

Supporting Information

Surface Reconstruction and Defect Healing of MAPbI₃ Perovskite Microcrystalline Thick Films for Sensitive and Self-Powered X-ray Detectors

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Experimental Section

Materials: Lead (II) iodide (PbI_2 , 99.9%), butylamine bromide (BABr) and gamma-butyrolactone (GBL, 99%) were purchased from Aladdin Reagent Ltd. Methylamine ethanol solution (32%) was purchased from Sinopharm. Methylammonium iodide (MAI) was synthesized as reported previously.^[1] Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS (Clevious P VP AI 4083), fullerene (C_{60}) and bathocuproine (BCP) were purchased from Xi'an Polymer Light Technology Corp. N,N-dimethylformamide (DMF, 99.8%) was purchased from Sigma-Aldrich. All commercial materials were used without any further purification.

Preparation of MAPbI_3 polycrystalline films: PEDOT:PSS solution filtered with a 0.45 μm filter was spin-coated on indium tin oxide (ITO) substrates at 4000 rpms for 30 s, and then annealed at 135 $^{\circ}\text{C}$ for 15 min. The MAPbI_3 solution (1 M) in DMF was dripped onto the PEDOT:PSS-covered ITO substrate on a hot plate at 150 $^{\circ}\text{C}$, then swiped linearly by a blade coater. After blading, the resulting film was annealed at 120 $^{\circ}\text{C}$ for 10 min.

Growth of MAPbI_3 microcrystalline films: Appropriate amounts of PbI_2 and MAI were dissolved in GBL to obtain a 1.6 M MAPbI_3 crystal growth solution. Subsequently, MAPbI_3 polycrystalline films were immersed into a supersaturated solution at temperature of 90 $^{\circ}\text{C}$ and the microcrystalline films were grown by the inverse temperature crystallization (ITC) method. Finally, the microcrystalline films were taken out of the solution and annealed at 60 $^{\circ}\text{C}$ for 10 min to remove residual solvent.

Surface reconstruction and defect healing: For the surface reconstruction, the as-prepared MAPbI_3 microcrystalline films were placed on the mouth of 50 ml vials containing 10 ml methylamine ethanol solution for 5 s, 15 s and 20 s, respectively. The MA-treated microcrystalline films were placed in air at -4°C or room temperature until the treated microcrystalline films were completely dried after one day. For the defect healing, an appropriate amount of BABr solution (10 mg/ml in isopropyl alcohol) was dripped on the

microcrystalline films and spin-coated by rotating at 4000 rpm for 30 s without annealing treatment.

Device Fabrication: C₆₀ (30 nm), BCP (8 nm) and copper (Cu) (80 nm) were sequentially deposited on the microcrystalline films by thermal evaporation at rates of 0.2 Å s⁻¹, 0.2 Å s⁻¹ and 1 Å s⁻¹, respectively. A metal mask was used to define the active region (2.89 mm²) during the evaporation process.

Characterization: The surface and cross-sectional morphology of microcrystalline films were examined via a field-emission scanning electron microscope (SEM) (ZEISS, G300 FE-SEM System). X-ray diffraction (XRD) patterns were characterized using an X-ray diffractometer (SmartLab 3 KW, Rigaku). X-ray photoelectron spectra (XPS) spectroscopy was performed by an X-ray photoelectron spectrometer equipped with an Al K α X-ray radiation source (ESCALAB 250, ThermoFisher SCIENTIFIC). Steady-state absorption spectra were recorded with a U3500 Hitachi ultraviolet-visible spectrophotometer (UV/Vis). The steady-state photoluminescence (PL) spectra were carried out by a fluorescence spectrometer (FLS1000, Edinburgh Instruments). The time-resolved PL (TRPL) spectra were measured by a nanosecond pulsed diode laser (405 nm) as an excitation source with a repetition frequency of 1 MHz. The Current density-Voltage (*J-V*) characteristics of devices were recorded using a Keithley 2450 source meter under dark and illumination by a solar simulator with the light intensity of 100 mW cm⁻² (Sun 2000, ABET Technologies). The external quantum efficiency (EQE) spectra were measured by a QTEST HIFINITY 5 system (CROWNTECH, INC.) using a monochromatic light beam, calibrated by a reference silicon photodiode. High-resolution EQE was measured by Fourier transform photocurrent spectrometer (Enlitech FTPS spect-600). The nitrogen laser delivers 3.5 ns pulses at 337 nm with a repetition rate of up to 20 Hz was used to measure transient photovoltage attenuation. The noise current of detectors was obtained by a Fast Fourier transform (FFT) analyzer (Agilent, 35670A) combined with a current pre-amplifier (Stanford Research Systems, SR570) under zero bias. The respond speed of detectors was tested

by a current pre-amplifier coupled with a Keysight DSOX3104A oscilloscope under the excitation of a frequency modulated 570 nm LED at 1-10 kHz under 0 bias.

