface morphologies of the different perovskites showed surface roughness of 8.32 ± 2.31 nm for original MAPbI₃ perovskite (**Figure 3a**), 16.7 ± 3.50 nm for MAGA perovskite (**Figure 3b**) and 12.0 ± 1.85 nm for NH₄Br-modified MAGA perovskite (**Figure 3c**), respectively. Interestingly, the MAGA perovskite films displayed rougher surface than the original MAPbI₃ and NH₄Br-modified
MAGA perovskite films, which is consistent with the SEM observation (Figure 1b&c). Thus, incorporating a small dose of NH₄Br in GA rich perovskite films can facilitate the formation of dense and smooth perovskite films by the growth of large-size perovskite crystal from transient phase. We further conducted KPFM to compare the surface potential of the corresponding perovskite films (Figure 3d-f). It is worth noting that the surface potential fluctuation of NH₄Br-modified MAGA perovskite is much smaller than the others; its surface potential fluctuation difference is 95.4 mV, which is much lower than original MAPbI₃ (584 mV) and MAGA (114.7 mV) perovskite films. This suggests that the band bending and surface defects in the NH₄Br-modified MAGA samples are effectively inhibited [48]. This low surface potential fluctuation observed in NH₄Br-modified MAGA perovskite films is ascribed to its flat surface and a lower stress concentration at grain boundaries [49].

**Figure 3.** AFM morphologies of a) MAPbI₃ perovskite, b) MAGA perovskite and c) NH₄Br-modified MAGA perovskite. Surface potential difference of d) MAPbI₃ perovskite, e) MAGA perovskite and f) NH₄Br-modified MAGA perovskite. The scale bar: 200 nm.

To clarify the interaction between NH₄Br and the perovskite materials, the X-ray photoelectron spectroscopy (XPS) spectra for 2% NH₄Br-modified MAGA perovskite film was measured and shown (**Figure 4a&b**), using the crystallization method previously reported [39].
For reference MAGA perovskite, the two obvious Pb peaks centered at ~ 138.48 and ~ 143.38 eV and the two I peaks centered at ~ 619.38 and ~ 630.88 eV are clearly observed. Compared to the MAGA sample, the spin-orbit splitting peaks of the Pb 4f orbital in the 2% NH₄Br-modified MAGA perovskite film shift to lower binding energies ca. 138.38 and 143.28 eV, which indicates the passivation of uncoordinated Pb²⁺. These uncoordinated Pb²⁺ modifies the chemical stoichiometry of the films, which influences the electronic properties. Meanwhile, the two peaks of the I 3d orbital in the 2% NH₄Br-modified MAGA perovskite film also shift to lower binding energies (619.28 and 630.78 eV), indicating the amount of I in the perovskite film reduced. XPS of MAGA perovskite with the NH₄Br additive was conducted to confirm the existence of Br⁻ ions in the perovskite film (Figure S6, Supporting Information). The full XPS spectrum shows a trace amount of Br element in the perovskite film. A weak Br 3d signal was detected in the sample after introducing the NH₄Br additive. The elemental compositions of the MAGA perovskite with and without NH₄Br additive were also observed via energy-dispersive X-ray spectroscopy (EDS) measurements. The EDS mapping shows a uniform distribution of Br in the perovskite films (Figure S7a&b, Supporting Information).

