SOLAR CELLS

Homogenized chlorine distribution for >27% power conversion efficiency in perovskite solar cells

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The spatial heterogeneity of halogen distribution in perovskite thin films represents a critical factor currently limiting both the power conversion efficiency and stability of solar cells. We identified pronounced through-film inhomogeneity in chlorine distribution in formamidinium lead iodide films, with the generally used additive methylammonium chloride. We demonstrated that incorporating alkali metal oxalates could effectively homogenize the chlorine distribution. These compounds underwent thermal dissociation, releasing alkali metal cations that selectively bound chloride ions, which considerably suppressed surface defects and eliminated interfacial barriers. A certified steady-state power conversion efficiency (PCE) of 27.2% (device area and measured mask area: 0.108 square cm and 0.074 square cm, respectively) in perovskite solar cells was achieved, and devices retained 86.3% of their initial PCE after 1529 hours of continuous maximum power point tracking (MPPT) under 1 Sun condition. Moreover, the unpassivated device maintained 82.8% of its original PCE under MPPT at 85°C aging under 1 Sun illumination after 1000 hours.

Perovskite solar cells have achieved certified power conversion efficiencies (PCEs) >26%, advancements primarily attributed to progress in film crystallization control, charge transport layer optimization, and interfacial passivation (*1*–*3*). A key factor in attaining high performance, in both one- and two-step deposition processing, is the incorporation of methylammonium chloride (MACl) additive (*4*–), which reduced the nucleation barrier for intermediate state formation and decelerated crystal growth ( ). Notably, the migration of MACl and its ultimate escape from the perovskite layer are processes highly sensitive to ambient moisture (*10*, *11*). However, precisely controlling the environmental humidity remains challenging, and the presence of moisture could induce surface aggregation of Cl, which hinders charge transport (*12*).

We identified that the perovskite films exhibited surface enrichment of chloride when using MACl as the additive, resulting in vertical compositional heterogeneity. This inhomogeneity promoted trap-assisted recombination and misalignment of energy levels, thereby suppressing interfacial carrier extraction. To address this issue, we introduced a homogenized vertical chlorine distribution (HVCD) strategy by adding alkali metal oxalates, such as potassium binoxalate (PB), into the perovskite precursors. During thermal annealing, PB dissociated and released K^+, which effectively bound chloride anions, leading to a HVCD in the films. This approach suppressed interfacial defects and minimized interfacial energy barriers. We have achieved high-performing inverted perovskite solar cells with a certified steady-state PCE of 27.2% (device area/measured mask area: 0.108 cm^2/0.074 cm^2, respectively). The HVCD devices also showed improved stability and maintained 98.8 and 85% of their initial performance after storage under dark for >3000 hours and continuous 85°C aging for 750 hours, respectively. Also, the HVCD devices maintained 86.3% of their original PCE after 1529 hours maximum power point tracking (MPPT) under 1 Sun condition. The unpassivated HVCD device retained 82.8% of its original PCE under MPPT and 85°C aging upon 1 Sun illumination after 1000 hours.

Homogenized vertical chlorine distribution

We prepared the perovskite precursor solution based on formamidinium lead iodide ($FAPbI_3$) with the addition of 19.5 mol % MACl and 6.5 mol % PbI_2, corresponding to a PbI_2:MACl molar ratio of 1:3, which was critical for obtaining high-quality perovskite films (*13*). After spin coating and vacuum flashing, the precursor films were annealed in a nitrogen atmosphere (movie S1). For the HVCD perovskite films, we added 0.7 mol % PB of $FAPbI_3$ as an additive for crystallization modulating (see supplementary materials for details).

To investigate the optoelectronic homogeneity of the resulting films, steady-state photoluminescence (SSPL) measurements were conducted from both the top and buried surfaces. The control perovskite film exhibited distinct emission peaks at 811 nm and 818 nm on top and buried surfaces, respectively, indicative of vertical phase segregation (Fig. 1A). By contrast, both surfaces showed identical emission peaks at 819 nm in the HVCD perovskite film, indicating uniform composition and vertical homogeneity (Fig. 1B).

