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Elucidating compositional differences in halide perovskites for normal and inverted perovskite solar cells

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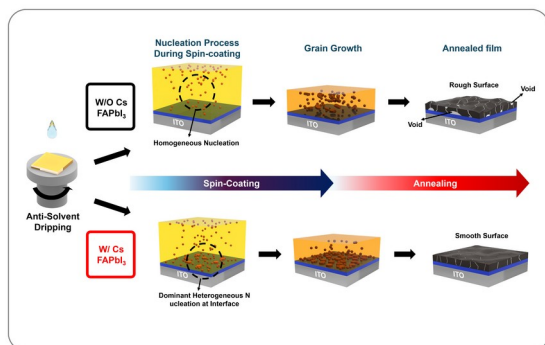
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Abstract

Over the recent few years, extensive research efforts have shifted from normal (n-i-p) to inverted (p-i-n) perovskite solar cells (PSCs), owing to their promising efficiency and operational stability, enabled by low-temperature processing. Despite a fundamentally identical operation principle (only structurally inverted), the optimized perovskite compositions for normal and inverted PSCs differ significantly across the literature, suggesting an underlying design principle for perovskite composition. Here, we unveil the role of cesium cation in enhancing interfacial contact between the perovskite layer and the underlying hole-transporting layer (HTL) in inverted PSCs. Comprehensive in situ and device characterization reveal that cesium incorporation promotes the formation of initial nucleation seeds for heterogeneous nucleation at the perovskite/hydrophobic HTL interface, thereby improving their contact. The resulting compositional heterogeneity explains the focus of recent studies on resolving this issue. This study provides mechanistic insight into designing perovskite compositions to further enhance the performance and longevity of PSCs.

TOC GRAPHICS



In recent years, inverted perovskite solar cells (PSCs) with a p-i-n architecture have attracted significant attention, with rapid progress in power conversion efficiency (PCE) catching up to that of their conventional n-i-p structured counterparts. With the certified PCE of 26.7%¹, their superior stability and low-temperature processability make them a compelling alternative to regular n-i-p structured devices². The development of p-type charge-transporting materials, optimized perovskite compositions, and passivation materials has significantly contributed to the recent breakthroughs in inverted PSCs.³⁻⁶

As inverted PSCs become the mainstream of reported PSCs, a common practice is emerging to achieve high-performance inverted PSCs. Browsing through the literature, we noted widespread practice in designing perovskite compositions for inverted PSCs, distinctive relative to those for regular n-i-p structured PSCs (**Figure 1a** and **Table S1**)^{1, 5-23}. The inverted PSCs predominantly utilize A-site composition modulation in formamidinium lead triiodide (FAPbI₃)-based perovskites, particularly by incorporating FA-Cs alloyed compositions; methylammonium (MA⁺) incorporation has mainly been avoided due to their volatility and phase instability^{24, 25}. Incorporating Cs⁺ at the A-site is known to optimize lattice tolerance factors, thereby enhancing structural stability and device performance^{24, 26}. However, this approach often entails bandgap widening and lattice microstrain, which adversely affect stability and efficiency.^{27, 28} As a result, the conventional n-i-p PSCs typically rely on nearly pure FAPbI₃ compositions without Cs⁺ incorporation.²⁷ While its necessity is widely acknowledged, the underlying mechanisms through which Cs⁺ affects device performance in inverted PSCs remain poorly understood.

In this study, we employ in-situ techniques to investigate the effect of Cs⁺ on perovskite formation and crystallization dynamics, with a focus on its role in enhancing interfacial contact and film morphology in inverted PSCs. Incorporating Cs⁺ reduces the nucleation energy barrier, facilitating the formation of α -phase seeds and promoting heterogeneous nucleation at the perovskite-HTL interface. This leads to enhanced interfacial contact and superior film morphology, effectively reducing voids to facilitate charge transfer, as confirmed by transient photocurrent and time-resolved photoluminescence (PL) measurements. The unraveled role of Cs⁺ should provide insight into the design of perovskite compositions to further enhance the performance and longevity of PSCs.

Figure 1a illustrates the evolution of certified efficiencies in single-junction perovskite solar cells (PSCs), categorized by n-i-p (normal structure) and p-i-n (inverted structure) architectures. A thorough review of perovskite compositions from the literature on record-setting certified efficiencies reveals distinct differences in A-cation compositions between the two types of configurations (see **Table S1** for detailed perovskite compositions). For normal structure devices, the perovskite composition shows a clear trend towards pure FA-based perovskites with a minimal amount of MA (typically <1%) to secure phase stability and sustain the ideal bandgap of pure α -FAPbI₃ (optical bandgap $\approx$ 1.54 eV), essential for achieving high-performance devices. In contrast, devices with inverted structure prevalently utilize compositions that incorporate the Cs⁺ (in the range of 5~10%) cation into FAPbI₃. Despite the inherent challenges of microstrain and bandgap widening^{27,28}, the widespread utilization of Cs⁺ in the perovskite composition of inverted PSCs appears crucial.

