## **Electronic Supplementary Information**

## Anisotropic Moisture Erosion of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Single Crystal

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## **Experimental Procedure**

MAPbI3 single crystal growth

The growth of MAPbI<sub>3</sub> single crystal was performed in saturated solution by slow cooling. All chemicals were used as received without further purification. Pb(CH<sub>3</sub>COOH)<sub>2</sub>•3H<sub>2</sub>O was of analytical grade from Sinopharm Chemical Reagent Co., Ltd., China. 57% HI aqueous solution with 0.75% H<sub>3</sub>PO<sub>2</sub> as stabilizer was from Acros and 40% CH<sub>3</sub>NH<sub>2</sub> aqueous solution was from Alfa. Briefly, 7.5 g of Pb(CH<sub>3</sub>COOH)<sub>2</sub>•3H<sub>2</sub>O was dissolved in 30 ml of a 57% HI aqueous solution contained in a Erlenmeyer flask under stirring condition in air. To make them dissolve sufficiently and quickly, the Erlenmeyer flask was put on a heating stage till the solution turned homogeneous bright yellow. An additional 6 ml of 57% HI solution with 2 ml of CH<sub>3</sub>NH<sub>2</sub> 40% aqueous solution was added to the solution drop by drop at 100 °C to ensure no black solid appear. The Erlenmeyer flask was put into an oven after sealing. Black single crystals were grown at the bottom of the Erlenmeyer flask by cooling this yellow solution to 60 °C in 10 days.

## Materials Characterization

The as-grown MAPbI<sub>3</sub> single crystals were oriented by X-ray crystal diffraction (XRD) instrument (Brüker P4) using Cu Karadiation at a scan rate of 12 degree/min under operation condition of 40 kV and 40 mA. Energy dispersive spectrum (EDS) was attached on a field-emission scanning electron microscope (FESEM, Gemini LEO 1530). Before the EDS test, samples were heated to 55 ° C under vacuum for 1 hour to make the MAI and possible I<sub>2</sub> escape from the surface of MAPbI<sub>3</sub> single

crystals, which would monitor the erosion process more accurately. The morphology of the each facet of MAPbI<sub>3</sub> single crystal was also observed by a confocal laser scanning microscope (CLSM, Olympus OLS 4100). The optical reflection spectra of the three facets of MAPbI<sub>3</sub> single crystal before and after water erosion were collected using a UV–vis–NIR spectrophotometer (Perkin Elmer Lambda 950) with an aperture of 2 mm. The Auger electron spectroscopy was collected by nanoscale Auger system (PHI 710, ULVAC-PHI). The lon beam voltage was 2 kV when sputtering.

In the I-V test, Au strips of 50 nm in thickness were deposited on the surface of three facets of the single crystal by a conventional thermal evaporation method through a stainless steel mask. The channel width (W) was 800  $\mu$ m, and the channel length (L) was 50  $\mu$ m. We tested the I-V under the dark condition and under the solar simulator condition (The power density was 100 mw cm<sup>-2</sup>).



**Fig. S1** Schematic illustration of water mist erosion apparatus for studying the anisotropy of moisture erosion of MAPbI<sub>3</sub> single crystal. MAPbI<sub>3</sub> single crystal exposing (100) facet, (112) facet and (001) facet with same degree of surface roughness was clamped with random orientation and put into the sample cell. Water mist was diffuse and had same opportunity to contact with each facet.



**Fig. S2** Optical photographs with different shooting angle of (100) facet, (112) facet and (001) facet of the MAPbI3 single crystal before (left) and after (right) suffering from the water mist erosion for 60 s.



**Fig. S3** CLSM observation of the cross-section of (001) facet of the MAPbI<sub>3</sub> single crystal after suffering from water mist erosion for 30 s (A) and 60 s (B). It can be found that the eroded single crystal surface is yellow and the interior remains intact. The thickness of the erosion layer increases with the lapse of erosion time. After water mist erosion for 60 s, the thickness can reach 10  $\mu$ m (B).



**Fig. S4** Dark-current and Photocurrent versus voltage curves on (100) facet, (112) facet and (001) facet of MAPbI<sub>3</sub> single crystal before and after water mist erosion for 60 s. Compared to the other two facets, the current on (001) facet is more reduced, especially the photocurrent. The degeneration of electrical properties might be caused by the destruction of the crystal structure and the shielding of light by  $PbI_2$ , which was more serious on (001) facet due to the fastest erosion rate.