X-ray photoelectron spectroscopy (XPS) revealed the chemical changes of the top surfaces. After annealing of the control precursor film, the surface concentration of Cl increased by more than one order of magnitude (Fig. 1C). This increase was attributed to the solvent's volatilization-induced migration of Cl^- anions from the bulk to the surface during annealing. This redistribution of anions resulted in substantial surface aggregation of Cl and consequently induced inhomogeneous crystallization and vertical phase segregation within the film (*14*–*1*). For the HVCD perovskite films, the surface concentration of Cl^- anions remained nearly the same after annealing, suggesting that the Cl^- anions were immobilized within the bulk (Fig. 1D).

Grazing-incident x-ray diffraction (GIXRD) was performed to investigate the crystal variation from the top surface (*1*). In the control perovskite film, a shift of (200) plane toward smaller diffraction peaks was observed by varying the grazing incident angle from 0.4° to 4° (Fig. 1E), whereas negligible changes occurred in the HVCD films (Fig. 1F). Similar results were obtained for the (100) planes (fig. S1). Conventional x-ray diffraction (XRD) of the control perovskite film (fig. S2) revealed a broadening diffraction peak corresponding to the (100) plane of cubic $FAPbI_3$, along with a shoulder peak at 28.15° associated with the (004) plane. These observations indicated the emergence of a tetragonal phase, which we attributed to the aggregation of MACl (*1*). In HVCD perovskite films, sharp and symmetric diffraction peaks of (100) and (200) planes were observed with no shoulder present.

Time-of-flight secondary-ion mass spectroscopy (ToF-SIMS) was further utilized to investigate the spatial vertical distribution of Cl^- anions. In the control film, pronounced Cl accumulations on both the top and bottom surfaces were observed (Fig. 1G), whereas throughout the HVCD films the distribution of Cl was uniform (Fig. 1H). These findings provided further evidence of the vertical inhomogeneity and surface accumulation of Cl in the control film, accounting for the distinct emission peaks from the top and buried surfaces in SSPL (Fig. 1A) and the shift of the diffraction peaks in GIXRD (Fig. 1E).

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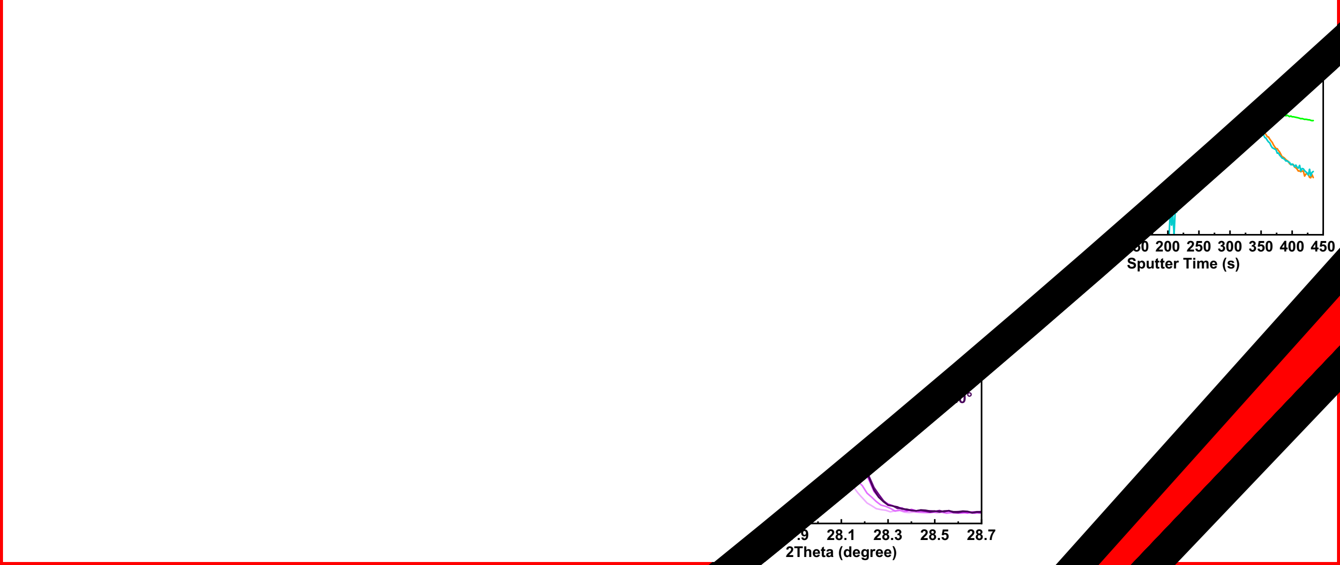

