Supplementary Information

Nanoscale Light- and Voltage-Induced Lattice Strain in Perovskite Thin Films

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1. MATERIALS AND METHODS

Perovskite sample preparation. Indium tin oxide (ITO) coated glass substrates (Colorado Concept Coating, LLC) were sequentially cleaned by sonication in acetone, 2-propanol, and deionized water for 5 min each, followed by UV-ozone treatment for 10 min. Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS) (Clevios PH, Heraeus) was spin-coated at 3000 rpm for 60 s onto the ITO substrates and annealed on a hotplate at 150 ºC for 20 minutes. $MAPbI_3$ perovskite thin films were then deposited through a two-step process in a nitrogen-filled glovebox. First, lead iodide (PbI_2, Lumtec, 99.999%) and methylammonium iodide (MAI, Lumtec, >99.5%) were dissolved in *N,N*-dimethylformamide and 2-propanol, respectively, with concentrations of 450 mg/mL and 25 mg/mL. Both solutions were heated to 70°C before use. The preheated warm PbI_2 solution was spin coated onto the PEDOT:PSS coated ITO/glass at 6000 rpm for 45 s and then annealed on a hotplate at 70 °C for 10 min. MAI solution was then spin coated onto the dry PbI_2 layer at 6000 rpm for 45 s and annealed on a hotplate at 100 °C for 40 min to form a 300 nm-thick tetragonal phase perovskite film.[1]

Piezoresponse force microscopy. Strain mapping was performed under dark conditions and solar simulator light (approximately 4.5 suns) in a nitrogen-filled glovebox, using an AIST-NT CombiScope 1000 atomic force microscope (AFM). The AFM employs a laser with a wavelength of 1300 nm for cantilever detection, which is outside the absorption range of the perovskite layer. Pt-coated cantilevers (Budget Sensors HQ:NSC18/Pt) with a spring constant of 2.8 N/m and resonance frequency of 75 kHz were used. An AC bias with an amplitude of 2 V and frequency of 0.8 kHz was applied to the conductive probe, unless otherwise noted. During the PFM measurements, the probe was maintained in contact with the sample surface, using an applied load of 5 nN. The strain response of the sample was detected via the lateral (torsional) and vertical (normal) oscillation amplitudes of the cantilever, recorded at the second harmonic frequency (1.6 kHz) relative to the applied AC voltage. The selected AC probe voltage (2 V) provided a maximized signal while rarely inducing surface modification under illumination, such as that shown in Figure 5.

Higher voltages induced increased surface rearrangement, while lower voltages exhibited a reduced signal (see Figure S10). Minimally invasive strain mapping can be achieved with a voltage between 1 and 2 V. As shown in Figure S5, the strain response is most prevalent below 1 kHz.

2. X-ray Diffraction

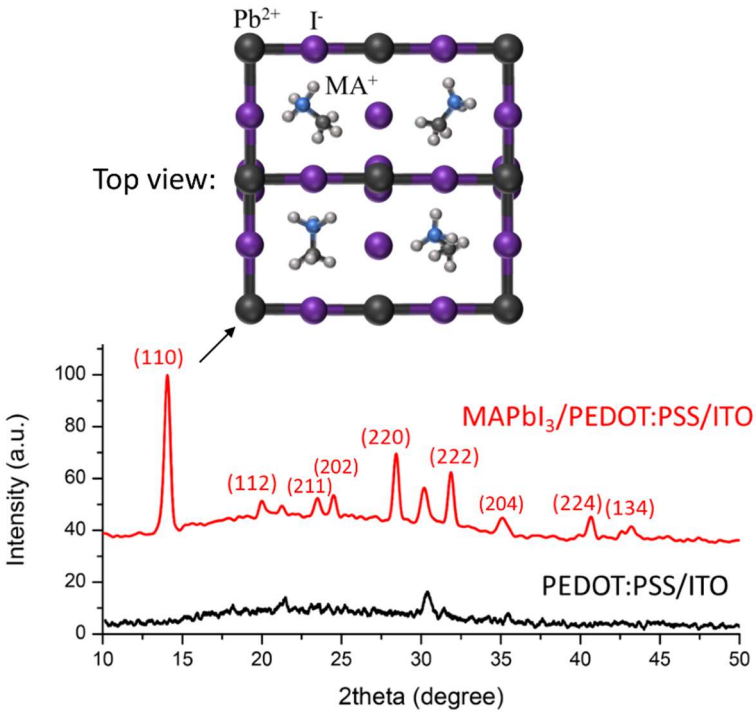
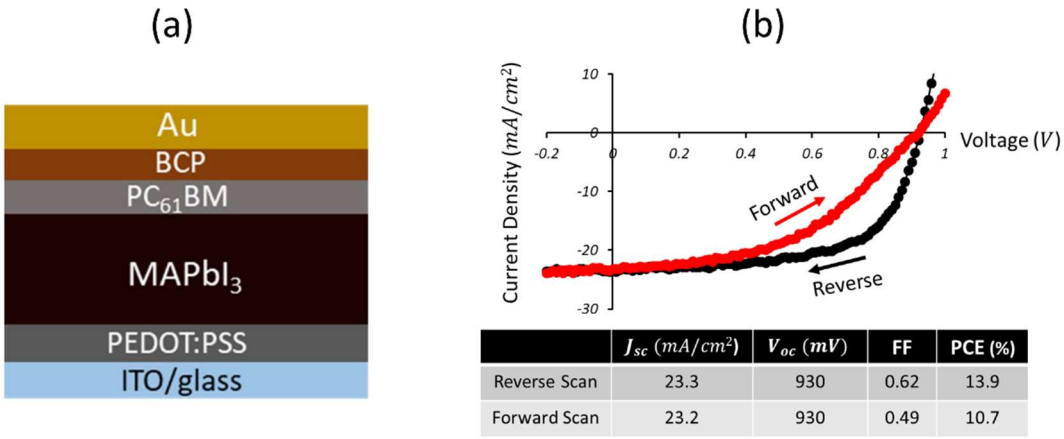


