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Supplemental Information

Layer-by-Layer Degradation of Methylammonium Lead Tri-iodide Perovskite Microplates

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Supplemental Information

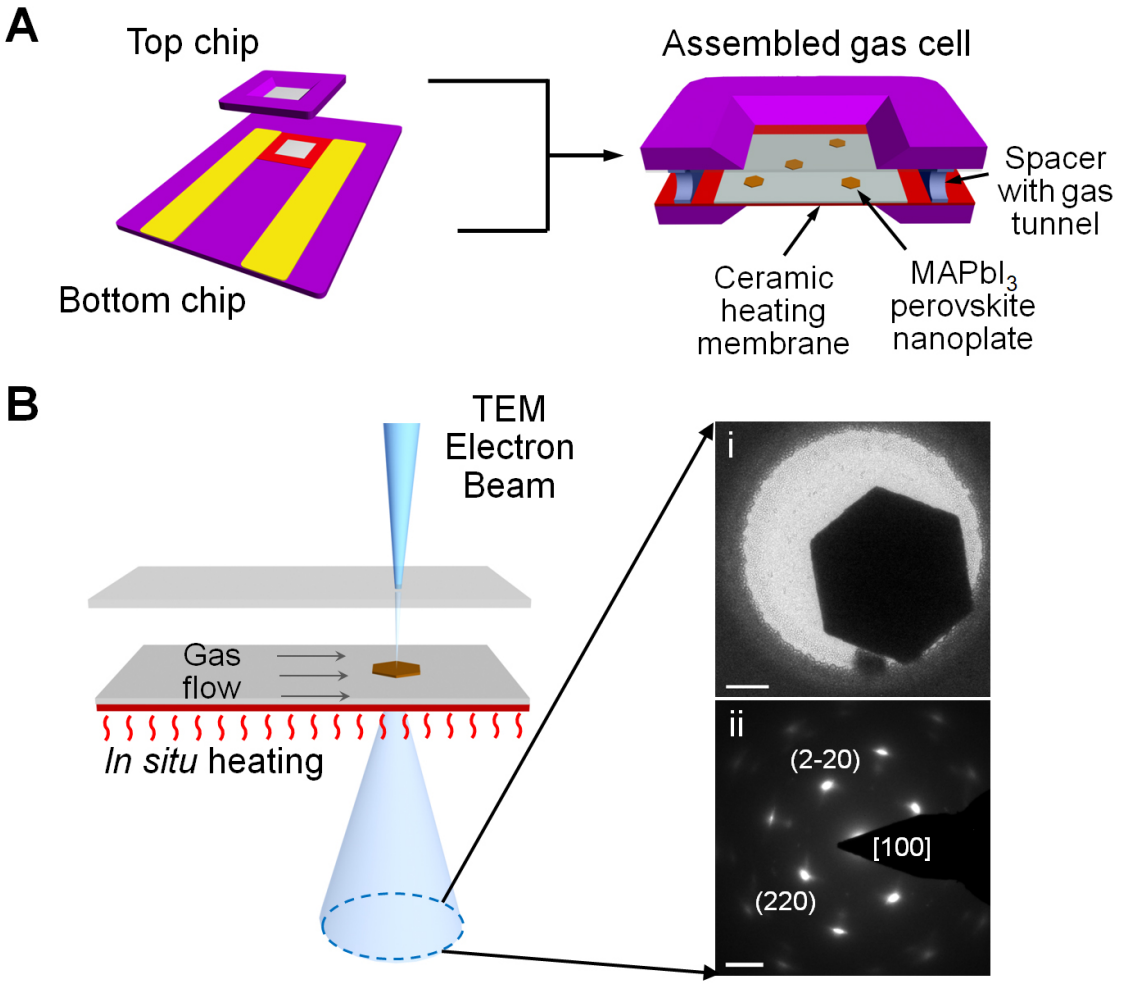

Figure S1. Schematic illustrating the *in situ* TEM observation of thermal-heating-induced $MAPbI_3$ degradation in a TEM gas cell. (A) A top chip is assembled with a bottom chip to form a gas cell for TEM visualization by using a TEM gas holder. **(B)** Schematic of the *in situ* characterization of $MAPbI_3$ microplate. Insets show the low-magnification observation of microplate **(i)** and the according electron diffraction pattern **(ii)**. Scale bar, 2 nm^{-1}.