X-ray Detector Characterization: X-rays with a maximum energy of 50 keV were produced by an Amptek Mini-X2 tube. The X-ray dose rates were adjusted by tuning the tube current and inserting different thicknesses of metal foil, calibrated using a Radcal Accu- Gold+ 10X6-180 ion chamber dosimeter. The irradiation stability of the devices without encapsulation was measured in ambient air using a Keithley 2400 source under continuous X-ray irradiation of $2.46 \mu\text{Gy}_{\text{air}} \text{ s}^{-1}$. Imaging of the "U" mark was accomplished using a microcrystalline detector with a pixel size of $1.5 \times 1.5 \text{ mm}^2$ in a linear stage driven X-Y scan mode. The X-ray detector measurements were performed at $55 \pm 2 \%$ humidity conditions.

References

- [1] Y. Dang, Y. Liu, Y. Sun, D. Yuan, X. Liu, W. Lu, G. Liu, H. Xia, X. Tao, *CrystEngComm*, 2015, **17**, 665.

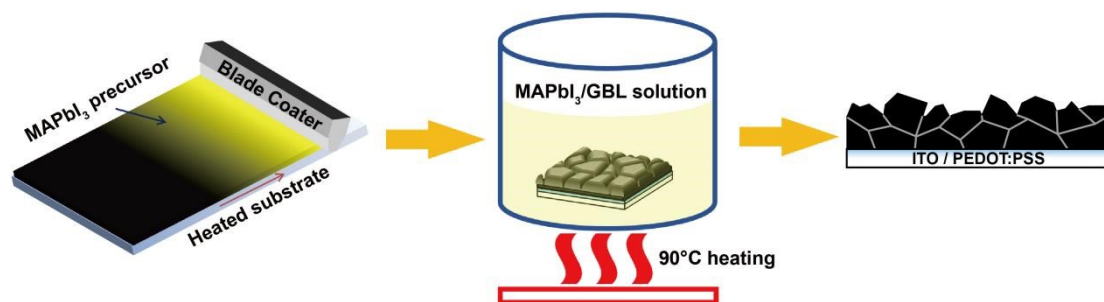


Figure S1. Schematic preparation process of MAPbI₃ microcrystalline film.

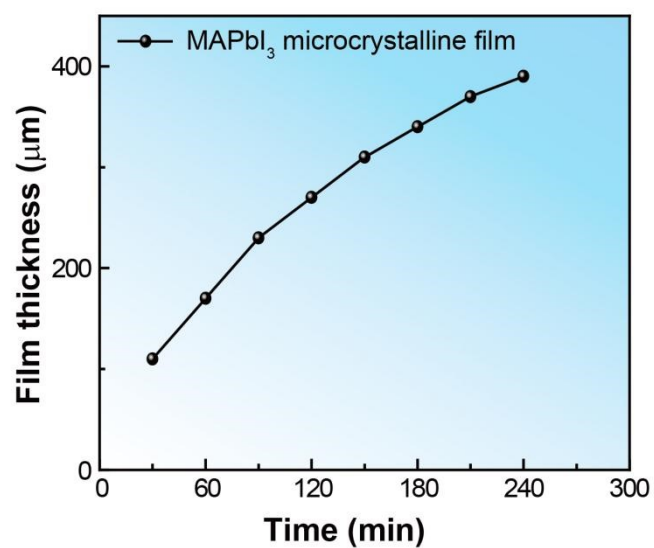


Figure S2. Thickness of microcrystalline films as a function of growth time. MAPbI₃ microcrystalline films with thickness of 400 μm could be obtained after 4 hours of growth.