To confirm the distinctive role of Cs⁺ cation for both normal and inverted structures, we fabricated the model devices based on the perovskite compositions without and with 10 mol% Cs⁺ cation (pure FAPbI₃ or Cs_{0.1}FA_{0.9}PbI₃ composition, both with a 30 mol% MACl additive) deposited via a one-step spin-coating process with diethyl ether antisolvent dripping followed by two-step thermal annealing (100 °C for 5 min under N₂ and 150 °C for 10 min under 15 % RH).²⁹ The device structures for the normal (ITO/SnO₂/perovskite/spiro-MeOTAD) and inverted (ITO/2PACz/perovskite/LiF/C₆₀/BCP/Ag) configurations are illustrated in the insets of **Figures 1b and c**, respectively. **Figures 1b and c** show the current density-voltage (*J-V*) curves for both configurations of PSCs, with and without Cs⁺ incorporation. The measured photovoltaic parameters are summarized in **Figure S1 and Table S2**. Incorporating Cs⁺ into normal structure devices does not significantly alter device photovoltaic performance, as evidenced by PCEs of $19.35 \pm 0.49\%$ for 0% Cs⁺ and $19.00 \pm 0.63\%$ for 10% Cs⁺. By contrast, the inverted structure devices exhibit a significant difference in the PCE depending on the presence of Cs⁺: $9.25 \pm 1.94\%$ for 0% Cs⁺ and $18.44 \pm 0.78\%$ for 10% Cs⁺. All the photovoltaic parameters are superior to those incorporating Cs⁺. Such a performance trend is consistently observed with other hole-transporting materials used in inverted PSCs (**Figure S2 and Table S3**). Moreover, a gradual improvement in photovoltaic performance with increasing incorporation of Cs⁺ into the perovskite composition supports the distinctive and crucial role of the Cs⁺ cation in inverted PSCs (**Figure S3 and Table S4**). While the above trends were derived from model devices, the champion inverted FAPbI₃

devices with Cs⁺ incorporated and surface passivation achieve 24.28% PCE (stabilized PCE = 23.83%) under optimized conditions (**Figure S4**).

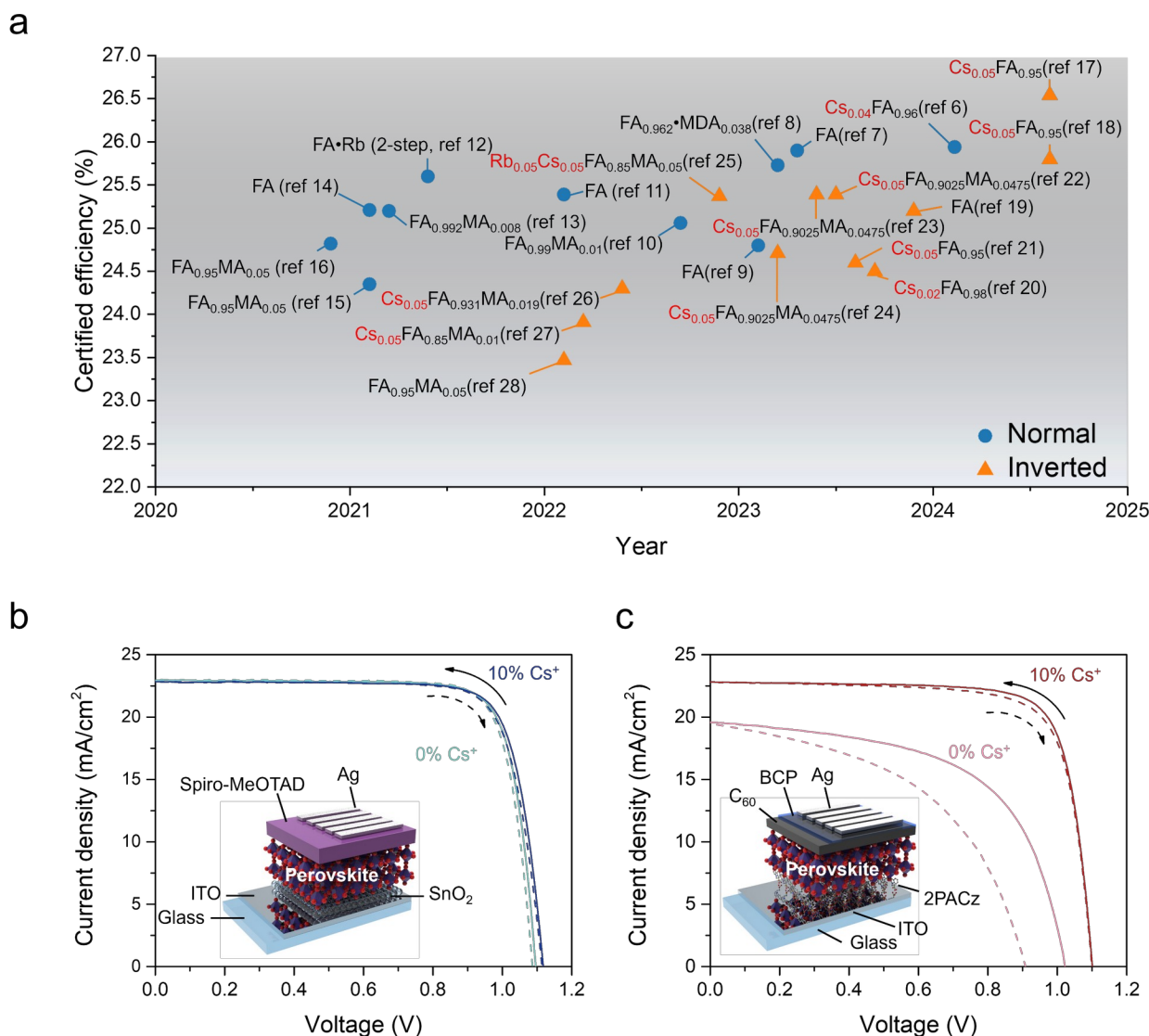


Figure 1. (a) A-site-cation compositions for n-i-p (normal structure, blue circles) and p-i-n (inverted structure, orange triangle) devices with certified record-setting efficiencies. (b and c) Current-voltage (I-V) curves for perovskite solar cells with normal (b) and inverted (c) structures, based on the perovskite compositions without and with Cs⁺ cation (pure FAPbI₃ or Cs_{0.1}FA_{0.9}PbI₃ composition). Insets show device architecture for each configuration. The references corresponding to each data point shown in (a) are listed in **Table S1**.

