

# Resolving Nano-Morphologies: A Pathway to Cross-Grain Homogeneous Cation Distribution in Perovskites

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Recent breakthroughs in the engineering of compositions, microstructures, and phases in perovskite thin films have led to remarkable improvements in both the power conversion efficiencies (PCEs) and the operational stability of perovskite solar cells (PSCs). At the forefront of these developments, state-of-the-art PSCs predominantly rely on formamidinium lead triiodide (FAPbI<sub>3</sub>) as the perovskite absorber, owing to its nearly ideal bandgap, which is highly suitable for efficient light harvesting [1]. However, a significant challenge persists: FAPbI<sub>3</sub> is inherently unstable and prone to phase transitions into non-perovskite structures, which can severely compromise device performance. To mitigate this issue, cesium (Cs) cations are commonly introduced into the perovskite lattice, forming formamidinium-cesium (FA-Cs) mixed-cation perovskites [2]. This approach has proven effective in stabilizing the crystal structure and achieving high-performance PSCs.

Despite these advancements, the long-term stability of Cs-containing perovskites remains a critical concern. One of the primary issues is cation segregation, a phenomenon where Cs cations unevenly distribute in the perovskite film. This cation inhomogeneity not only affects the component integrity but also poses challenges for long term consistent PSC performance. Furthermore, the relationship between the distribution of cation and their direct impact on the PCE and stability of PSCs is still not fully understood. Unraveling this complex interplay is essential for developing strategies to suppress phase segregation and enhance the durability of various perovskite-based devices. Even though efforts by researchers have made strides in addressing these inhomogeneities from the out-of-plane and in-plane FA-Cs cation inhomogeneities of the entire perovskite thin films, the understanding and tailoring of grain-to-grain cation inhomogeneity down to the nanoscale remains elusive, enhancing the grain-to-grain uniformity is essential for advancing the overall performance of PSCs [3,4].

Recent work by Zhou's group has shed light on the

deviations of individual grains from their ideal cationic compositions, which compromise the optoelectronic properties and durability of the layers [5]. They found that the cross-grain cation homogenization was highly related to the thermodynamics-driven morphologic grooving of as-formed GBs. These grooves tend to merge at triple junctions, as schematically illustrated in Fig. 1a, forming trap-like nanostructures on the film surface. These structures segment the surface and create nanoscale traps at grain junctions, which impede cation mixing and contribute to compositional inhomogeneity. The geometry of nanoscale groove traps (nano-GTs) is determined by the interfacial energy relationship. By pre-incorporated butylammonium acetate (BAAC), they decreased the average nano-GT depth from 15.3 nm to 4.4 nm. The incorporated BAAC can enhanced heterointerface energy, then driven the formation of shallowed nano-GT perovskite films. As compared in high-resolution atomic force microscopy (AFM) images of the two samples, more flatten geometry can be observed, illustrating shallowed nano-GTs in the perovskite film (Fig.1 b, c).

Then they conducted cathodoluminescence (CL) microscopy hyperspectrally reveal the relationship of the grain-to-grain cation distribution and the depth of nano-GTs of the perovskite films. The combination usage of scanning electron microscopy (SEM) and the local CL emission mapping in the pristine sample (Fig. 1d, f) illustrates the evident different CL emissions in different grains with the boundary of GBs, which contributed by the cation (FA-Cs) inhomogeneity among the grains. By contrast, no discernible change has been observed in CL emission mapping among grains in the shallowed nano-GT films (Fig.1 e, g), which attests to the  $d_{GT}$  dependence of cation homogenization. Besides, formation of rod-shaped  $\delta$ -CsPbI<sub>3</sub> in the initial perovskite phase impurity has also been suppressed. They proposed a thermodynamic model illustrating how nano-GT depth affects cross-grain cation homogenization in FA-Cs perovskite films. Supersaturation during crystallization causes nucleation and growth of grains

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with varying cation compositions. As the grains merge, cationic interdiffusion leads to homogenization. The surface-dominated microstructure of the film directs interdiffusion across multi-grain surfaces, with nano-GTs acting as traps that hinder cation movement and influence the overall cation distribution across the film (Fig. 1h).