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K$^+$ cations with [redacted] ace to the substrate [redacted] avior was likely attrib- [redacted] alt in perovskite precursor, [redacted] saturation increased (table S1). [redacted] and K$^+$ in were further validated [redacted] ults (fig. S4 and table S2). The weight [redacted] it percent, which was quantified by induc- [redacted] mass spectrometry (fig. S5).

[redacted] f PB in the perovskite formation, XRD was [redacted] PbI_2-MACl systems both with and wi [redacted] ence of PB, the XRD pattern of [redacted] 0) peak at 14.1° (fig. S6A) [redacted] ration resulting fro [redacted]

Atomic force micro [redacted] (fig. S9). The enh [redacted] prolong the ch [redacted]

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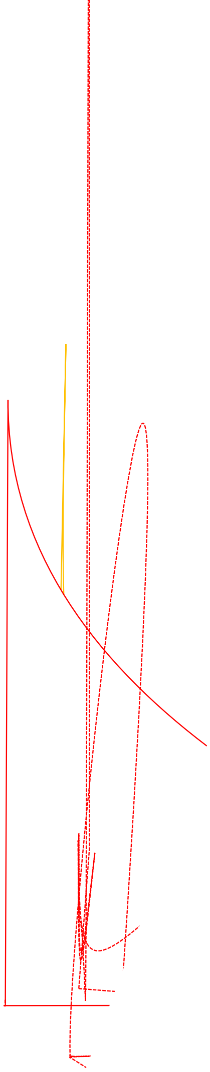
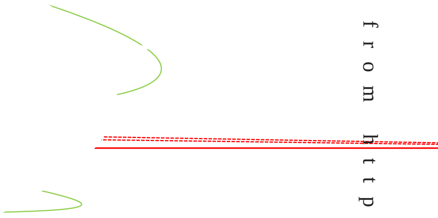
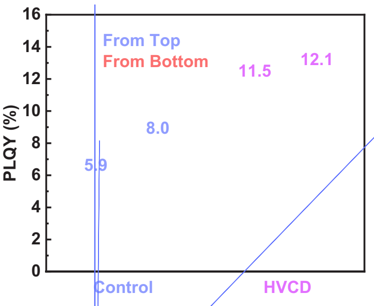
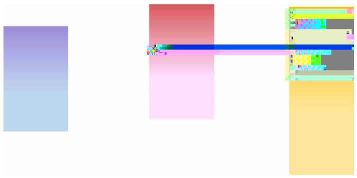