Figure S1. X-ray diffraction pattern for a $MAPbI_3$ film on PEDOT:PSS-coated ITO glass. The labelled peaks correspond to the tetragonal perovskite phase.[1-2] The top view of the (110) plane is depicted above.[2]

3. Solar Cell Device Performance



	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
Reverse Scan	23.3	930	0.62	13.9
Forward Scan	23.2	930	0.49	10.7

Figure S2. (a) Inverted perovskite solar cell film structure and (b) current-voltage characteristics and device parameters recorded under forward and reverse voltage sweep directions and 1 sun illumination. The gap between the two curves signifies significant photocurrent hysteresis.

4. Strain Dependence on Illumination

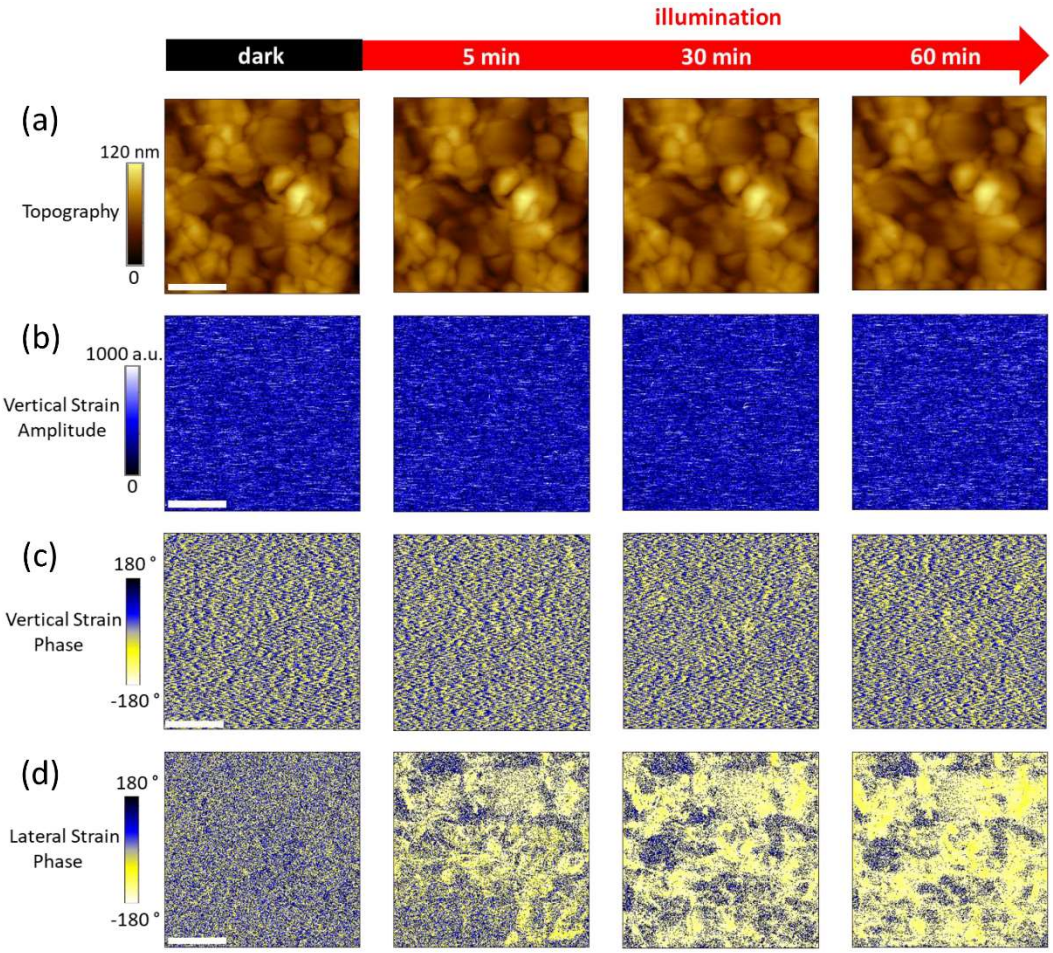


Figure S3. (a) Topography, (b) vertical second harmonic strain amplitude, (c) phase, and (d) lateral second harmonic strain phase under dark and illumination, as indicated by the arrow above. The scale bars represent 600 nm. The recorded sample area is the same as Figure 2 in the main text. No spatial contrast is visible in the vertical strain amplitude or phase. The lateral strain phase exhibits a change in contrast under illumination.

