Electronic Supplementary Information

Photoluminescence Enhancement and High Accuracy Patterning of Lead Halide Perovskite Single Crystals by MeV Ion Beam Irradiation

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1. Experimental Methods

Growth of $MAPbBr_3$ single crystals

Typically, 1M solution of MABr and $PbBr_2$ was prepared in DMF. The solution was then filtered using PTFE filter with 0.2-mm pore size and the filtrate was placed in a vial that was placed in a heating block at 60 °C. Next, the temperature was increased gradually to 80 °C and the vial was left undisturbed for 3 hours. The obtained crystals were dried in a vacuum oven at 40 °C overnight then the crystals were stored in the glovebox until needed.

Absorbance measurements

Steady-state absorbance measurement of the $MAPbBr_3$ single crystal was carried out in transmission mode using a Cary 5000 spectrophotometer equipped with an integrating sphere.

XRD measurements

X-ray Diffraction analysis was performed using Panalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and a PIXcel3D 2 × 2 area detector, operating at 45 kV and 40 mA. The single crystal was studied under ambient conditions using the parallel beam bragg Brentano geometry. XRD data was collected with a step size of 0.013° and a scan speed of 0.013°/s and the analyses was carried out using the HighScore 4.1 software from PANanalytical.

X-ray Photoelectron Spectroscopy (XPS)

A Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα source (photon energy = 1486.6 eV) was used for XPS characterization. Relative atomic percentages of different species were computed from high-resolution spectra, fitted with Voigt functions using CasaXPS software.

Photoluminescence imaging

The spectrally resolved images were recorded with an emission detection bandwidth of 2.5 nm over a spectral wavelength of 498-578 nm. We used 10× and 20× air (Nikon CFI Plan Apo Lambda 10×0.45 NA) objective lens. The spectral profiles of ion beam exposed and un-exposed area were obtained by drawing rectangular regions of interest around.

FLIM measurements

Photoluminescence was excited at 488 nm with a laser diode modulated at 10 MHz. The PL signal was detected in the spectral emission range 500-550nm. The frame size was set to 512×512 pixels and the scanning pixel-dwell time was set at 12.1 µs/pixel. Each FLIM image was obtained by averaging over 20 frames corresponding to an acquisition time of ~1 min. The FLIM data acquisition was managed by the VistaVision software (ISS). For each pixel, the FLIM system recorded a value of phase delay (ϕ) and de-modulation (M) at multiple frequencies with respect to the excitation signal. The FLIM data were visualized in the phasor plot where g=M cos(ϕ) and s=M sin(ϕ).[1] Before the experiments, the system was calibrated with a solution of Fluorescein in 1M NaOH, which has a known single exponential lifetime of 4.1 ns. In a typical FD FLIM measurement a sinusoidally modulated source excites the sample and the outcoming emission signal is still a sine wave, but has undergone modulation and phase shift with respect to the source. The modulation ratio (M) and phase change (ϕ) are derived from Phasor plot and their corresponding lifetime contributions (modulation lifetime (τ_M) and phase lifetime (τ_ϕ)) are given by[2]

$$\tau_M = \frac{1}{\omega}\left(\frac{1}{M^2} - 1\right)^{\frac{1}{2}} \quad (1)$$

$$\tau_\phi = \left(\frac{1}{\omega}\right)tan\phi \quad (2)$$

TCSPC measurement

TCSPC measurements were performed for bulk pristine sample without any irradiation using Edinburgh instrument fluorescence spectrometer (FLS 920). The PL decay traces were recorded by exciting the sample at 405 nm with a pulsed diode laser with a 50 ps at a repetition rate of 0.05-1 MHz.

ToF- ERDA Measurement

In order to quantify the low Z elements of $MAPbBr_3$ single crystals, Time of flight elastic recoil detection analysis (ToF-ERDA) measurements were carried out. 36 MeV iodine beam was collimated using a circular aperture in the beamline and focused to a spot size of ~1 mm on the sample surface, while the sample was titled 62.5 degrees w.r.t beam direction and the recoiled elements were captured by a ToF detector which is kept 13.75 degrees in the direction of the incident beam. Since the sample was titled w.r.t the incident beam direction the beam shape turns into an elliptic.