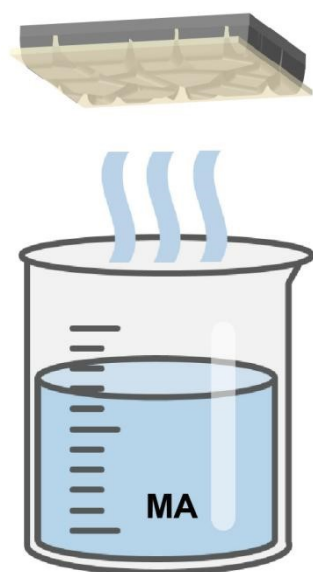


Figure S3. Schematic diagram of MA gas treatment of MAPbI_3 microcrystalline films.

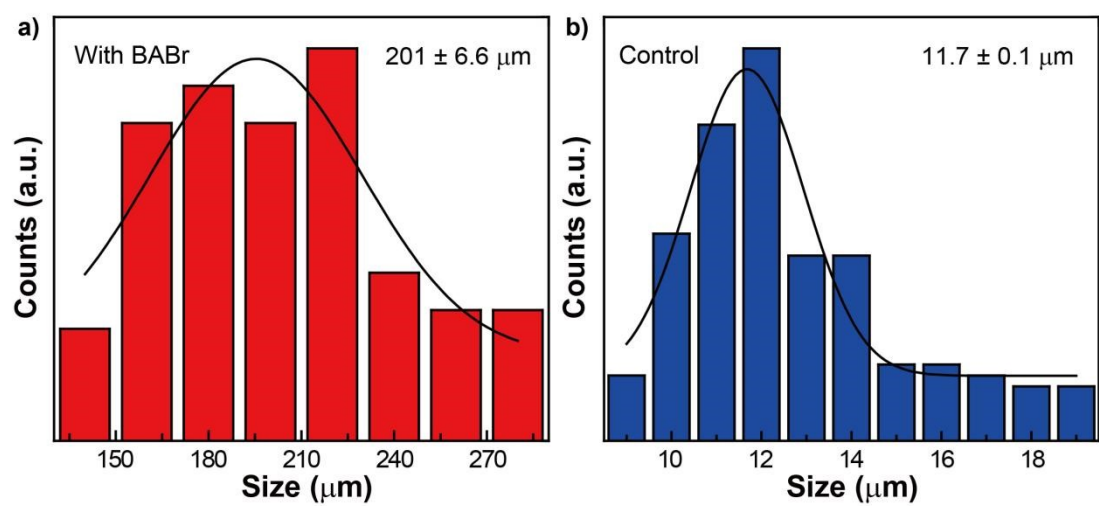


Figure S4. Grain size distribution on the surface of MAPbI₃ microcrystalline films (a) before and (b) after MA treatment.

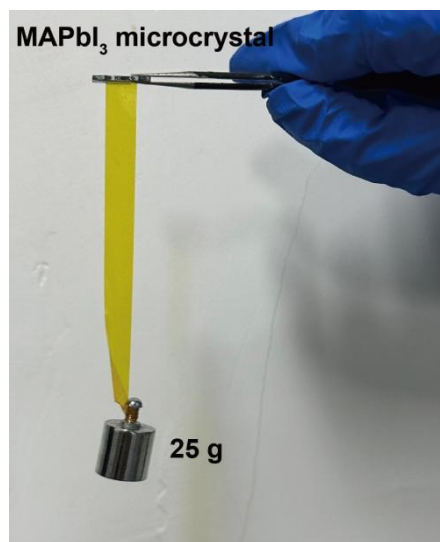


Figure S5. Surface-reconstructed MAPbI₃ microcrystalline films with 25 g of weight attached to the surface.

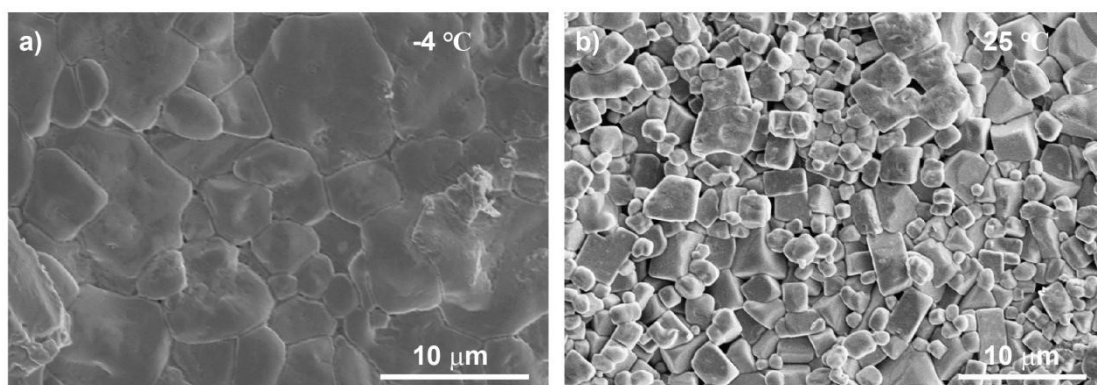


Figure S6. Top-view SEM images of MA-treated MAPbI₃ microcrystalline films after drying at (a) -4°C and (b) 25°C.