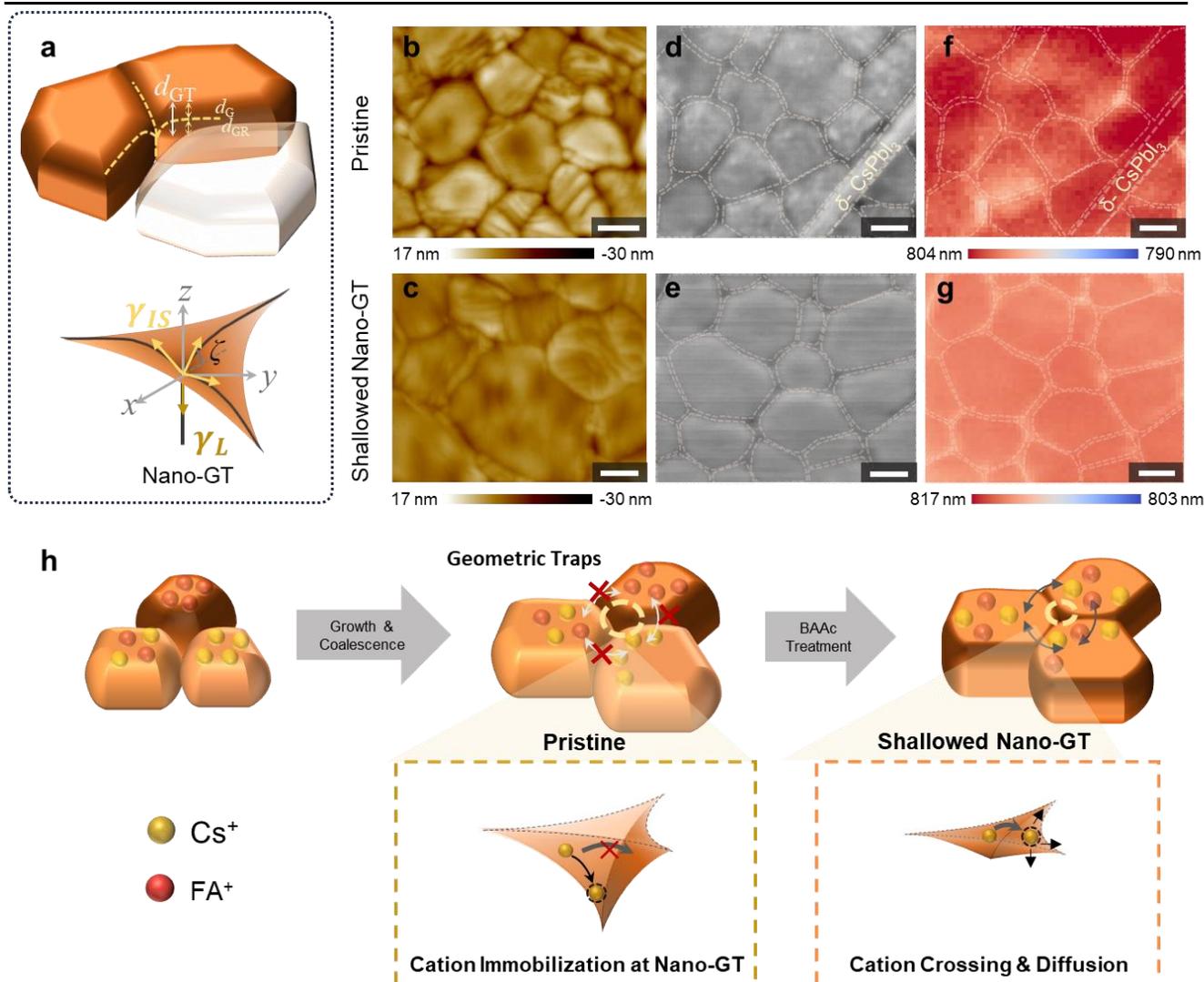
The *p-i-n* PSCs fabricated with shallowed nano-GT not only achieved enhanced power conversion efficiencies (PCE) of up to 25.62% but also demonstrated significantly improved stability under rigorous international testing standards due to the less voids at the buried interface and enhanced FA-Cs homogenization. In the maximum power point (MPP) tracking test conducted with the ISOS-L-11 protocol, the PSCs with shallower nano-GTs retained an impressive 90.2% of their initial PCE after 1000 hours of continuous one-sun-intensity light illumination, outperforming the pristine PSCs, which retained only 80.0% of their PCE after 170 hours. Furthermore, in the thermal cycling test (MQT11) under the IEC 61215:2021 standard, the shallower nano-GT PSCs maintained 95.7% of their initial PCE after 300 thermal cycles, significantly higher than the 74.8% retention observed for the pristine PSCs. Similarly, in the damp heat tests (MQT13) under the IEC 61215:2021 standard, the shallower nano-GT PSCs retained 90.5% of their initial PCE after 1,000 hours, compared to just 42.8% for the pristine PSCs.

This work first represents the correlation between nanoscopic microstructure and atomic-level homogeneity in perovskite films, unlocking the potential to achieve highly efficient and stable PSCs through precise nanoscale control of material properties. This fundamental research provides a novel perspective for advancing PSCs, complementing existing strategies. Beyond the FA-Cs system, the nanoscopic cross-grain compositional engineering demonstrated in this work can also be extended to enhance the homogeneity of metal cations and halide anions in mixed Pb-Sn and mixed I-Br

perovskites, which are critical for the development of tandem devices, pushing the boundaries of photovoltaic efficiency beyond the limits of single-junction devices. This method can also be transferred to large-scale module fabrication, offering a scalable pathway for the industrial production of high-performance PSCs. By integrating this approach with existing manufacturing processes, it is possible to achieve homogenous properties across large-area perovskite films, which is essential for maintaining high efficiency and stability in commercial-scale devices. The ability to precisely control the nanoscale composition and microstructure of perovskite films will significantly reduce performance variations and defects, leading to more reliable and reproducible PSC modules. This breakthrough lays the foundation for next-generation photovoltaic technologies with superior performance, durability, and scalability, driving forward the progress of sustainable energy solutions.

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**Figure 1.** (a) The Schematic illustration of a nano-GT in a typical polycrystalline perovskite film, the 3D view of the line tension equilibrium at the nano-GT, as well as the energy relationship at nano-GT.  $d_{GT}$ ,  $d_g$  and  $d_{GR}$  represent the depth of nano-GT, grain-boundary groove and the groove root, respectively.  $\gamma_{LS}$  and  $\gamma_{TL}$  are the groove root line tension energy and the triple line tension energy of the nano-GTs, respectively.  $\zeta$  is the angle between the groove root and the horizontal film plane. (b, c) AFM images of the microstructure of a pristine perovskite film and the film with shallowed nano-GT, respectively. (d, e) SEM images of pristine and shallowed nano-GT film and the according CL emission mapping (f, g). (h) Schematic illustration of how nano-GT depth influences cation homogeneity in the pristine and shallowed nano-GT film. Adapted from Ref. [2]. Copyright Springer Nature 2025.

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