The effects of NH₄Br addition to the perovskite films were further investigated by Fourier transform infrared (FTIR) spectrum. The FTIR spectrum of pristine MAPbI₃ perovskite powder reveals characteristic peaks of the C-N stretching vibration at ~ 1470 cm⁻¹ (Figure 4c) and the C-N and N-H compound stretching vibration at ~ 1570 cm⁻¹ respectively [50]. The films with GA⁺ show the C=N stretching vibration at ~ 1660 cm⁻¹. For the NH₄Br-modified MAGA perovskite films, these peaks are maintained. Note that the characteristics peak (1380 cm⁻¹) of the NH₄Br could not be found in the NH₄Br-modified MAGA perovskite, further indicating that the introduced NH₄⁺ disappears and no external residues remain. We also carried out FTIR of the PbI₂ and NH₄Br-addicted PbI₂ to further explain the formation of intermediate phase (Figure 4d). One can see that a peak occurs at ~ 3200 cm⁻¹ in the NH₄Br sample, and a peak at ~ 3400 cm⁻¹ appears in the NH₄Br-addicted PbI₂ sample, both of which are attributed to N-H stretching vibration. The shift of N-H stretching vibration peak in the NH₄Br-addicted PbI₂ sample might be deduced to be originating from the micro-environment change of the N-H bond in the intermediate phase NH₄PbI₃ [51, 52].
Figure 4. XPS spectra of a) Pb 4f core level and b) I 3d core level of the MAGA perovskite and NH₄Br-modified MAGA perovskite. FTIR spectra of c) different perovskites and d) PbI₂ without and with NH₄Br e) PL curves of different perovskites.

From the XRD, SEM and AFM characterizations, we find that introduction of NH₄Br can modulate the high dose GA-based perovskite crystallization, which would greatly influence the surface states of the perovskite films. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were carried out to study the trap-induced recombination in the perovskite films. In Figure 4e, the PL emission intensity increases after GA⁺ is added into the MAPbI₃ film, which might be originated from the overall larger grain size, despite the presence of voids. As we expected, the emission intensity is further increased with the addition of NH₄⁺, originated from the larger grain size together with void-free surface morphology. Besides the enhanced intensity, an indistinct blue-shift of the PL emission peak is observed in the NH₄Br-modified MAGA perovskite film, associated with a larger optical bandgap(Figure S8, Supporting Information). The TRPL spectra of the perovskites were also assayed (Figure S9, Supporting Information). A bi-exponential function is applied to fit the curves as follows (Equation (1)):
where $A_1$ and $A_2$ are the amplitudes. The fast decay component of $\tau_1$ indicates a non-radiative recombination and the slow decay component of $\tau_2$ implies a radiative recombination, respectively [53]. Herein, the average carrier lifetimes ($\tau_{\text{ave}}$) are 68 ns for MAPbI$_3$ perovskite, 110 ns for MAGA perovskite, and 158 ns for NH$_4$Br-modified MAGA perovskite, respectively (Table S2, Supporting Information). The higher PL intensity and longer lifetime of the NH$_4$Br-modified MAGA perovskite film confirm the less defects in the NH$_4$Br-modified MAGA perovskite film, in accordance with the improved surface morphology (Figure 2c) and the enhanced crystallinity (Figure 1d).

Figure 5. a) Schematic device architecture for SCLC measurement. The SCLC curves for b) MAPbI$_3$, c) MAGA and d) NH$_4$Br-modified MAGA devices.

The defect densities of different samples were evaluated by the space-charge-limited current (SCLC) measurements with the device structure of ITO/SnO$_2$/perovskite/[6,6]-phenyl-C61-butyric acid methyl ester/Ag [54-56], as shown in Figure 5a. At low bias voltage (Figure 4b-d), the linear correlation (red lines) demonstrates an ohmic response. After the bias voltage upgrades above the turning point, the current is immediately boosted with a nonlinear correlation (gray line). This illustrates that the traps in the samples are effectively reduced. The trap-filled limit voltage ($V_{\text{TFL}}$) is the bias voltage related to the kink point between the linear and nonlinear correlation. The defect density ($N_t$) is determined by the Equation (2):

$$N_t = \frac{2\varepsilon_0 V_{\text{TFL}}}{qL^2}$$

where $\varepsilon_r$ represents the relative dielectric constant, $\varepsilon_0$ represents the vacuum permittivity, $V_{\text{TFL}}$
represents the onset voltage of the trap-filled limit region, \( q \) represents the elementary charge, and \( L \) stands for the thickness of the absorber layer [57]. Here, the calculated defect density is \( 9.65 \times 10^{15} \text{ cm}^{-3} \) for the pure MAPbI\(_3\), \( 7.04 \times 10^{15} \text{ cm}^{-3} \) for MAGA, and \( 4.43 \times 10^{15} \text{ cm}^{-3} \) for NH\(_4\)Br-modified MAGA perovskite films, respectively, demonstrating that the NH\(_4\)Br-modified MAGA perovskite shows a decreased defect density.