To investigate the origin of the distinctive performance change in inverted PSCs upon Cs^+ incorporation, we first conducted scanning electron microscopy (SEM) to examine differences in the morphology of the perovskite films in the devices. **Figure 2a–c** presents surface, cross-sectional, and buried interface SEM images of perovskite films with 0% and 10% Cs^+ incorporation, fabricated on the ITO/2PACz substrate. We carefully peeled off the perovskite layer to expose the buried bottom surface using previously reported methods (**Figure S5a**).^{30,18} The SEM images reveal significant morphological differences resulting from the incorporation of Cs^+ . The film's top surface with 0% Cs^+ shows the sparse presence of voids (**Figure 2a, left**). The void exists across the cross-section, and a larger number was observed at the buried bottom surface (**Figure 2b and c, left**). In contrast, morphological improvements were observed with 10% Cs^+ incorporation, with no voids evident on either the top or the buried bottom surfaces. The observed voids decrease with increasing Cs^+ amount, indicating a close correlation between Cs^+ incorporation and morphological change (**Figures S5b–e and S6**). This void-suppressing effect was similarly observed in perovskite films deposited on alternative HTLs such as [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic Acid (MeO-2PACz), [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic Acid (MeO-4PACz), and Poly(triaryl amine) (PTAA) (**Figure S7 and S8**), suggesting that the morphology-enhancing role of Cs^+ is not limited to 2PACz but is broadly applicable across inverted device architectures. However, such morphological differences were not observed in conventional normal structure devices regardless of Cs^+ incorporation. Both surface and cross-sectional SEM images of perovskite films on the SnO_2 underlying layer show no noticeable morphological variation, and no voids are observed in either condition (**Figures S9 and S10**). It should be noted that evaporated carbazole-based SAMs typically exhibit denser molecular packing and more uniform surface potential compared to solution-processed SAMs, leading to improved surface wettability and interfacial energy distribution^{41–43}. Nevertheless, Cs^+ is consistently incorporated in both types of SAM-based perovskite solar cells, regardless of the deposition method, implying its universal role in promoting enhanced interfacial contact. Although fabrication parameters may influence film formation to some extent, under identical processing conditions, the occurrence of voids appears to be inherent to the inverted device architecture, and the incorporation of Cs^+ effectively suppresses poor interfacial formation.

Since the voids at the buried 2PACz/perovskite interface in the Cs^+ -free films were particularly severe, we examined how this interfacial defect affects charge-carrier transport within the device. To do

this, we first performed time-resolved photoluminescence (TRPL) decay measurements using a 405 nm laser directed at the ITO glass (see **Figure 2d**) to verify the carrier dynamics. The fast-decaying τ_1 component, responsible for the charge transfer from the perovskite to the underlying HTL^{31,32}, was 0.14 ns for the 10% Cs⁺ film, which is faster than the 0.23 ns for the 0% Cs⁺ film. TRPL measurements further validated this trend on perovskite films incorporating increasing concentrations of Cs⁺ (0%, 2%, 5%, and 10%) (**Figure S11 and Table S5**). The fast decay component (τ_1), associated with interfacial charge transfer to the hole transport layer, decreased from 0.23 ns (0% Cs⁺) to 0.17 ns (2% Cs⁺), 0.16 ns (5% Cs⁺), and 0.14 ns (10% Cs⁺). As the Cs⁺ content increases, the gradual improvement in film morphology and interface quality correlates with enhanced charge transfer from perovskite to HTL layer (**Figures S5 and S6, and Tables S5 and S6**). This trend may reflect more efficient interfacial charge extraction, although contributions from enhanced non-radiative recombination at interface defects cannot be excluded. The average carrier lifetime (τ_{avg}) also decreased from 2.54 ns to 1.20 ns with 10% Cs⁺ incorporation, suggesting improved charge extraction through better interfacial contact. Additionally, transient photocurrent (TPC) decay measurements were performed using the complete device architecture (**Figure 2e, Figure S12, and Table S6**). The 0% Cs⁺ device exhibits a decay time of 3.26 μs , more than threefold slower than 0.95 μs observed for the 10% Cs⁺ device, indicating that the presence of voids at the interface between perovskite and charge-transporting layers hinders the collection/extraction of photo-generated carriers in the device with 0% Cs⁺.