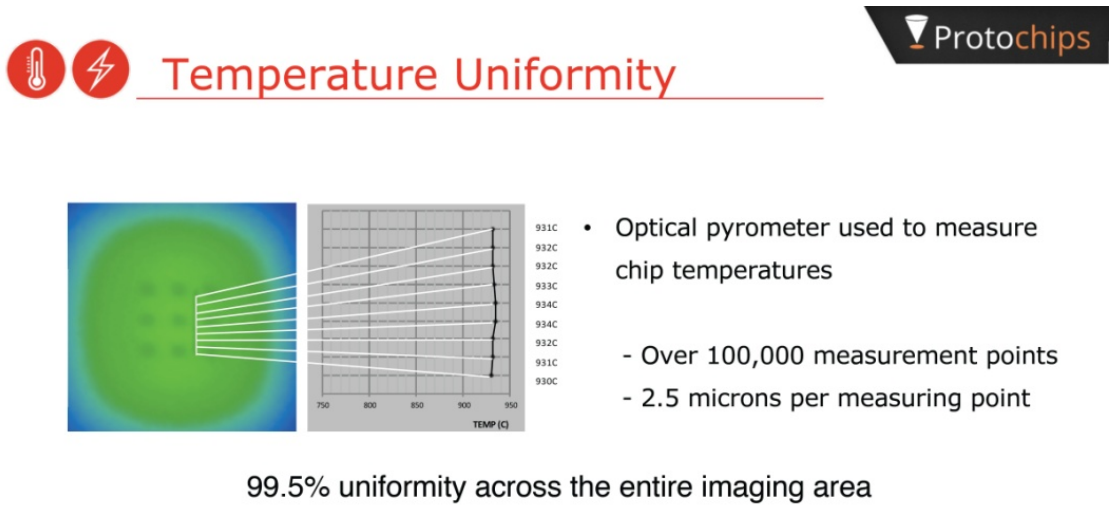

Figure S2. Temperature map of E-chip measured by optical pyrometer.

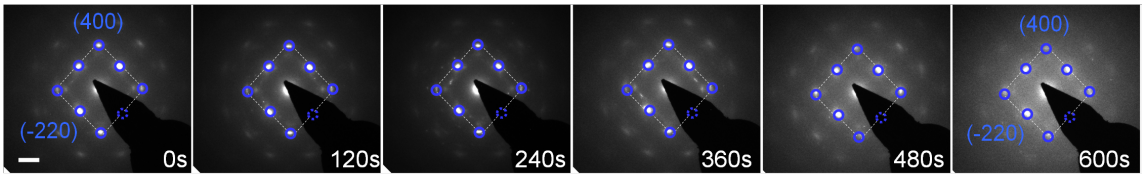

Figure S3. The control experiment of the beam damage on $MAPbI_3$ without thermal effect. The strict control experiment without heating demonstrates that the beam dosage used in our *in situ* studies has no apparent impact to our samples.Scale bar, 2 nm^{-1}.