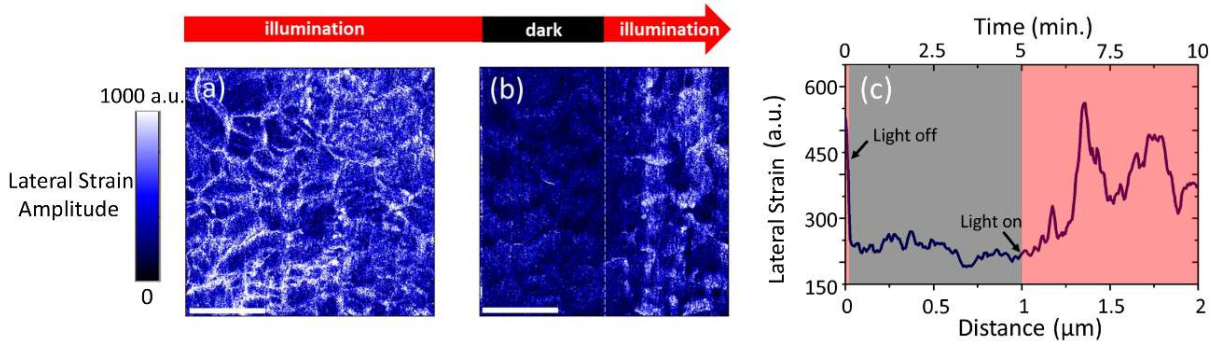


Figure S4. Consecutive lateral strain amplitude maps (a) under illumination (illuminated for 30 min prior to measurement), and (b) after turning the light off and then on again, as indicated with the arrow above and the dashed vertical line. The slow scan direction for (a) and (b) is from left to right. The scale bars represent 600 nm. (c) Average horizontal line profile from (b).

5. Strain Dependence on AC Bias Frequency

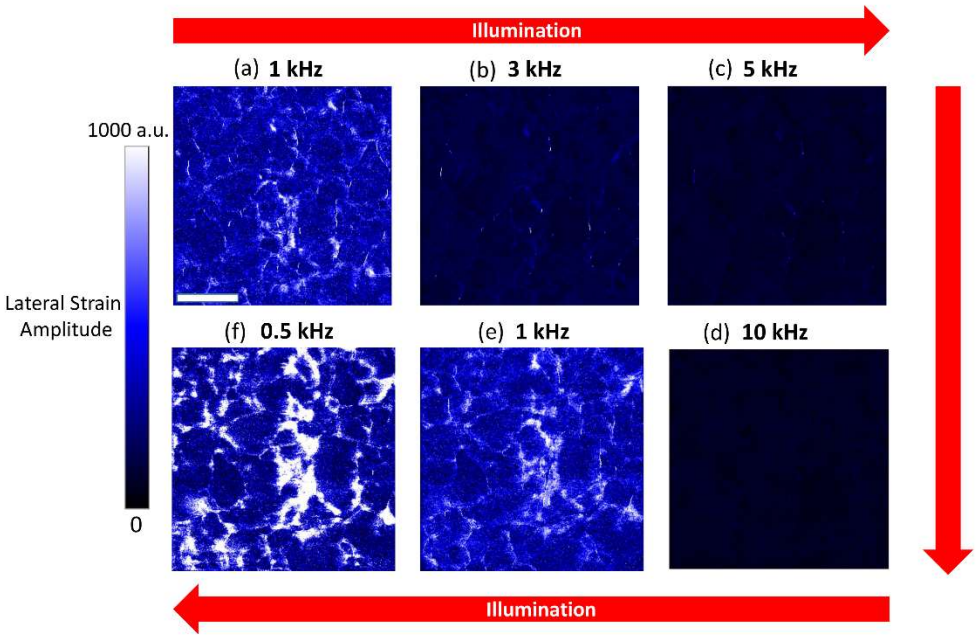


Figure S5. Consecutive lateral second harmonic strain amplitude obtained under continuous illumination with bias frequencies of: (a) 1 kHz, (b) 3 kHz, (c) 5 kHz, (d) 10 kHz, (e) 1 kHz, and (f) 0.5 kHz. The first image was recorded following 10 min of light soaking. Each scan took about 10 min to record. The scale bar represents 600 nm and the strain amplitude range is the same for all images. These measurements show that the lateral second harmonic strain amplitude is greatly reduced above bias frequencies of about 1 kHz.