To explore the influence of the NH\(_4\)Br-assisted perovskite crystallization on the device performance, carbon-based devices were prepared based on the MAPbI\(_3\) perovskite, the MAGA perovskite and the NH\(_4\)Br-modified MAGA perovskite. The schematic diagram of a typical structure of ITO/SnO\(_2\)/perovskite/C is shown in Figure S10a&b, Supporting Information. Statistics on the device performance of these different perovskites are summarized in Figure 6a&b. The reference MAGA C-PSCs deliver an average efficiency of 12.78% with an open-circuit voltage (\( V_{OC} \)) of 1.02 V, a short circuit current (\( J_{SC} \)) of 22.02 mA cm\(^{-2} \), and a fill factor (\( FF \)) of 56.10%. The average PCE of NH\(_4\)Br-modified MAGA C-PSCs further is boosted to 15.48%. Despite a smaller optical bandgap (Figure S8, Supporting Information), a higher average \( V_{OC} \) of 1.05 V is observed for the NH\(_4\)Br-modified MAGA film. It is attributed to the eliminated voids and pinholes in the perovskite absorber layer, thus effectively inhibiting the trap-induced recombination, and therefore significantly decreasing the \( V_{OC} \) loss and leading to a better \( FF \). The champion device based on the 2% NH\(_4\)Br-modified MAGA perovskite has a PCE of 16.19% with a \( V_{OC} \) of 1.10 V, \( J_{SC} \) of 22.74 mA cm\(^{-2} \), and an \( FF \) of 64.62%. The transformation of the device properties corresponding to the GA\(^+\) and NH\(_4\)\(^+\) is summarized in Table S3&S4, Supporting Information.

We further analyzed the carrier transport and transfer in PSCs by electrochemical impedance spectroscopy (EIS) measurements. Nyquist plots of devices in dark condition and in light condition are shown in Figure 6c&d. The NH\(_4\)Br-modified MAGA perovskite shows a largest semicircle with the distinct outline in dark condition, corresponding to the suppressed non-radiative recombination, and a smallest semicircle in light condition corresponding to promoted interfacial contact in PSCs. This demonstrates a faster charge transfer and weaker transmission loss. Apparently, in the device with NH\(_4\)Br, the recombination resistance (\( R_{rec} \)) is significantly increased and the transfer resistance (\( R_{tr} \)) is decreased, which indicated the restrained charge recombination and promoted electron extraction [13], thereby resulting in a higher \( FF \).

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Figure 6. J-V characteristic curves of a) PSCs based on different perovskite and b) MAGA PSCs with different NH$_4$Br additive doses, Nyquist plots in c) dark and d) light conditions. e) EQE spectra and the corresponding integrated photocurrent densities. f) The stabilized maximum power output measurement of the PSCs.

Figure 6e illustrates the external quantum efficiency (EQE) spectra and the integrated $J_{SC}$ values versus wavelength for the C-PSCs based on different perovskites. The addition of NH$_4^+$ inhibits the destruction of the perovskite film from sunlight, accounting for the distinct increase of the EQE. The highest EQE value of 93% is observed. Meanwhile, the integrated $J_{SC}$ of C-PSCs based on NH$_4$Br-modified MAGA perovskite increases from 22.13 to 22.59 mA cm$^{-2}$. The stabilized power output of the C-PSCs based NH$_4$Br-modified MAGA is shown in Figure 6f. Upon applying an external bias close to the maximum power output point (0.80 V), the determined stabilized photocurrent for the C-PSC based on NH$_4$Br-modified MAGA is 18.80 mA cm$^{-2}$, implying the excellent illumination stability of the device fabricated with NH$_4$Br-modified MAGA perovskite.
Figure 7. Statistical stability results for different PSCs. a) PCE decays of the corresponding solar cells stored under ambient condition. b) PCE decays of devices stored in ambient at 65 °C condition. c) PCE decays of devices under the continuous sunlight illumination.