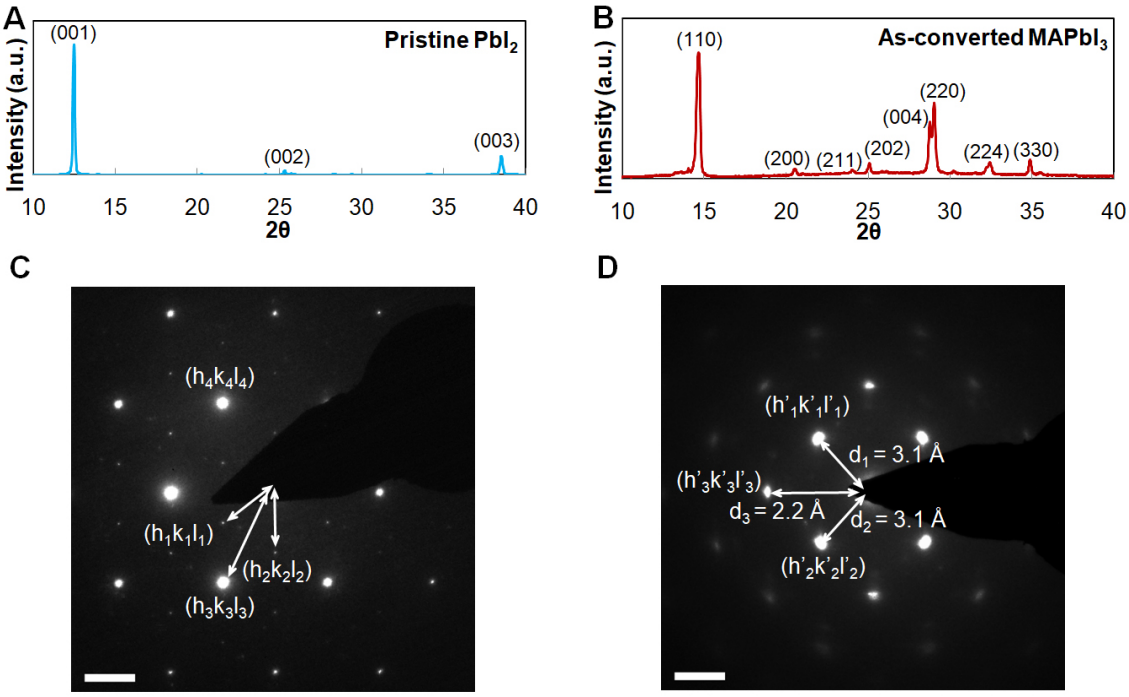

Figure S4. XRD characterization of the microplate and the index of the ED pattern. (A) The XRD pattern of the pristine PbI_2. **(B)** The XRD pattern of the as-converted $MAPbI_3$. **(C)** The index of the trigonal PbI_2 ED pattern. Scale bar, 2 nm^{-1}. **(D)** The index of the tetragonal $MAPbI_3$ ED pattern based on the measured lattice spacing. Scale bar, 2 nm^{-1}.

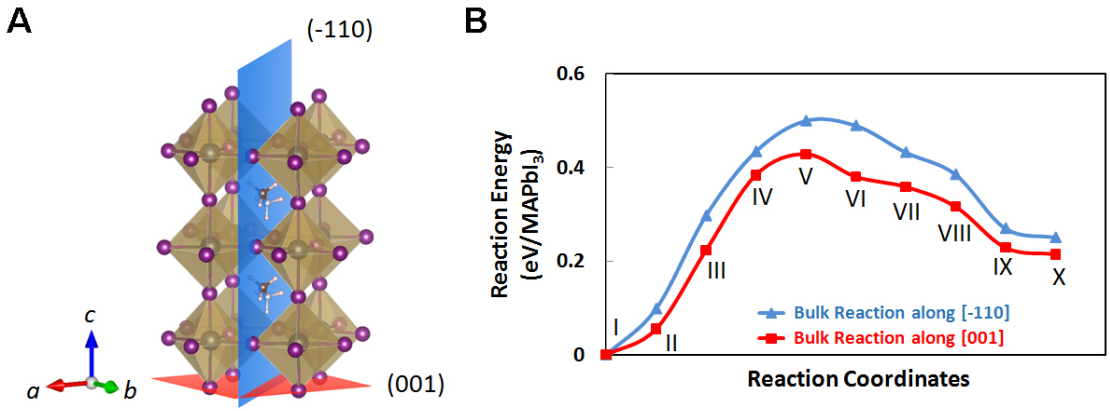

Figure S5. $MAPbI_3$ bulk decomposition. (A) The facet of (001) and (-110) in the tetragonal $MAPbI_3$. **(B)** The calculated minimum energy path of $MAPbI_3$bulk decomposition along [-110] and [001] axis. The decomposition barrier of [001] pathway is 0.43 eV per $MAPbI_3$ unit, lower by 0.07 eV than that of [-110] pathway.