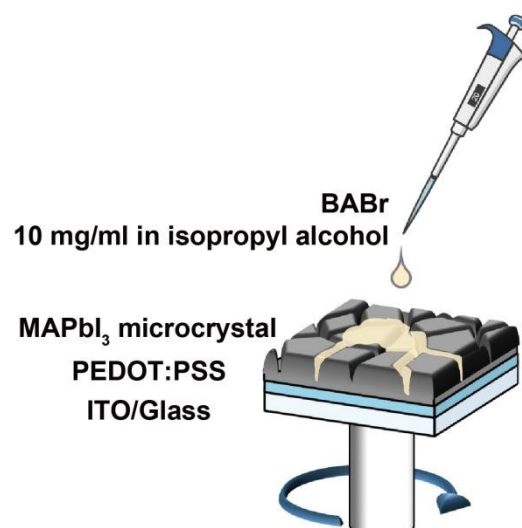


Figure S7. Schematic diagram of BABr modification of MAPbI₃ microcrystalline films.

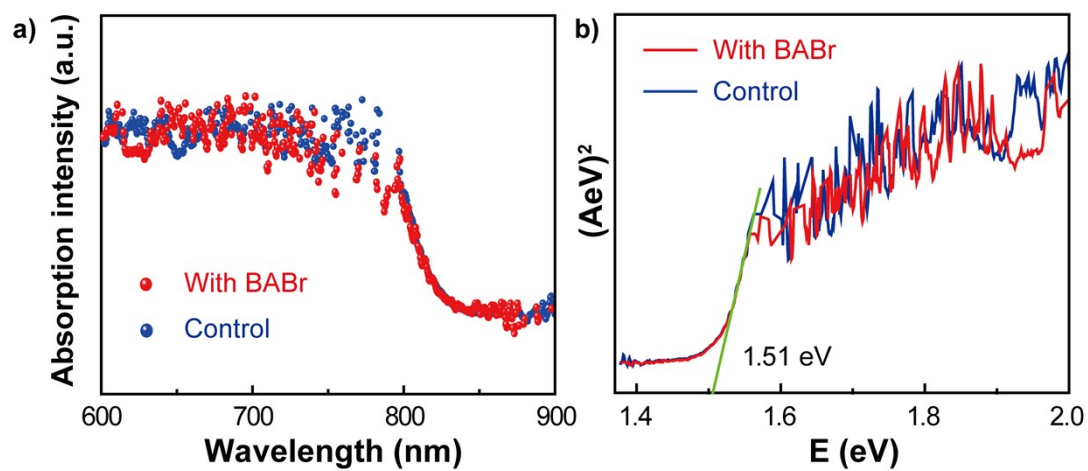


Figure S8. (a) UV-vis absorption spectra and (b) Tauc plots of control and BABr-modified MAPbI₃ microcrystalline films.