6. Strain versus Scan Direction

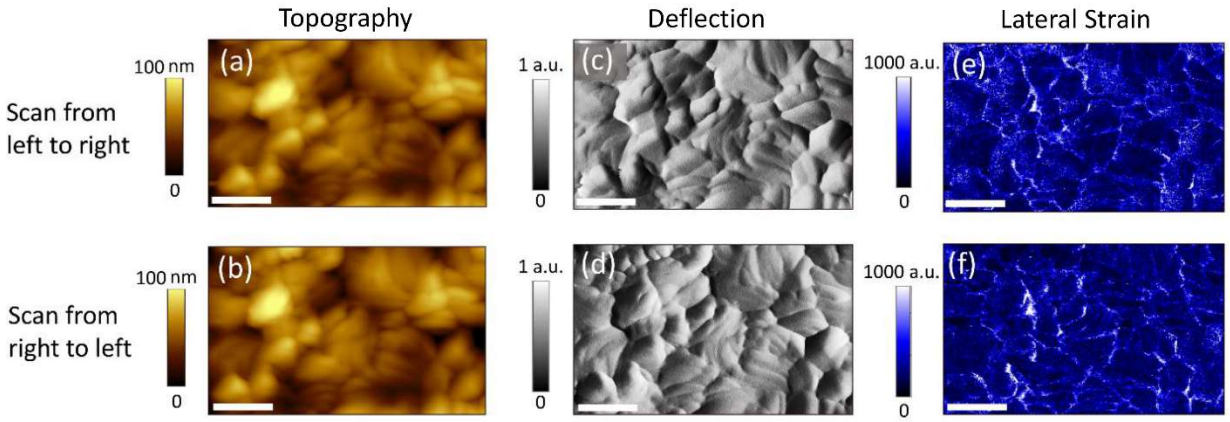


Figure S6. (a, b) Topography, (c, d) cantilever deflection, and (e, f) lateral strain amplitude under illumination, scanning (a, c, e) from left to right and (b, d, f) from right to left. The scale bar represents 600 nm. The strain images (e, f) exhibit highly similar features near grain boundaries, showing that the measured strain is not influenced by the scan direction.

7. Scanning Capacitance Microscopy

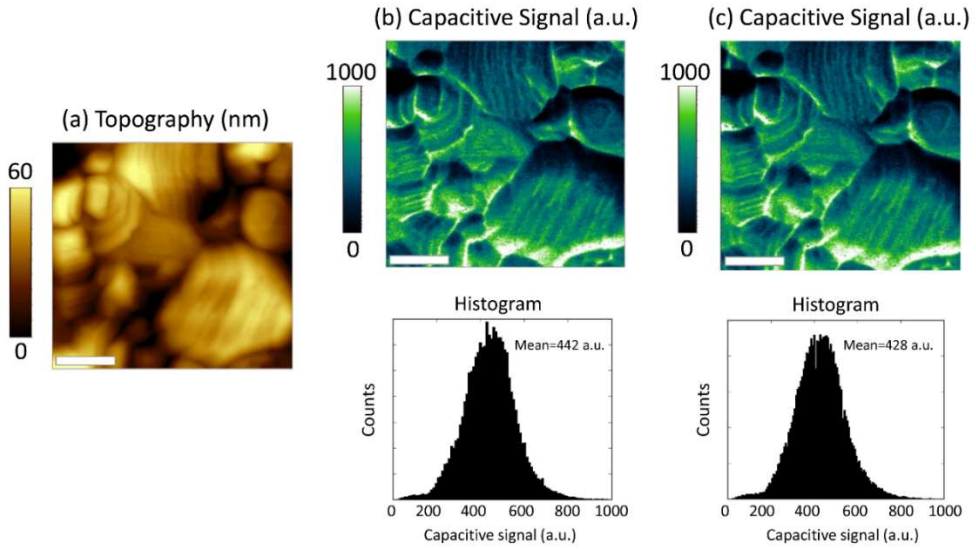


Figure S7. (a) AFM topography and (b, c) scanning capacitance microscopy (SCM) measurements: (b) under dark, and (c) under illumination following 30 min of light soaking. The scale bars represent 250 nm. Corresponding histograms are shown below. The SCM maps under dark and illumination exhibit no noticeable contrast differences and a comparable histogram, indicating that the capacitive response of the sample is not influenced by light. The SCM signal corresponds to the second harmonic term during frequency-modulated Kelvin probe force microscopy (FM-KPFM).[3-4] An AC bias amplitude of 3 V and a frequency of 1 kHz was applied to the probe and Pt-coated cantilevers (Budget Sensors HQ:NSC18/Pt) with a spring constant of 2.8 N/m and resonance frequency of 75 kHz were used. A two-pass approach was employed, with a lift height of 10 nm.