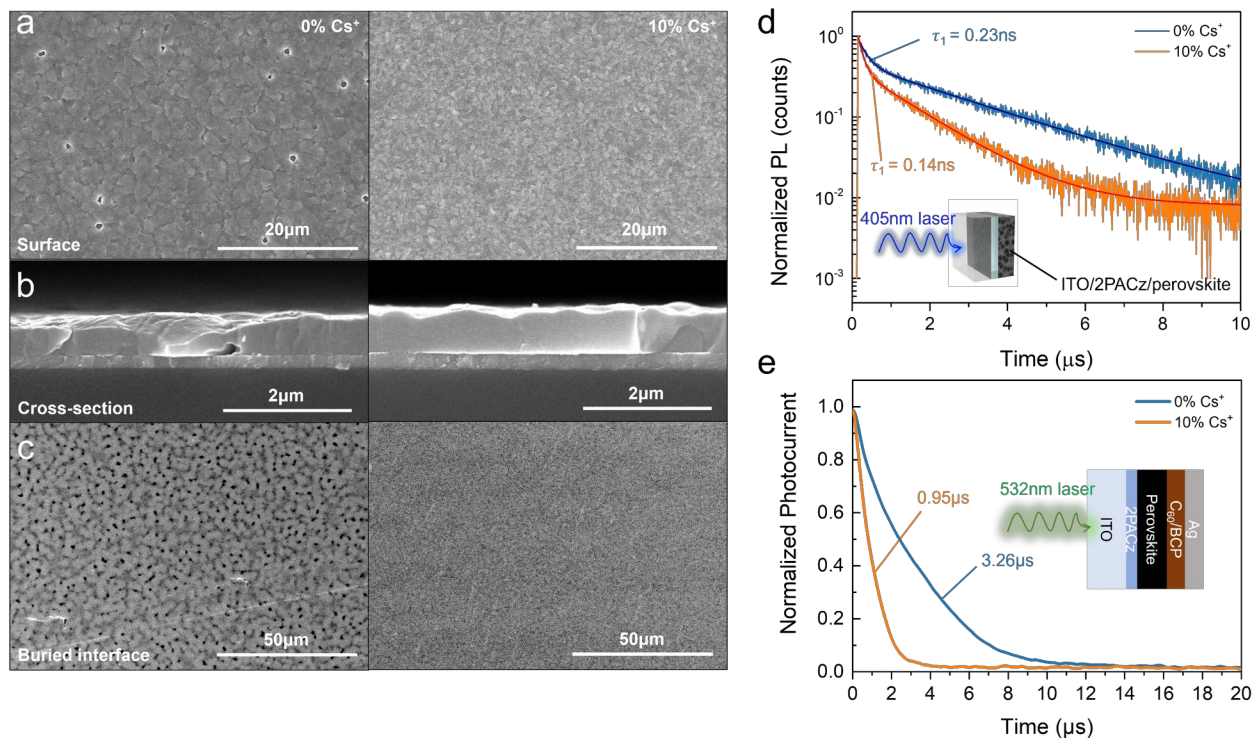


Figure 2. Scanning electron microscopy (SEM) images of perovskite films with 0% and 10% Cs⁺ incorporation fabricated on an ITO/2PACz substrate: (a) top surfaces, (b) cross-sections, and (c) buried bottom surfaces. (d) Normalized time-resolved photoluminescence (TRPL) decay of perovskite films with 0% and 10% Cs⁺. The inset depicts the film structure with 405 nm laser incidence from the ITO/2PACz substrate. (e) Normalized transient photocurrent decay curves of perovskite films with 0% and 10% Cs⁺ obtained within the complete inverted PSC device architecture.

To elucidate the mechanisms driving the observed morphological differences resulting from Cs⁺ incorporation, we performed in situ photoluminescence (PL) coupled with grazing-incidence wide-angle X-ray scattering (GIWAXS) during perovskite film formation, using a customized setup that replicates the device fabrication environment (**Figure 3a**). The antisolvent (diethyl ether) was introduced approximately 10 seconds after the initiation of the spin-coating process to promote crystallization. **Figure 3b** displays the in-situ PL spectra during the film formation with Cs⁺ incorporation from 0% to 10%. After the anti-solvent dropped, the immediate, though weak, appearance of a PL signal around 1.76 eV likely originates from quantum-confined nanocrystalline α-phase perovskite nuclei.^{29, 33} A gradual red shift to approximately 1.63 eV over time reflects the nuclei growth process (see **Figure S13**