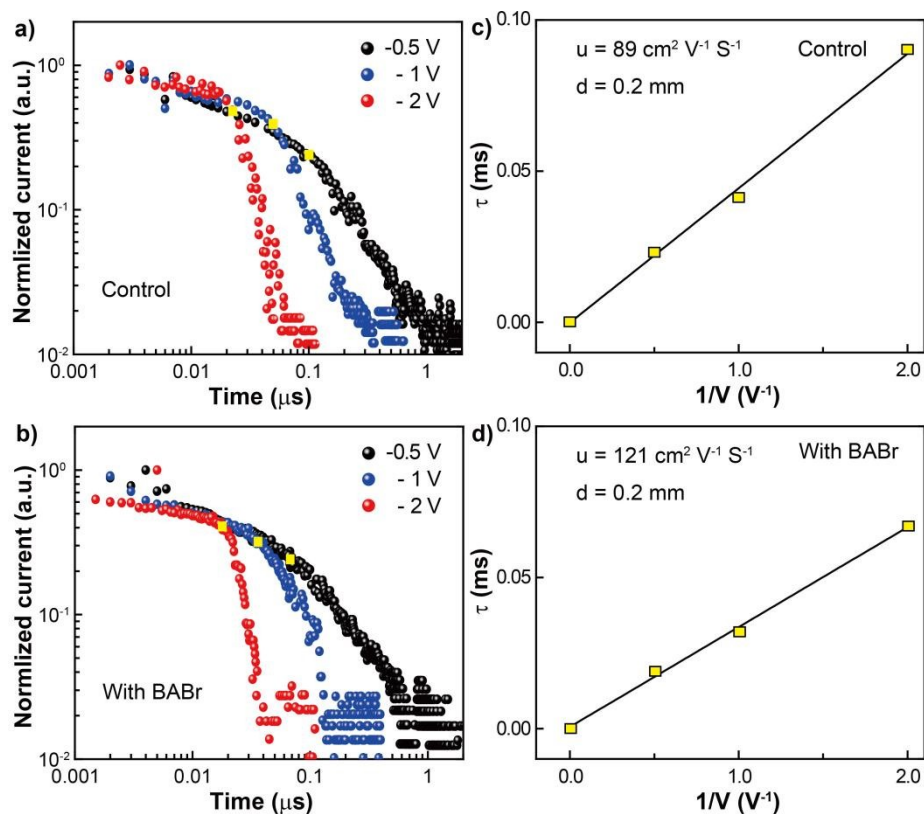


Figure S9. Normalised transient current curves for (a) control and (b) BABr-modified devices under various biases. Linear fit of transit time versus inverse voltage V^{-1} for (c) control and (d) BABr-modified devices.

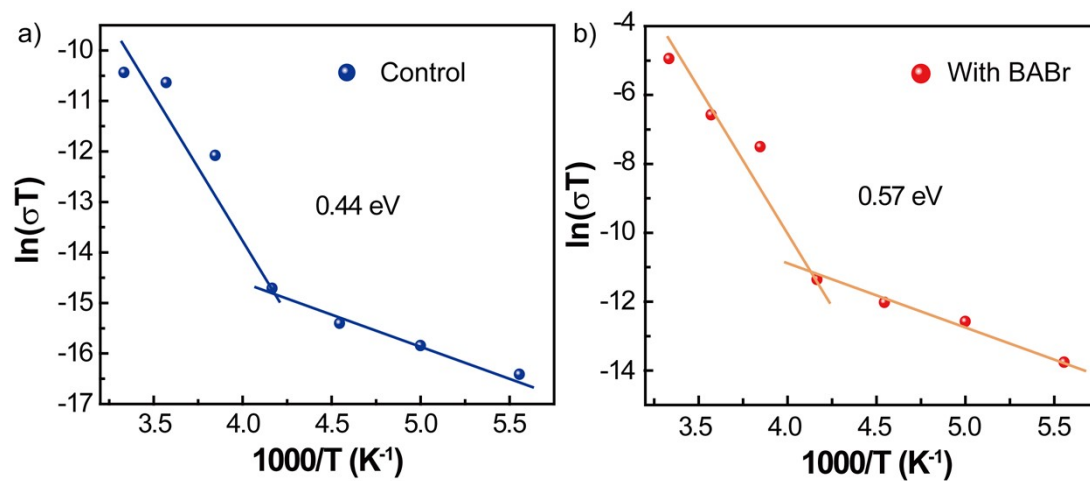


Figure S10. Temperature-dependent conductivity of (a) control and (b) BABr-modified single crystals.

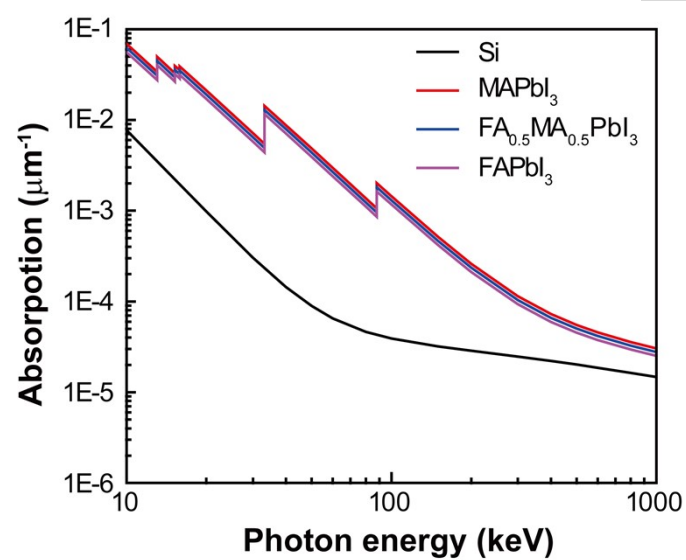


Figure S11. Absorption coefficients of Si and lead-iodide perovskite with different A-site cation as a function of X-ray photon energy.