8. Strain versus Applied Force

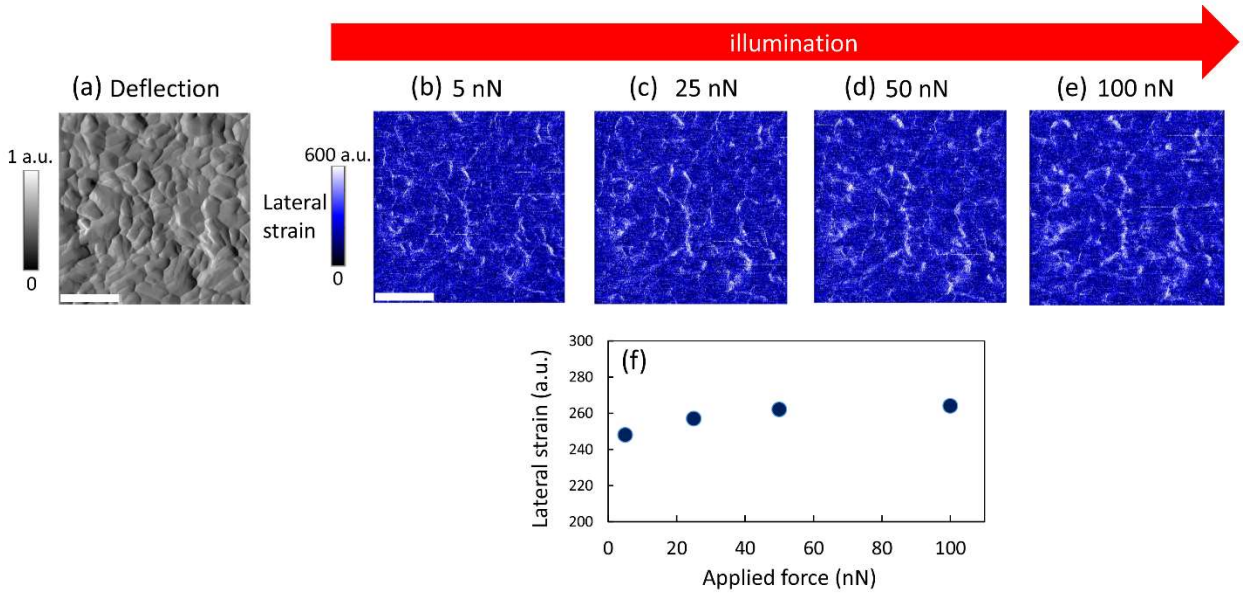


Figure S8. (a) AFM cantilever deflection and lateral second harmonic strain obtained with an applied force of (b) 5 nN, (c) 25 nN, (d) 50 nN, (e) 100 nN, all recorded under illumination. The scale bar represents 600 nm. (f) Average strain versus applied force, showing that the strain is nearly independent of the probe-sample force.