for individual PL spectra). The relatively low PL intensity with 0% Cs⁺ throughout the spin-coating process indicates a lower nuclear density than in the 10% Cs⁺ film. It is supported by the corresponding photographs and GIWAXS (discussed below). The higher initial PL intensity, followed by a pronounced increase with 10% Cs⁺, indicates the formation of more rapid and robust α -phase nuclei in the film (**Figure 3b**). This observation is further supported by the composition- and time-dependent evolution of PL intensity extracted from the in-situ PL spectra (**Figure S14b**). Notably, the evolution of the PL peak energy reveals a transient blue shift in the 5% and 10% Cs⁺ incorporated perovskite films, occurring at approximately 12 ~ 13.6 s and 17 ~ 18 s, respectively, followed by a gradual red shift (**Figure S14a**). The gradual red shift is attributed to the growth of quantum-confined α -phase nuclei into larger domains with reduced confinement.³³ The transient blue shift observed with higher Cs⁺ contents might indicate the formation of a Cs⁺-rich phase with a relatively higher bandgap. This feature likely arises from kinetically induced compositional redistribution of Cs⁺ toward the early-formed nuclei during rapid solvent extraction, which transiently enriches the local composition with Cs⁺. Consequently, this feature is absent from the 0% Cs⁺ film. **Figures 3c** illustrate in-situ GIWAXS measurement data, which concurrently track the formation of crystallographic phases during the spin-coating process. In the 0% Cs⁺ film, the non-perovskite hexagonal δ -phase scattering peak at $q \approx 0.84 \text{ \AA}^{-1}$ forms immediately after antisolvent dripping and persists as the dominant phase throughout the spin-coating duration.^{29, 33} We note that the PL signal observed for 0% Cs⁺ in **Figure 3b** likely corresponds to the initial nucleation stage of a small fraction of α -phase seed formation, which is expected to exist in a nanocrystalline polymorphic structure at this stage, with a certain amount of α -phase present as nuclei that are less ordered and less extensive than a fully developed perovskite lattice.^{29, 33, 34} On the other hand, the 5% and 10% Cs⁺ films exhibit a noticeable signal from the α -phase ($q \approx 0.99 \text{ \AA}^{-1}$). The intensity of the α -phase gradually increases with higher Cs⁺ content in the composition (**Figure 3c**). The insets in **Figure 3b** display the as-spun perovskite films ranging from 0% to 10% Cs⁺ incorporation. The darker appearance of the as-spun 10% Cs⁺ film relative to the 0% Cs⁺ one suggests a higher density of α -phase formation, correlating with PL and GIWAXS measurements. The differentiated phase-formation process is evident in the integrated peak area calculated from in-situ GIWAXS (**Figure 3d**). For the 0% Cs⁺ film, the integrated peak area of the δ -phase gradually increases. In contrast, the 10% Cs⁺ film shows a gradual increase in the α -phase peak area, along with a simultaneous decrease in the δ -phase peak. The promotion of the α -phase formation in the 10% Cs⁺ film is attributed to the facilitation of perovskite

phase formation by the smaller Cs^+ cation incorporation, reducing the tolerance factor of FAPbI_3 , thereby driving α -phase stabilization at room temperature.^{24, 26}

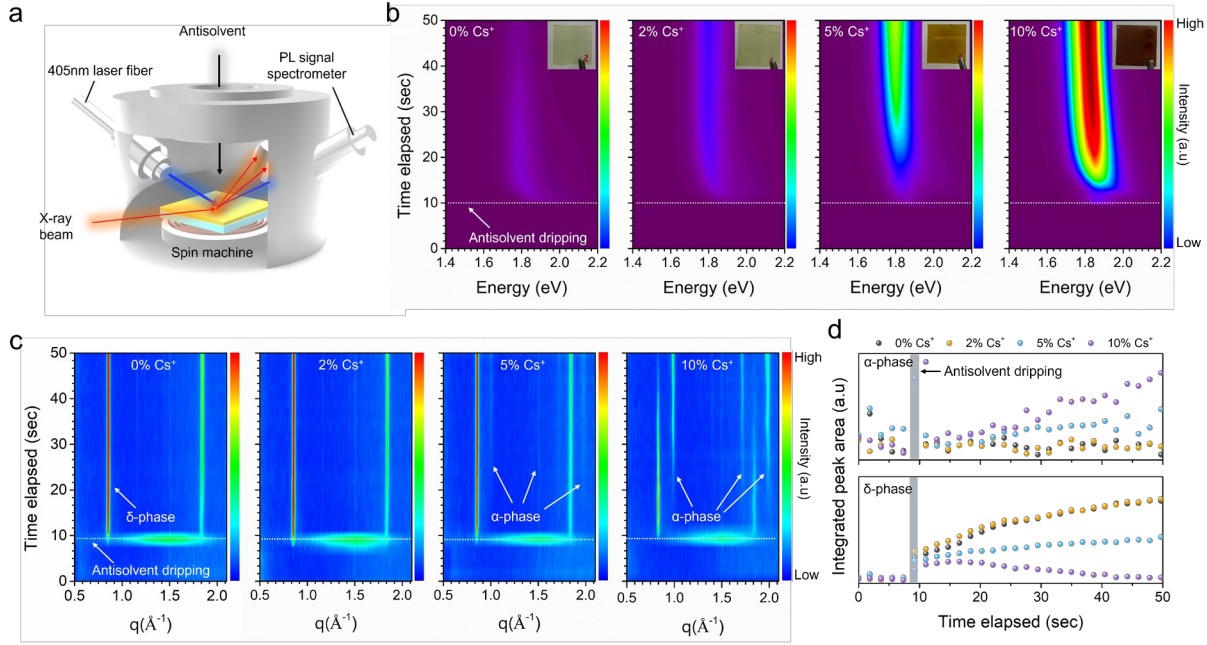


Figure 3. In-situ investigations on the crystallization of perovskite films with varying Cs^+ incorporation during the spin-coating process on an ITO/2PACz substrate. (a) Schematic illustration of the custom-built setup enabling simultaneous in-situ PL and GIWAXS measurements with antisolvent dripping. (b) In-situ PL spectra of as-spun films with 0%, 2%, 5%, and 10% Cs^+ incorporation, together with corresponding photographs of the as-spun perovskite films (insets). (c) In-situ GIWAXS patterns of perovskite films with different Cs^+ contents, showing the transition from δ -phase to α -phase. (d) Integrated peak areas of α - and δ -phases extracted from in-situ GIWAXS, highlighting that Cs^+ incorporation promotes early α -phase nucleation while suppressing δ -phase persistence.

