

The atomic-scale microstructure of metal halide perovskite elucidated via low-dose electron microscopy

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Understanding the atomic-scale crystallographic properties of photovoltaic semiconductor materials such as silicon, GaAs, and CdTe has been essential in their development from interesting materials to large-scale energy conversion industries. However, studying photoactive hybrid perovskites by transmission electron microscopy (TEM) has proved particularly challenging due to the large electron energies typically employed in these studies.[1] In particular, the very close structural relationship between a number of crystallographic orientations of the pristine perovskite and lead iodide has resulted in severe ambiguity in the interpretation of EM-derived information, severely impeding the advance of atomic resolution understanding of the materials.

Here, we successfully image the archetypal $\text{CH}(\text{NH}_2)_2\text{PbI}_3$ (FAPbI₃) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) hybrid perovskites in their thin-film form with atomic resolution using a carefully developed protocol of low-dose STEM (see Figure 1).[2] Our images enable a wide range of previously undescribed phenomena to be observed, including a remarkably highly ordered atomic arrangement of sharp grain boundaries and coherent perovskite/PbI₂ interfaces, with a striking absence of long-range disorder in the crystal (see Figure 2). These findings explain why inter-grain interfaces are not necessarily detrimental to perovskite solar cell performance, in contrast to what is commonly observed for other polycrystalline semiconductors. Additionally, we observe aligned point defects and dislocations that we identify to be climb-dissociated, and confirm the room-temperature phase of $\text{CH}(\text{NH}_2)_2\text{PbI}_3$ to be cubic. We further demonstrate that degradation of the perovskite under electron irradiation leads to an initial loss of $\text{CH}(\text{NH}_2)_2^+$ ions, leaving behind a partially unoccupied, but structurally intact, perovskite lattice, explaining the unusual regenerative properties of partly degraded perovskite films. Our findings thus provide a significant shift in our atomic-level understanding of this technologically important class of lead-halide perovskites.

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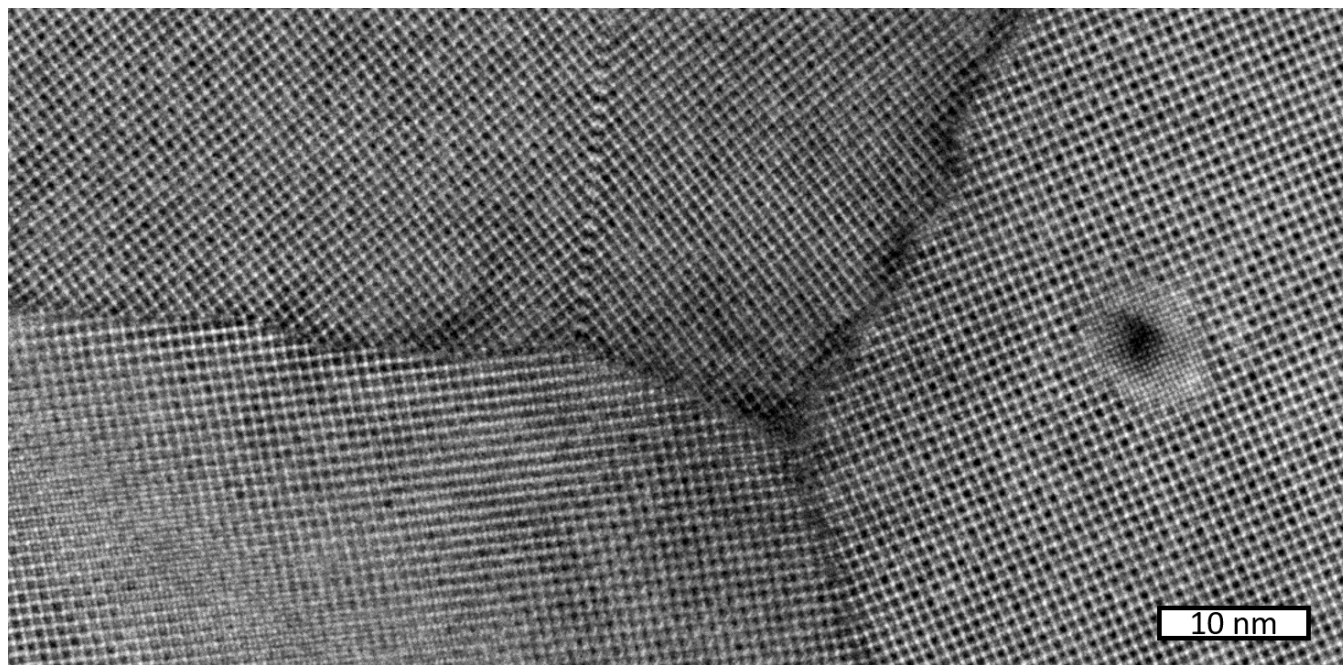


Figure 1. Low-angle annular dark-field scanning transmission electron micrograph illustrating several crystallographic phenomena of a FAPbI₃ thin film. Visible are high-angle and low-angle grain boundaries, a triple grain boundary, stacking faults, secondary phase inclusion, and a burned area containing the precursor PbI₂ phase where the beam was parked for a brief moment.