9. Strain Dependence on AC Bias Amplitude

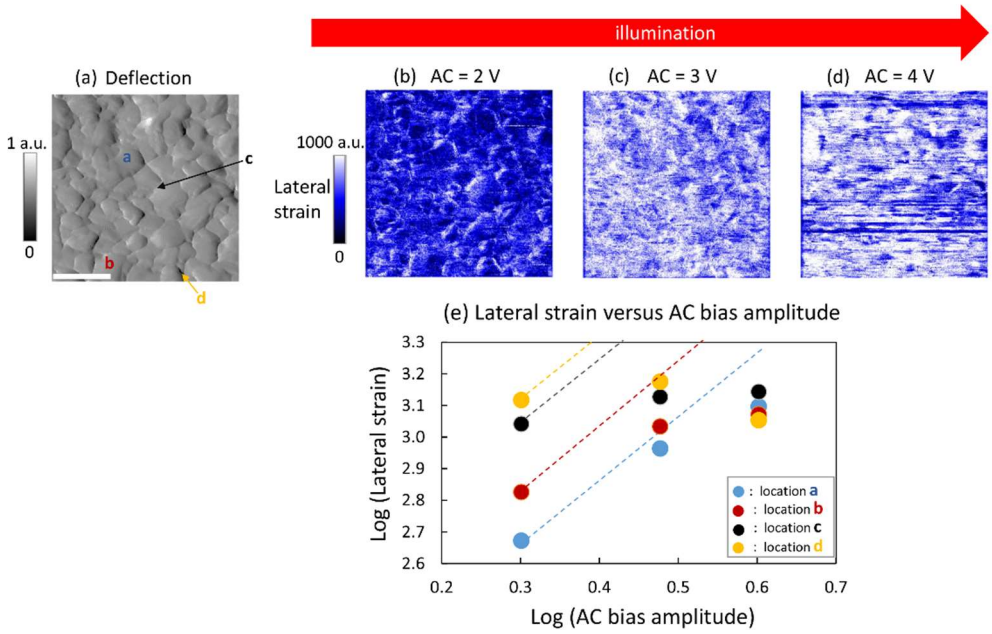


Figure S9. (a) AFM cantilever deflection and lateral second harmonic strain with an AC bias amplitude of (b) 2 V, (c) 3 V, (d) 4 V, all recorded under illumination. The scale bar represents 600 nm. (e) Log of second harmonic lateral strain versus log of AC bias amplitude at four selected locations labeled in (a), averaged over 10 pixels at each location. The dashed lines represent the predicted slope of 2 for a quadratic increase (Joule heating). As shown in (e), the increase in lateral second harmonic strain differs from location to location and is not quadratic, suggesting that Joule heating is not responsible for the observed strain signal.

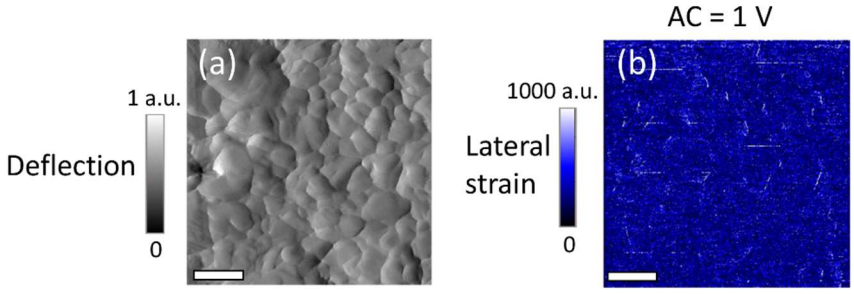


Figure S10. (a) AFM cantilever deflection and lateral second harmonic strain obtained with an AC bias amplitude of 1 V and frequency of 0.8 kHz, recorded under illumination following 30 min light-soaking. The strain response is weak and lacks contrast at a bias voltage of 1 V and below. The scale bars represent 400 nm.

10. Strain Dependence on DC Bias

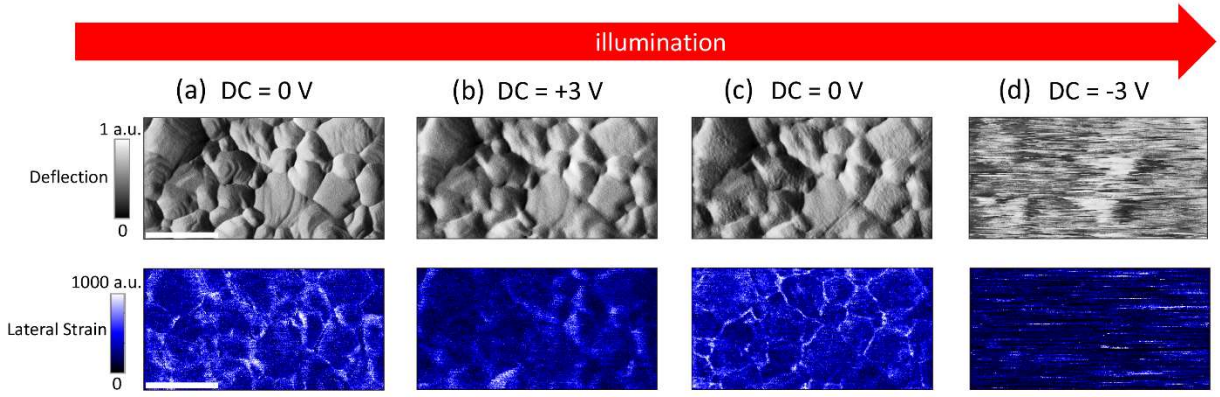


Figure S11. Mapped cantilever deflection and lateral second harmonic strain amplitude under illumination with an additional DC bias applied to the probe (on-field measurement) to induce current flow; consecutive images were obtained with a DC probe bias of (a) 0 V, (b) +3 V, (c) 0 V and (d) -3 V. The scale bars represent 600 nm. The lateral second harmonic strain with an added DC bias shows a suppressed response, suggesting that Joule heating due to current flow is not a factor.