To further investigate how Cs^+ incorporation influences the morphology and interfacial contact of the perovskite film in inverted PSCs, we examined the formation of nuclei depending on the Cs^+ content (**Figure 4**). To locate the formed nuclei during the spin-coating process, steady-state PL measurements were performed, with the samples excited through the top and bottom surfaces of the as-spun films using a 405 nm laser (**Figure 4a**). As shown in **Figure 4b**, the steady-state PL measurements reveal a notable difference in PL intensity measured from the top (surface) and bottom (buried interface) sides, depending on the Cs^+ content. For the 0% and 2% Cs^+ films, the top side exhibits PL intensity

comparable to or higher than that of the bottom side. In contrast, the bottom-side PL intensity is higher than the top-side PL intensity for films with 5% and 10% Cs⁺. The progressively increased PL intensity from the bottom surface indicates that the nucleation density of the α -phase at the buried interface rises with Cs⁺ incorporation. This finding suggests that Cs⁺ incorporation facilitates heterogeneous nucleation of α -phase domains at the HTL/perovskite interface (inset of **Figure 4b**). The nucleation energetics underlying these observations can be rationalized by Gibbs free energy considerations (**Figure 4c**). In classical nucleation theory, the barrier for heterogeneous nucleation ($\Delta G_c^{\text{hetero}}$) is relatively lower than that of homogeneous nucleation (ΔG_c^{homo}). This results in a smaller critical radius (r_c) of stable nuclei formed at the substrate surface. Due to the enhanced surface energy contribution, the smaller nuclei resulting from heterogeneous nucleation are likely to form as the α -phase.³⁵ As Cs⁺ content increases, the heterogeneous nucleation of the stabilized α -phase seems to be further promoted, which might contribute to improved interfacial contact between perovskite and substrate. The schematic in **Figure 4d** summarizes these findings: Cs⁺-free films have sparse interfacial nuclei that turn into voids, whereas Cs⁺ incorporated films display dense α -phase nuclei at the 2PACz/perovskite interface, forming compact and void-free morphology of the annealed film. The heterogeneous nucleation of Cs⁺ incorporated α -phase and facilitated Cs⁺ diffusion during the growth stage might result in a Cs⁺ rich phase observed at the interface between the perovskite and substrate. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) performed in our study also reveals Cs⁺ accumulation at the bottom interface of the perovskite layer, consistent with findings from a previous study (**Figure S15**, Note that formation of Cs⁺ rich phase might influence interfacial energetics and impact p-i-n structured devices; the interfacial morphology change seems to be a major factor causing performance difference observed in our study).⁶ Although perovskite crystallization has typically been described as a top-to-bottom growth process in previous reports^{36, 37}, such a unidirectional pathway does not sufficiently explain the enhanced interfacial contact observed here. We therefore suggest that crystallization in Cs⁺ incorporated films proceeds via concurrent top-to-bottom and bottom-to-top growth, where interfacial heterogeneous nucleation plays a pivotal role in establishing intimate contact at the HTL/perovskite interface.