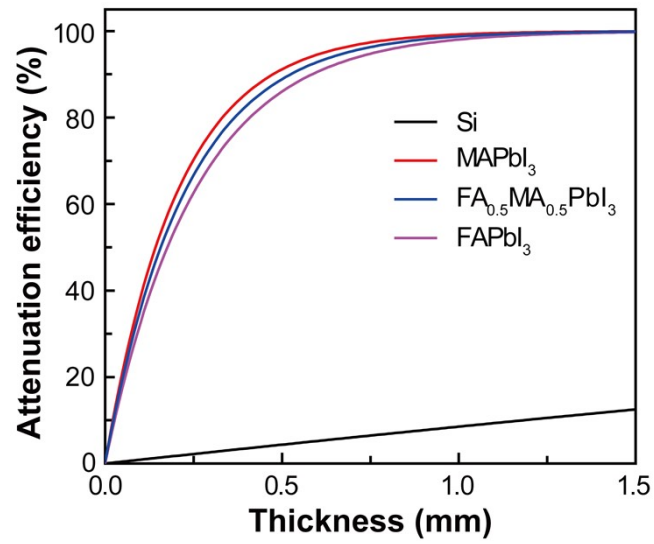


Figure S12. Calculated attenuation efficiencies of perovskites and silicon for 50 keV X-ray photons versus thickness.

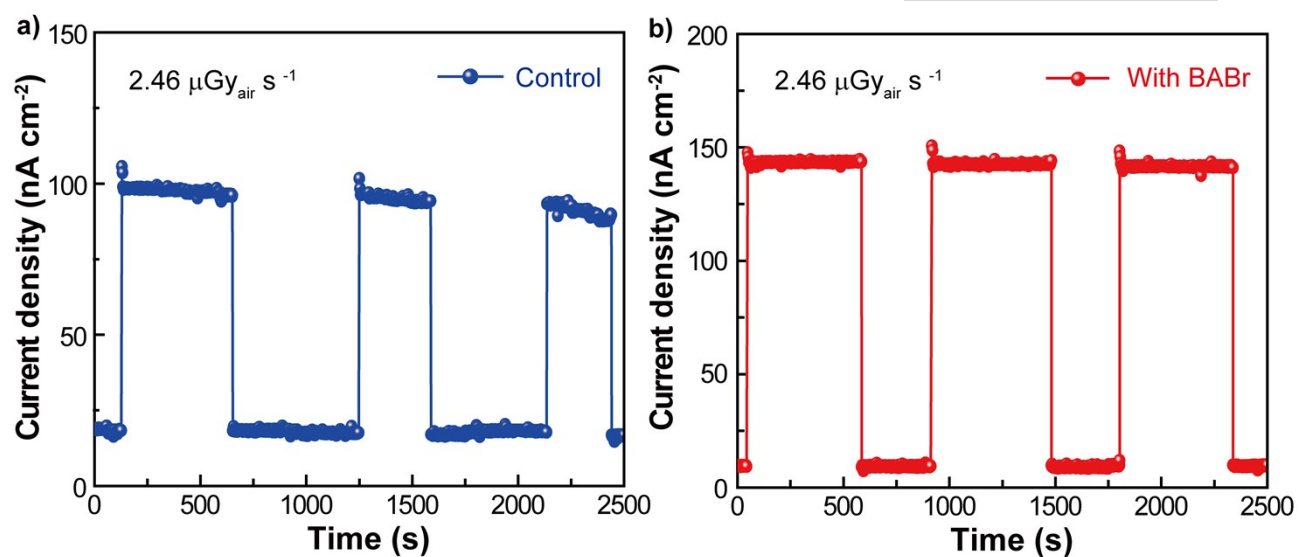


Figure S13. X-ray radiation stability of (a) control and (b) BABr-modified MAPbI₃ microcrystalline detectors under 0 V bias.