11. Influence of Bias under Dark Conditions

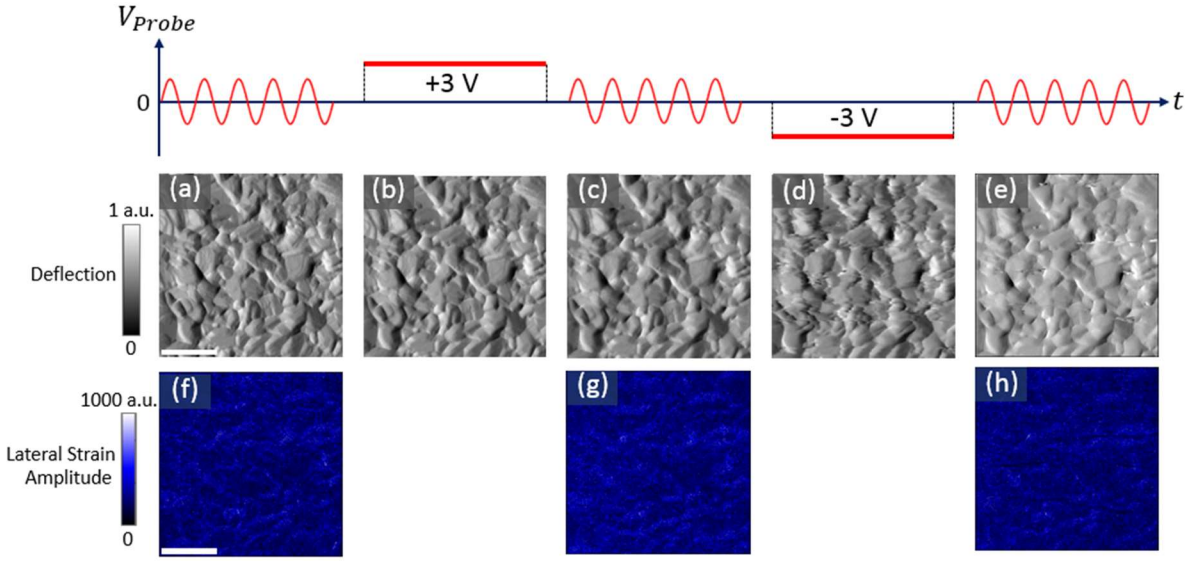


Figure S12. (a, c, e) Deflection and (f, g, h) lateral second harmonic strain amplitude images obtained under dark. (b, d) Deflection images obtained with contact mode AFM with (b) +3 V and (d) -3 V applied to the probe. The scale bars represent 600 nm.

12. Influence of Bias and Probe-Sample Contact on Morphology

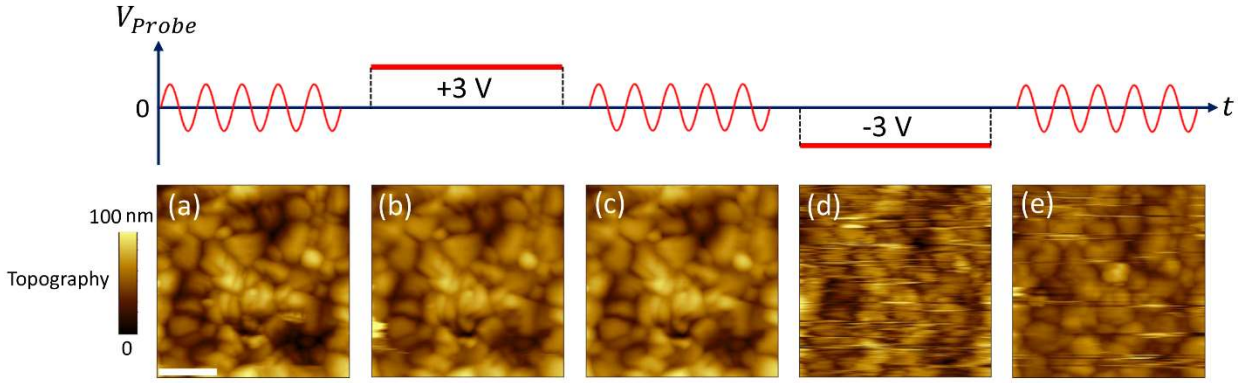


Figure S13. Topography obtained under illumination with an AC or DC bias applied to the probe as indicated. The scale bar represents 600 nm. The recorded sample area is the same as Figure 4 in the main text.