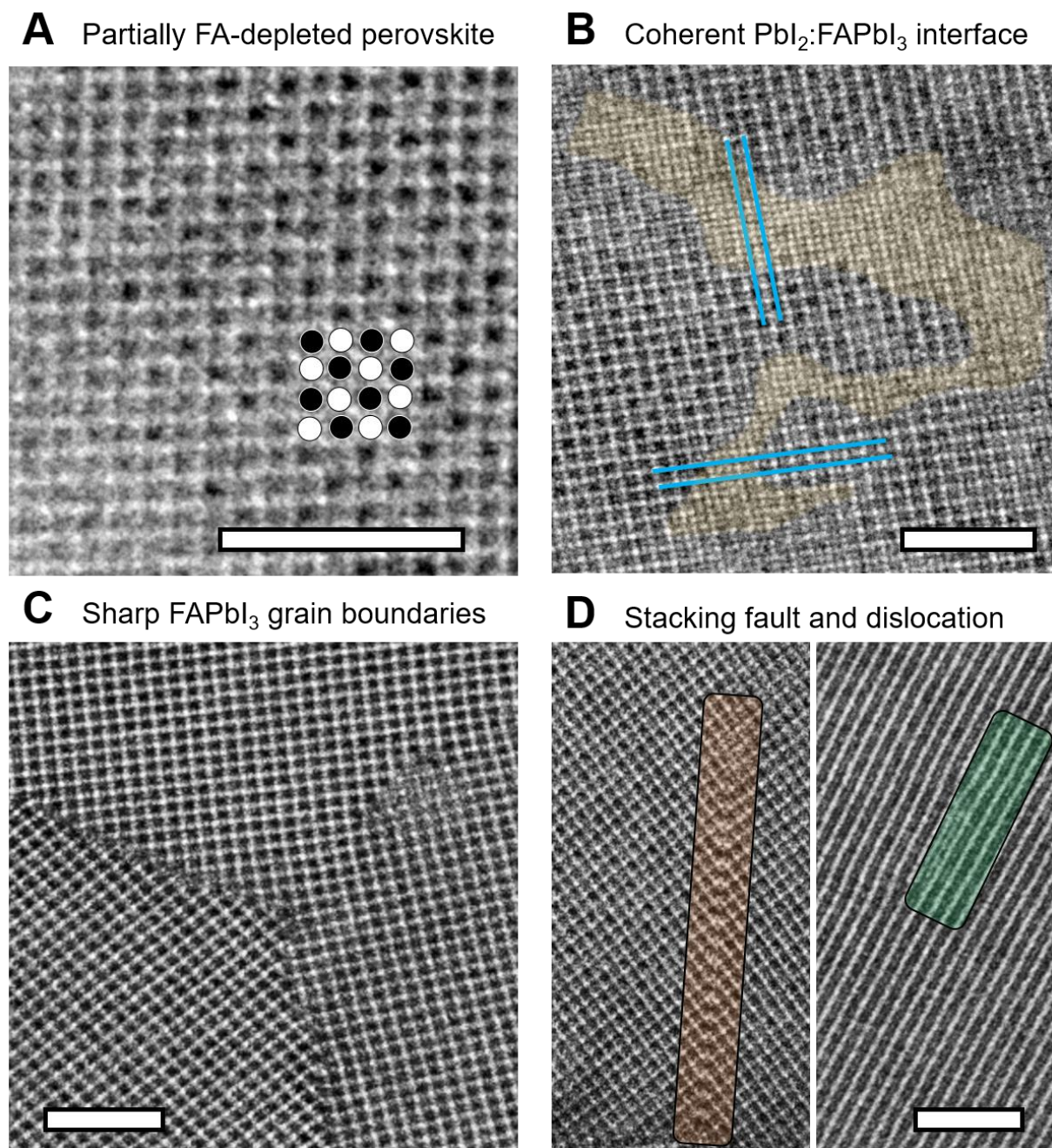


Figure 2. Overview of some key crystallographic properties of hybrid perovskite thin films including (A) a partially depleted crystal lattice after brief beam exposure, (B) highly coherent interfaces between FAPbI_3 and PbI_2 , sharp grain boundaries with minimal distortions near the boundary, and (D) planar defects including stacking faults and dislocations.

References

- [1] *Adv. Mater.* 2018, 30, 1800629
- [2] *Science* 370, eabb5940 (2020)