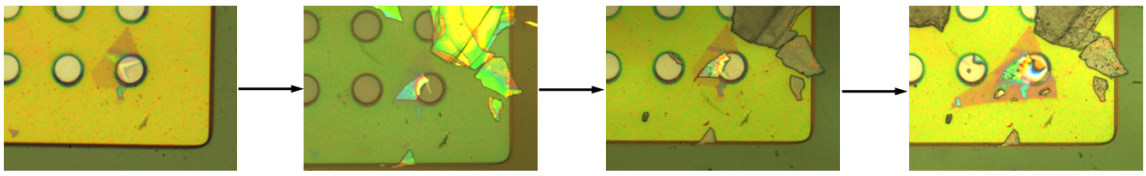

Figure S6. Fabrication process of BN-perovskite-BN heterostructure.

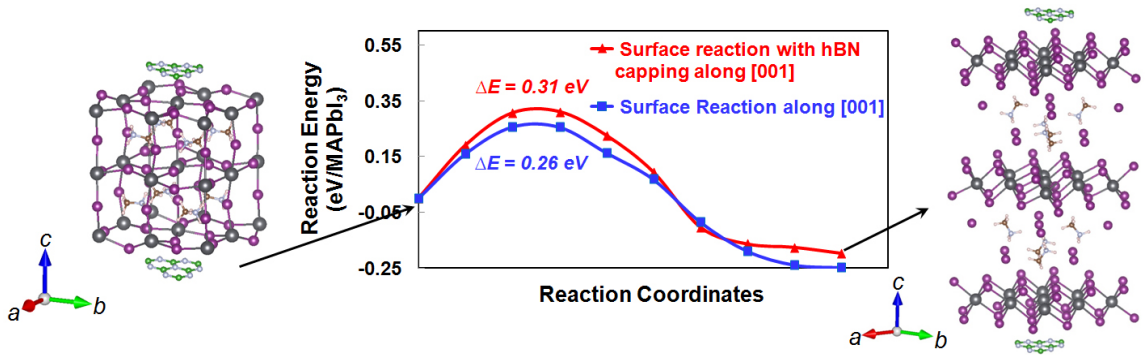

Figure S7. The DFT calculated minimum energy path for $MAPbI_3$ with hBN capping under thermal loading. The decomposition barrier of the MAPbI3 surface with hBN capping is about 0.31 eV, which is 0.05 eV higher than the pristine MAPbI3 surface under thermal loading, corresponding to 7-fold slower reaction rate.

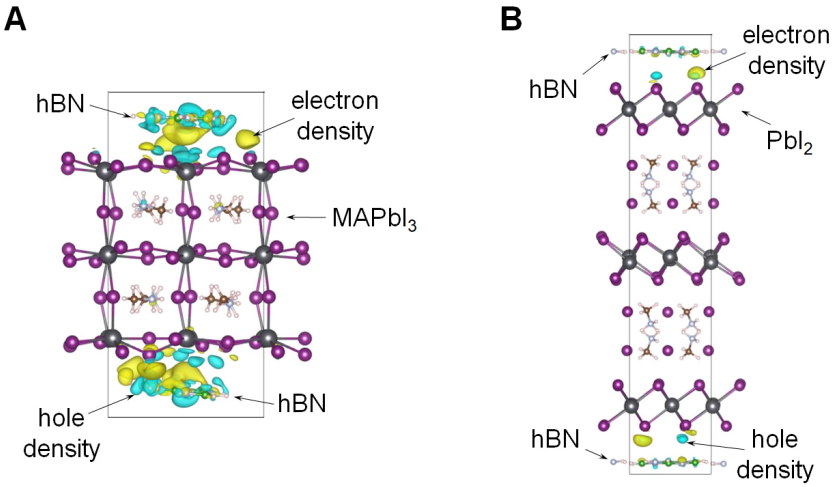

Figure S8. Charge density difference (ρ_{diff} = ρ(hBN@$MAPbI_3$) − ρ(hBN) − ρ($MAPbI_3$)) maps of (A) initial structure and (B) degradation product. The yellow color stands for electron density, and the cyan color for hole density. The contour is plotted with density cutoff of 0.0003 *e*/$Bohr^3$.