Further, we performed long-term stability measurements for cell devices with NH₄Br and without NH₄Br in different environments (Figure 7). During the long 2400 h timescales of the steady state measurements in ambient air, the PCE degradation of the NH₄Br-modified C-PSCs is rather low, ranging from initial 100% to 95.1%. To examine the thermal stability, the fabricated C-PSCs were then placed in a constant 65 °C environment in an air atmosphere. The champion NH₄Br-device remained almost 92% of their initial PCE after over 1000 h of continuous heating, whereas the reference MAGA C-PSC decreased to 83% of its primary PCE over the same period, demonstrating the significantly improved thermal stability of NH₄Br modified devices. Finally, we placed the devices under 100 mW cm⁻² sunlight for continuous illumination analysis, and counted the changes of PCEs after 40 devices were illuminated. Notably, after 800 hours of continuous illumination, the average PCE of the devices drops to 96% of the initial value, superior to that of the unoptimized devices (90%) (Figure 6c).

3. Conclusion

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In this work, we successfully prepared NH₄Br-modified GA rich perovskite films characteristics of dense and smooth surface by a two-step process. The XRD and AFM characterizations demonstrated that NH₄Br induces the formation of the intermediate phase NH₄PbI₃ and alleviates the disorder of the PbI₆ octahedron caused by adding big GA. The resultant perovskite absorber layers enhance the tolerance for the roughness fluctuation and decrease the risk of appearing voids and pinholes. The C-PSCs made of the MAGA hybrid perovskite films in the ambient condition produce a champion PCE of 16.19% which shows strong resistance against ambient-air, heat and sunlight in long period. This work provides a feasible approach to prepare stable and low-defect perovskite films for optoelectronic device production.

4. Experimental Section

**Materials:** ITO glass substrates with sheet resistance of 15 Ω cm² were obtained from Shenzhen South China Xiang Cheng Science & Technology Company Limited. The SnO₂ (tin (IV) oxide, 15% in H₂O colloidal dispersion) was bought from Alfa Aesar. N, N-Dimethylformamide (DMF, 99.8%), ethanol (99.5%) and isopropanol (IPA, 99.5%) were bought from J&K Chemical Ltd. Dimethyl sulfoxide (DMSO, 99.9%) was obtained from Aladdin. PbI₂ (99.9985%) was got from the Xi’an Polymer Light Technology Corp. MAI (99%) was obtained from Dyesol. NH₄Br (99%) was obtained commercially from Sigma- Aldrich. The GAI (99%) was obtained from TCI. And the carbon paste was obtained from Guangzhou Seaside Technology Co.Ltd. Note that all the materials mentioned above were used directly without further modification.

**Perovskite Films Preparation:** The perovskite absorber layer was prepared through a modified two-step sequential procedure. First, 1.3 mM PbI₂ DMF/DMSO mixed solution (V_{DMF} : V_{DMSO} = 9 : 1) was spin-coated on the SnO₂/ITO surface at 3000 rpm for 30 s, and heated at 60 °C for 1 min. NH₄Br (at molar ratios of NH₄Br to PbI₂ of 1%, 2%, 3%) were added to the PbI₂ solution to obtain the desired NH₄⁺ content. Thereafter, a mixture solution of MAI&GAI in IPA (at molar ratios of GAI to MAI of 10%, 15%, 20% and 25%) was dropped on the as-cast PbI₂ film at 3000 rpm for 30 s, followed by evaporating the solvent at 130 °C for 10 min and naturally cooling.