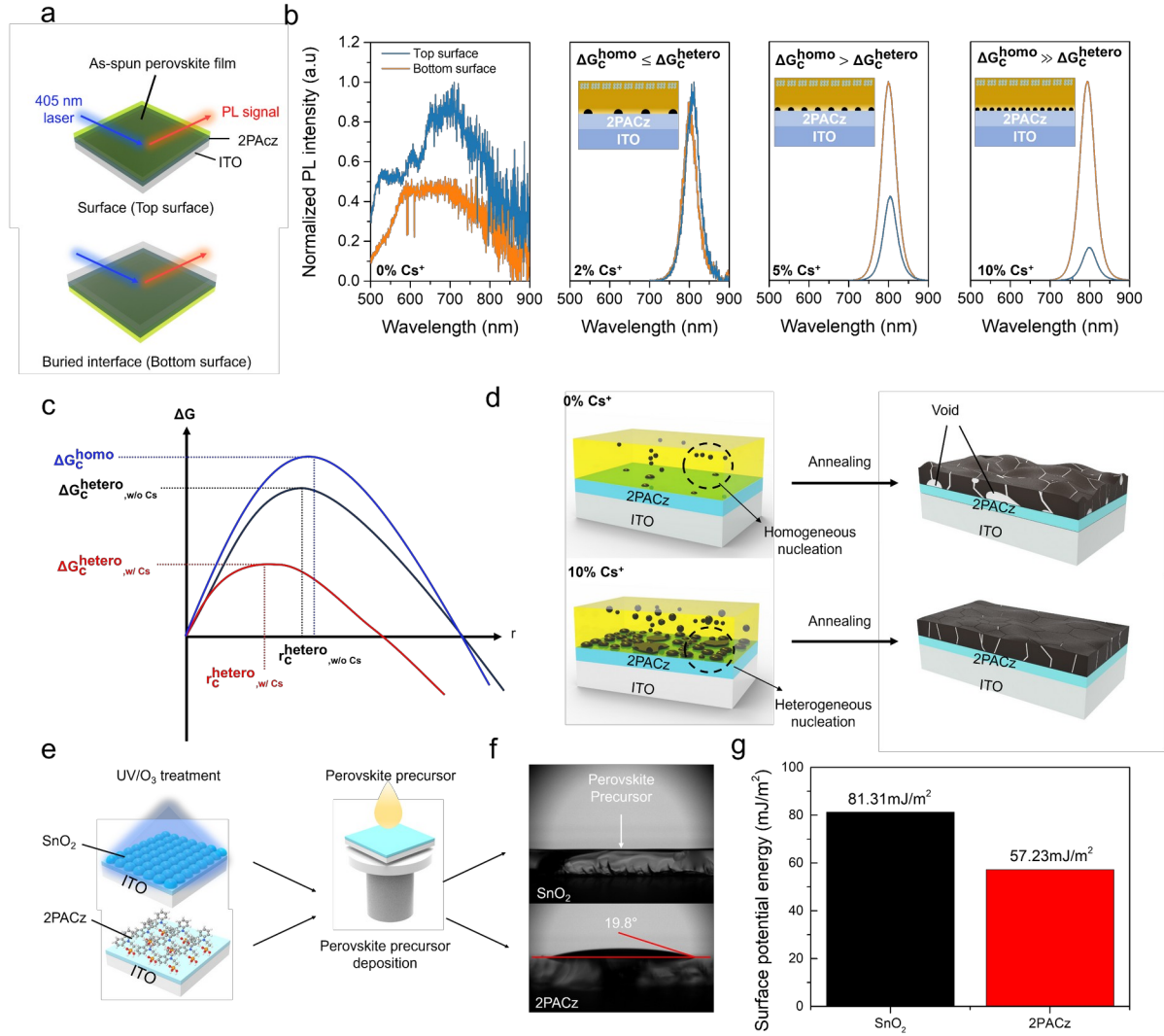


Figure 4. (a) Schematic illustration of steady-state PL measurement with excitation from the top (surface) or bottom (buried interface) side of the as-spun perovskite film. (b) Steady-state PL spectra of perovskite films with varying Cs^+ contents (0-10%), measured from the top and bottom sides. (c) Gibbs free energy diagram for homogeneous and heterogeneous nucleation cases, where ΔG_c^{homo} and $\Delta G_c^{\text{hetero}}$ represent the critical Gibbs free energies for each nucleation pathway, and r_c^{homo} and r_c^{hetero} are the corresponding critical radii. (d) Schematic illustration of the nucleation process for 0% and 10% Cs^+ incorporated films and the resulting film morphology after annealing. (e) Schematic illustration of perovskite precursor deposition on SnO_2 and the 2PACz charge transport layer for the spin-coating process. (f) Contact angle measurement for a perovskite precursor on SnO_2 (UV/ O_3 treated) and 2PACz layers, indicating surface wettability. (g) Calculated surface potential energy profiles for UV/ O_3 -treated SnO_2 and 2PACz layers.

To elucidate the driving factors behind the promoted heterogeneous nucleation upon Cs^+ incorporation, we assessed whether changes in the precursor solution's wettability could account for it. The Cs^+ incorporation does not induce significant variation in contact angle across different HTLs (**Figure S16**), suggesting that the effect does not originate from altered wettability. DFT calculations further support this conclusion: the binding energy between Cs^+ and 2PACz (0.71 eV, dipole moment 8.51 D) is weaker than that of FA^+ (1.02 eV, 14.6 D), and the interfacial binding energy of Cs^+ incorporated FAPbI with 2PACz (0.71 eV) is also lower than that of pure FAPbI₃ (0.90 eV) (**Figure S17**). These results demonstrate that Cs^+ does not improve the chemical interaction of the perovskite layer and the underlying HTL.

To identify alternative driving factors, we investigated the solubility of precursors with varying Cs^+ contents—FAPbI₃ (0% Cs^+), $\text{FA}_{0.5}\text{Cs}_{0.5}\text{PbI}_3$ (50% Cs^+), and CsPbI_3 (100% Cs^+). We observed that increasing Cs^+ content decreases precursor solubility, with higher Cs^+ fractions exhibiting reduced miscibility and visible precipitation upon mild disturbance (**Figure S18**). Moreover, under slow solvent evaporation, 10% Cs^+ solutions yielded dense black α -phase crystals, while Cs^+ -free solutions left only amorphous white residues (**Figure S19**). XRD analysis confirmed that the formed crystals with Cs^+ incorporation exhibited a dominant (002) diffraction peak originating from α -phase perovskite (**Figure S20**). These results indicate that Cs^+ incorporation promotes local supersaturation and facilitates the nucleation of the α -phase. Thus, the enhanced supersaturation might lower both ΔG_c^{homo} and $\Delta G_c^{\text{hetero}}$ while the reduced $\Delta G_c^{\text{hetero}}$ critically improves the interfacial contact between the perovskite and the underlying substrate.

Given the contrasting impact of Cs^+ incorporation, significantly enhancing performance in inverted structured devices while having minimal effect in normal structured devices, we sought to investigate the mechanisms underlying these differences. **Figure 4e** provides a schematic illustration of the conventional surface treatments applied before perovskite precursor deposition in normal and inverted PSCs. In normal PSCs, the SnO_2 layer is typically treated with UV/ozone (UV/ O_3) or plasma to enhance surface energy and thus the wettability of the perovskite solution, resulting in an extremely low contact angle of the perovskite solution, as shown in the top panel of **Figure 4e**. In contrast, UV/ O_3 or plasma treatment is hardly applicable to substrates coated with organic HTLs for inverted PSCs, as these treatments can damage the HTL layer. Moreover, organic HTLs with aromatic ring functional groups

