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## Supporting information

## Stoichiometry-dependent local instability in MAPbI3 perovskite materials and devices

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Figure S1. Standard LVSEM surface morphological images of degraded (a) excess  $PbI_2$  pellet (b) stoichiometric MAPbI<sub>3</sub> pellet (c) high magnification image of (a) with nano plates on degraded surface (d) photo of stoichiometric MAPbI<sub>3</sub> pellet.



Figure S2. Standard LVSEM surface morphological images (a) degraded excess MAI pellet (b) magnified image of (a) shows the porous degraded structure



Figure S3. Standard LVSEM surface morphological images of degraded excess MAI pellet where we can see localised degradation with in the same SEM image.



Figure S4. Secondary electron hyperspectral images (SEHI) of excess MAI pellets at different energies. Dark grey areas at high energy (fig S4 a &c at 10.0 eV) showing contrast reversal at lower energy (fig S4 b &d at 3.5 eV). The appearance of these 'dark' regions is different in low energy SEHI imaging where they become brighter compared to the perovskite. It means, this phase emits low energy secondary electrons that cannot be detected effectively in standard SEM. Therefore, in standard SEM these 'dark' regions could be mistaken for voids. This is in good agreement with our previous report, where, we observed similar behaviour for bromide based perovskite materials.<sup>[1]</sup>





Figure S5. (a) Cross sectional view of dissipated energy in MAPbI<sub>3</sub> perovskite with 1kV accelerating voltage using CASINO Monte Carlo program, <sup>[2]</sup> (b) Magnified image of the black doted region of fig. S6 (a). Magnified image showing that the 90 % of beam energy dissipated within top 2.5-3.0 nm thick MAPbI<sub>3</sub>.



Figure S6. (a-i) Standard LVSEM surface morphological images of excess MAI perovskite pellets for first, second and third scan respectively for three different regions. Here we observed that some grain boundaries are more unstable under the electron beam. It suggests that they profoundly non-stoichiometric in nature and decompose fast compared to the corresponding grains under the identical electron beam conditions.



Figure S7. LVSEM surface morphological images of excess MAI perovskite pellets. We can see electron beam induced crack propagation through the MAPbI<sub>3</sub> perovskite. These cracks propagate through the grains fig S6 (b & c) (indicated by red arrow) and also across the grain boundaries fig S6 (d, e & f) due to the long exposure to the electron beam.



Figure S8. Standard LVSEM surface morphological images of stoichiometric MAPbI<sub>3</sub>, (a) thin film, (b) pellet (inset showing the MAPbI<sub>3</sub> pellet image)



Figure S9. Differentiated SE spectra of stoichiometric MAPbI<sub>3</sub> pellets and thin films



Figure S10. J-V characteristics of the stoichiometric and non-stoichiometric (5% excess PbI<sub>2</sub>) MAPbI<sub>3</sub> solar cell devices before and after the bias degradation.

Table S1 Photovoltaic Performance of stoichiometric and non-stoichiometric (5% excess PbI2)
perovskite solar cell devices before and after the bias degradation.

Sample name	V <sub>oc</sub> (Volts)		J <sub>sc</sub> (mA.cm <sup>-2</sup> )		Fill factor		PCE	
	Fresh	Bias degrade d	Fresh	Bias degrade d	Fresh	Bias degrade d	Fresh	Bias degrade d
Stoichiometri c	0.98	0.85	18.50	17.40	60	41	10.80	6.10
Non- stoichiometric	1.01	0.87	19.90	10.90	59	48	11.80	4.50



Figure S11. (a-d) Cross-sectional LVSEM images of bias (1 V for 1.50 h) degraded excess PbI<sub>2</sub> MAPbI<sub>3</sub> solar cell devices for first and second scan respectively. Degraded grains exhibit bright nano structures (indicated by black circle) which grow further during prolonged exposure. The structures are similar to those that appeared in the excess MAI perovskite pellet (fig S8 and fig 3 a-c in the main paper) due to the variation local stoichiometry. Above results indicate the local variation in MAPbI<sub>3</sub> stoichiometry throughout the thickness of the active layer that might cause this non-uniform degradation under forward bias.



Figure S12. Cross-sectional LVSEM images of excess  $PbI_2$  perovskite solar cell devices before and after the bias degradation. Degraded devices (fig S12 b&d) shows the rearrangements of grains and wider grain boundaries as compared to the non-degraded devices (fig S12 a&c). Above results suggests faster decompositions at grain boundaries and the rearrangement of grains due to forward electrical bias. However, this pattern is not noticeable for stoichiometric MAPbI<sub>3</sub> (fig 4 a&b in the main paper).



Figure S13. Cross-sectional LVSEM images of stoichiometric and non- stoichiometric perovskite solar cell devices after bias degradation. We observed a different degradation pattern between the two MAPbI<sub>3</sub> compositions where stoichiometric MAPbI<sub>3</sub> starts to degrade near to top (indicated by blue arrow) electron transport layer (PCBM-BCP/ MAPbI<sub>3</sub> interface, fig S13 a&b), while non-stoichiometric (excess PbI<sub>2</sub>) degraded near to the hole transport (indicated by red arrow) layer (NiOx/MAPbI<sub>3</sub> interface, fig S13 c&d).



Figure S14. Cross-sectional LVSEM images of stoichiometric and non- stoichiometric perovskite solar cell devices without any bias degradation. For non-stoichiometric perovskite materials, excess PbI<sub>2</sub> detected (due to the appearance of bright nano structures indicated by blue arrows) near to the hole transport layer (NiO<sub>x</sub>/MAPbI<sub>3</sub> interface, fig. S14 d-f) which can promote the degradation at this interface as appeared in fig. S13 c&d.

References:

[1] V. Kumar, W. L. Schmidt, G. Schileo, R. C. Masters, W. Wong-stringer, D. C. Sinclair, I. M. Reaney, D. Lidzey, C. Rodenburg, Nanoscale Mapping of Bromide Segregation on the Cross Sections of Complex Hybrid Perovskite Photovoltaic Films Using Secondary Electron Hyperspectral Imaging in a Scanning Electron Microscope. *ACS Omega*, **2017**, *2*, 2126–2133.

[2] H. Demers, N. Poirier-Demers, A. R. Couture, D. Joly, M. Guilmain, N. de Jonge, D. Drouin, Three-dimensional electron microscopy simulation with the CASINO Monte Carlo software. *Scanning*, **2011**, 33(3), 135-14.