16
14
12
10
8
6
4
2
0
PLQY (%)
From Top
From Bottom
11.5
12.1
8.0
5.9
Control
HVCD



while annealing the perovskite in ambient air with the relative humidity of 30 to 40%, which is a general procedure for MACl-containing perovskites (3 , 3). The performance of HVCD device was also better than that of the control (fig. S16A and table S10), although it was inferior to that of the devices processed in a nitrogen environment. We tested other alkali metal oxalates as an alternative additive, and a similar beneficial effect was validated using sodium oxalate (fig. S16B and table S11). The enhanced performance of HVCD devices primarily originated from the improvements in $_{OC}$ and the fill factor ( ), reaching values of 1.195 V and 85.6%, respectively, both approaching 95.6% of their theoretical limit (3 , 3). The short-circuit current densities ( ) of the control and HVCD devices were 26.4 mA cm^{-2} and 26.6 mA cm^{-2}, respectively, consistent with the external quantum efficiency (EQE) results (fig. S17). Additionally, the reproducibility of the HVCD strategy was confirmed across multiple device batches fabricated under varying external conditions (fig. S18).

We sent our champion devices to two accredited third-party institutions, the National Photovoltaic Industry Measurement Test Center (NPVM) and the National Institute of Metrology (NIM), for independent certifications. Both of the certified steady-state PCEs were 27.2% from NPVM (device area/measured mask area: 0.108 cm^2/0.074 cm^2) and NIM (device area/measured mask area: 0.135 cm^2/0.108 cm^2) (figs. S19 and S20). Also, PCEs of 26.4 and 26.2% from reverse and forward scans, respectively, have been achieved in the HVCD device with an active area of 1 cm^2 (fig. S21).

The presence of free Cl^- anion at interfaces and grain boundaries could introduce instability, which accelerated performance degradation over time under harsh conditions (*40*). We therefore measured the device stability under various conditions, including shelf stability, photo/thermal stability, or a combination thereof. Unencapsulated HVCD devices maintained 98.8% of their original PCE after >3000 hours in dark under an N_2 environment (fig. S22). The HVCD devices without reflection and encapsulation maintained 86.3% of their original PCE [26.6% measured at room temperature (RT)] after 1529 hours of MPPT under 1 Sun illumination (100 mW/cm^2) at 40~50°C in an N_2 environment, outperforming the control which retained only 73.0% (initial PCE of 25.9% measured at RT) (Fig. 4C and fig. S23).

To further confirm the improved stability after HVCD, we investigated the accelerated aging stability including thermal (85°C) and photothermal stability (MPPT at 85°C) of the devices. The HVCD device showed a T_{85} lifetime of 750 hours (initial PCE of 26.5% measured at RT) after 85°C aging, which was better than the control (initial PCE of 25.8% measured at RT) with 497 hours (Fig. 4D and fig. S24). By analyzing the behavior of the unpassivated devices upon 85°C aging (fig. S25), the performance decay in the passivated control device (Fig. 4D) was mainly caused by the degradation of both the perovskite and passivators, whereas the decline in the passivated HVCD device was mainly attributed to the passivators. As a result, we removed the passivation layer and then reevaluated the photothermal stability. The unpassivated HVCD device maintained 82.8% of its initial PCE (24.6%, measured at RT) after 1000 hours MPPT at 85°C, whereas the unpassivated control device degraded to 66.5% (initial PCE of 23.6% measured at RT) (Fig. 4E and fig. S26). From these results, it is unambiguous that the HVCD strategy enhanced both the device efficiency and stability by stabilizing the Cl with the formation of KCl and homogenizing the distribution of Cl^- anions that mitigated halide segregation.

Discussion

A PCE of >27% for perovskite solar cells with promising stability was obtained through the HVCD strategy. To further approach the theoretical limit of $FAPbI_3$ systems, we could focus on two aspects: (i) Although improved homogeneity of Cl distribution in the perovskite film was achieved by the HVCD strategy, further optimizations are required to achieve even more uniform phase distribution and reduced spatial heterogeneity. (ii) Although the defect density was reduced to 10^{13} cm^{-3} in the top surface, the buried interface still has a defect density as high as 10^{15} cm^{-3}, which requires a method to further reduce the buried interface defects.

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SUPPLEMENTARY MATERIALS

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Materials and Methods; Supplementary Text; Figs. S1 to S26; Tables S1 to S11;
References (. –); Movie S1

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