typically exhibit hydrophobic properties. Unlike the surface-treated SnO₂ layer, the perovskite solution consequently shows a higher contact angle on the 2PACz/ITO substrate (**Figure 4f**). The quantitative analysis of the surface energy revealed a higher surface energy of 81.31 mJ/m² for the SnO₂-coated substrate than 57.23 mJ/m² for the 2PACz-coated substrate (**Figure 4g**). Additionally, we also measured MeO-2PACz to compare the wetting properties of the SAM layer; MeO-2PACz was found to have a relatively lower contact angle compared to 2PACz (surface potential energy = 63.88 mJ/m²), attributable to the methoxy (-OCH₃) groups and a short alkyl chain (C₂H₄) (**Figure S21**).³⁸ We found that differences in wetting properties determine the quality of interfacial contact between the perovskite layer and the underlying charge transport layer (**Figure S22**). Consequently, the poor interfacial contact from the 2PACz layer is attributed to its low surface energy, which raises the nucleation energy barrier and ultimately reduces the nucleation rate and the number of nuclei formed, as evidenced by the low PL intensity and thus initial nucleation rate observed in the in-situ PL results.³⁹ (**Note S1** and **Figure S23**). While the hydrophobic surface of the 2PACz layer and thus higher $\Delta G_c^{\text{hetero}}$ promotes improved crystallinity of perovskite phases and the growth of larger grain sizes⁴⁰ (**Figures S24, S25, and S26**), the reduced wettability poses challenges for heterogeneous nucleation and interfacial contact in the absence of Cs⁺ (**Figure S24**). As described in **Supplementary Note 1**, the SnO₂ layer in normal PSCs has intrinsically high surface energy and good wettability, corresponding to a small contact angle (θ) that minimizes the correction factor ($\varnothing$) for $\Delta G_c^{\text{hetero}}$. This intrinsically lowers the $\Delta G_c^{\text{hetero}}$, making nucleation at the SnO₂ interface favorable even in the absence of Cs⁺ incorporation. In contrast, at the hydrophobic 2PACz interface of inverted devices, Cs⁺ is required to reduce the nucleation barrier, thereby improving morphology.

Previous studies have shown that during one-step solution processing, rapid crystallization at the film–air interface forms a dense top shell that traps high-boiling-point solvents, such as DMSO, within the film bulk, which are slowly released during annealing, leading to the formation of interfacial voids and accelerated film degradation³⁷. To quantitatively analyze the DMSO content in perovskite films, ¹H NMR spectroscopy was performed on samples prepared on SnO₂ and 2PACz substrates with and without Cs⁺ incorporation (**Figure S27**). All perovskite films were thermally annealed at 100 °C for 10 min, carefully scraped from the glass substrates with stainless steel razors, dissolved in deuterium oxide (D₂O, ≈ 20 mM), and analyzed by 850 MHz NMR spectroscopy⁴¹. The DMSO content was determined from the integrated proton signals of DMSO and FA⁺, normalized by proton number. The quantified DMSO molar

contents relative to perovskite were 0.43 mol% (SnO₂–0% Cs⁺), 0.23 mol% (SnO₂–10% Cs⁺), 0.72 mol% (2PACz–0% Cs⁺), and 0.32 mol% (2PACz–10% Cs⁺). These results indicate that the SnO₂-based films exhibit inherently low DMSO residue regardless of Cs⁺ incorporation, reflecting the efficient DMSO release facilitated by the high-surface-energy SnO₂ interface. In contrast, the hydrophobic 2PACz-based films retain more DMSO when Cs⁺ is absent, while the incorporation of Cs⁺ significantly reduces this residue to a level comparable to that of SnO₂-based films. We therefore speculate that the enhanced heterogeneous nucleation induced by Cs⁺ at the hydrophobic 2PACz interface probably accelerates the formation of quantum-confined α -phase nuclei, thereby occupying interfacial free volume and possibly reducing the space available for DMSO trapping (**Figure S28**). While the heterogeneous nucleation in n-i-p devices is favorable, in p-i-n devices, Cs⁺ lowers the $\Delta G_c^{\text{hetero}}$, promoting both α -phase nucleation and more efficient solvent release at the buried interface. Collectively, these results suggest that Cs⁺ incorporation exerts a multifaceted effect on inverted PSCs. By altering precursor solubility and reducing the heterogeneous nucleation barrier, Cs⁺ enables robust α -phase nucleation at the buried interface, thereby enhancing interfacial contact and solvent trapping (**Figure S29 and Supplementary note 3**). This unified mechanism explains the decisive, structure-specific role of Cs⁺ in inverted architecture, ultimately leading to improved morphology, efficiency, and reproducibility.

In conclusion, we conducted systematic studies combined with in-situ techniques to elucidate the critical role of Cs⁺ in regulating crystallization dynamics, interfacial contact, and film morphology in inverted PSCs. Our findings reveal that Cs⁺ incorporation facilitates the heterogeneous nucleation of α -phase perovskite nuclei at the HTL/perovskite interface by enhancing supersaturation of precursor solution and thus lowering the overall nucleation energy barrier. Enhanced heterogeneous nucleation improves interfacial contact between the perovskite and the HTL and reduces solvent trapping at the interface. These results highlight the importance of integrated design rules for perovskite compositions compatible with inverted PSCs and provide insight into the design of more advanced compositions toward inverted PSCs with higher performance, reproducibility, and scalability for ultimate commercialization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/xx.xxx>.

Experimental details, materials and methods, in-situ PL and GIWAXS data, SEM images, TRPL and TPC analyses, ToF-SIMS depth profiles, NMR spectra, contact angle and DFT calculation results, and supplementary notes, tables, and figures (S1–S30).

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Notes

The authors declare no competing financial interest.

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