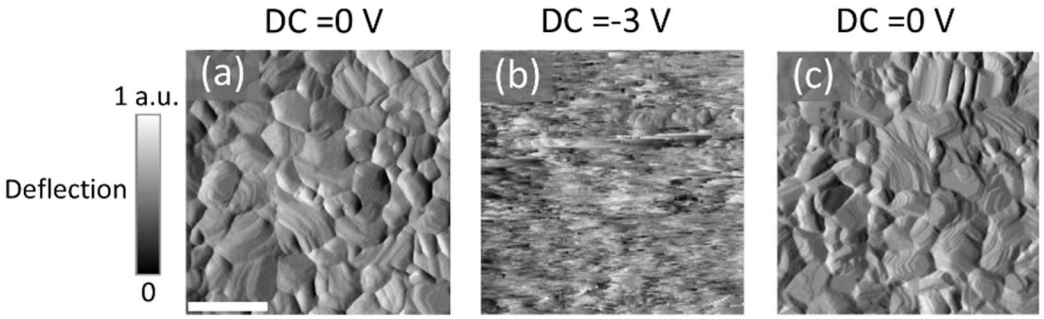


Figure S14. Consecutive contact mode deflection images with a DC bias of (a) 0 V, (b) -3 V, and (c) 0 V at a nearby location, all recorded using the same probe. These measurements confirm that the streaky appearance of images during the application of a negative voltage are not caused by probe damage. The scale bar represents 600 nm.

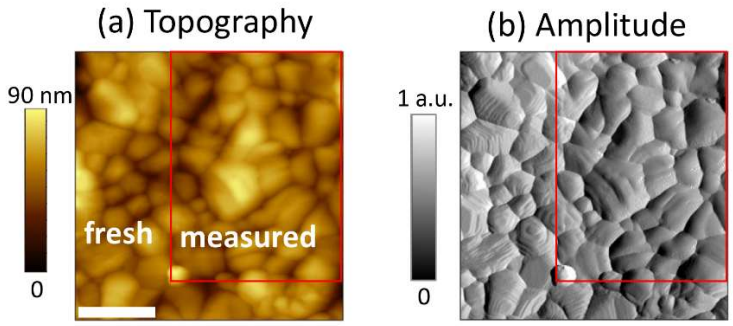


Figure S15. (a) Tapping mode topography and (b) amplitude obtained after PFM strain mapping in the indicated “measured region”. The “fresh region” represents a pristine surface that was not measured by PFM. The scale bar represents 600 nm. It can be seen in (b) that within the pristine region, the perovskite grains exhibit a layered texture, while within the region where PFM mapping was performed, the texture within the grains is smooth. These measurements exclude AFM probe degradation as the cause for the loss of surface texture following PFM measurements.

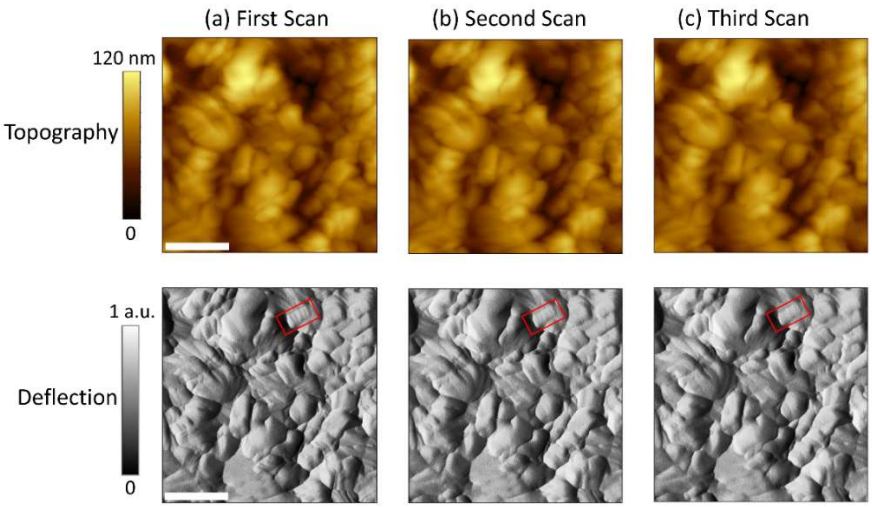


Figure S16. Contact mode topography and corresponding deflection images obtained after repeated measurement at the same location under dark conditions. The scale bars represent 600 nm. The deflection measurements reveal a smoothing of the surface (for example, within the red rectangle), even though the applied probe-sample load is small, about 5 nN.

13. References

(1) Cao, D. H.; Stoumpos, C. C.; Malliakas, C. D.; Katz, M. J.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. Remnant PbI_2, an unforeseen necessity in high-efficiency hybrid perovskite-based solar cells? *APL Materials* **2014,** *2*, 091101.

(2) Oku, T. Crystal Structures of CH3NH3PbI3 and Related Perovskite Compounds Used for Solar Cells. In *Solar Cells-New Approaches and Reviews*; Intech Open Science: **2015**; Chapter 3, p 80.

(3) Williams, C. C.; Slinkman, J.; Hough, W. P.; Wickramasinghe, H. K. Lateral dopant profiling with 200 nm resolution by scanning capacitance microscopy. *Appl. Phys. Lett.* **1989,** *55*, 1662-1664.

(4) Melitz, W.; Shen, J.; Kummel, A. C.; Lee, S. Kelvin probe force microscopy and its application. *Surface Science Reports* **2011,** *66*, 1-27.