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Device Fabrication: ITO substrates were sequentially washed by sonication in deionized water, ethanol and IPA for 20 min. Then cleaned ITO substrates were dried at 60 °C and processed with ultraviolet-ozone for 20 min. The SnO$_2$ electron transporting layer was deposited on the substrate by spin-coating the colloidal SnO$_2$ nanoparticle solution (2.67% in H$_2$O colloidal dispersion) at 3000 rpm for 30 s, and later dried at 150 °C for 30 min. The perovskite films prepared on the SnO$_2$ electron transporting layer through the method mentioned above. In the end, the carbon paste was coated on the perovskite layer without any other modification and then dried at 100 °C for 20 min. Especially, all sections prepared above were fabricated under an actual atmospheric environment.

The Transient Phase: The synthesized transient phase was prepared by blading a solution of NH$_4$I and PbI$_2$ at an equal molar ratio onto the ITO substrate and annealed at 60 °C.

XRD Measurement: The crystallinity was characterized by powder X-ray diffraction (XRD) using Cu Ka radiation ($\lambda = 0.15406$ nm) on a Rigaku D/max-2500 VB2+/PC diffractometer in the 2θ range of 5-60° at a scan rate of 3° min$^{-1}$.

SEM Study: SEM images were obtained from JEOL J-7800F to observe the surface and cross-sectional microstructure of the samples.

PL and TRPL Measurements: PL and TRPL spectra of the perovskite films were characterized on an Edinburgh Instruments FLS 980. The exciting was at 470 nm and the range of wavelength was from 720 nm to 860 nm.

UV-vis Absorption Spectroscopy: The optical performance of perovskite films was obtained by the absorption spectra characterized on a UV-vis spectrophotometer (Perkin Elmer Lambda 950 UV/VIS).

AFM and KPFM: The surface height and potential images of films were characterized on a Bruker Multimode 8 atomic force microscope with tapping mode.

FTIR Measurements: FTIR spectrum was carried out on a Bruker Vertex 70v spectrometer.

XPS Analysis and EDS Measurements: XPS was carried out with a Kratos X-ray photoelectron spectrometer (Thermo Fisher ESCALAB 250Xi) equipped with monochromatic Al K$\alpha$ (1,486.6 eV) and non-monochromatic HeI (21.22 eV) sources. EDS measurements were carried out using an X-ray energy dispersive spectrometer mounted on a JEOL-7610F microscope.
**TGA:** TGA curves were obtained on a Q50 TGA instrument with the range of 25-500 °C and a heating rate of 5 °C min\(^{-1}\) under atmospherical conditions.

**Devices Characterization:** The electrochemical testing (such as EIS) was measured on an electrochemical workstation (Zennium 400147) with the Keithley 2400 source meter under AM 1.5G. The EIS measurements were carried out by applying a bias of the open-circuit voltage with frequencies ranging from 106 Hz to 1 Hz. The current density-voltage (J-V) characteristics were obtained by a solar simulator (Oriel Sol3A). The photo-stability test at continuous MPP operation was carried out to match the voltage at VMPP and trace the current output. The VMPP at the maximum power point was obtained from the J-V curves of the devices. The external quantum efficiency (EQE) spectrum was obtained from an EQE system (Oriel instruments) using a 150 W xenon lamp (USHIO, Japan). Remarkably, all samples were stored and tested in an air-ambient environment.

**Declaration of Competing Interest**

The authors declare no competing financial interests.

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References


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We prepare rich guanidinium (GA) perovskite films via NH₄Br-assisted two-step process in air conditions, in which NH₄Br is introduced to facilitate the transient phase (NH₄PbI₃) formation and reduces voids and pinholes in films. The fabricated carbon-based perovskite solar cells (C-PSCs) in ambient air deliver the highest efficiency of 16.19% and exhibit excellent stability against moisture, heat and sunlight.

Keywords: Carbon-based perovskite solar cells; Rich guanidinium; NH₄Br-assisted two-step-processing; High stability in ambient air

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NH₄Br-Assisted Two-Step-Processing Rich Guanidinium Perovskite Films for Extremely Stable Carbon-Based Perovskite Solar Cells in Ambient Air