2. Ion penetration depth

Table S1. The penetration depths of used ions in $MAPbBr_3$ and Cu

	3MeV He^+	12.5MeV Br^{5+}	20MeV I^{7+}
Cu (µm)	5.49	2.43	2.91
$MAPbBr_3$ (µm)	24.7	11.4	14.3

3. PL maps and spectra peak analysis

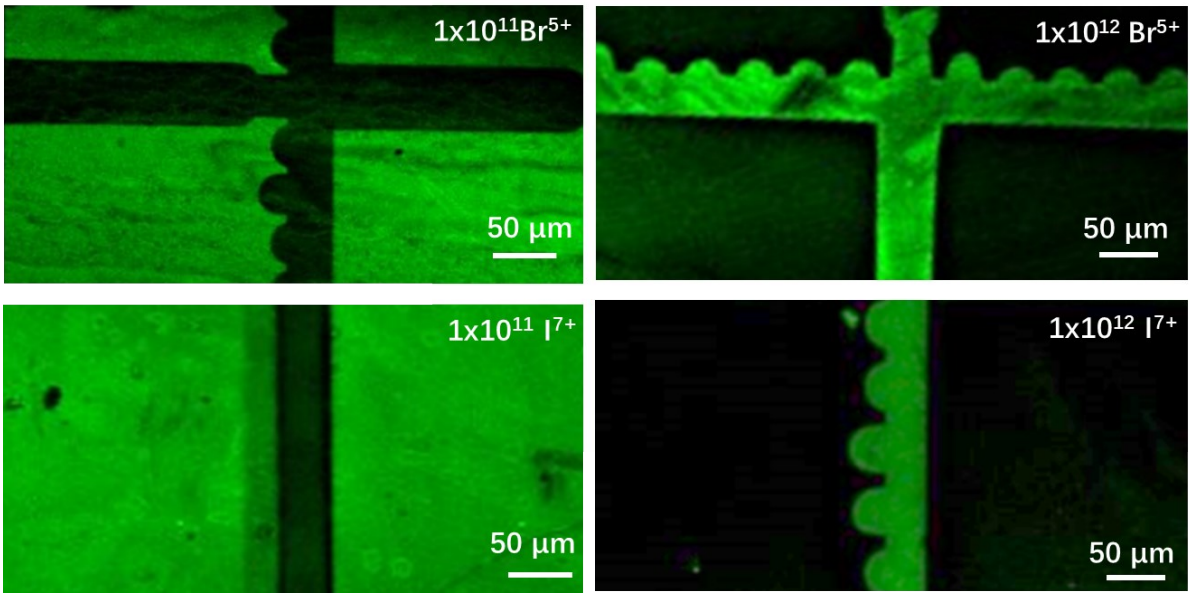

Fig. S1.1 PL confocal maps for patterned $MAPbBr_3$ crystal surfaces.

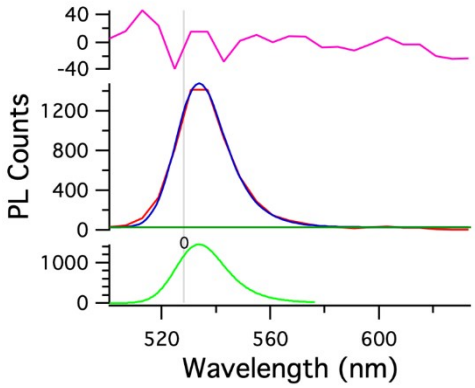

Fig. S1.2 PL spectra (red) obtained from masked (unexposed) $MAPbBr_3$ crystal and its fitting with expmodGauss function; where blue = fitted curve, green = peak1 and pink = residue after curve fitting.

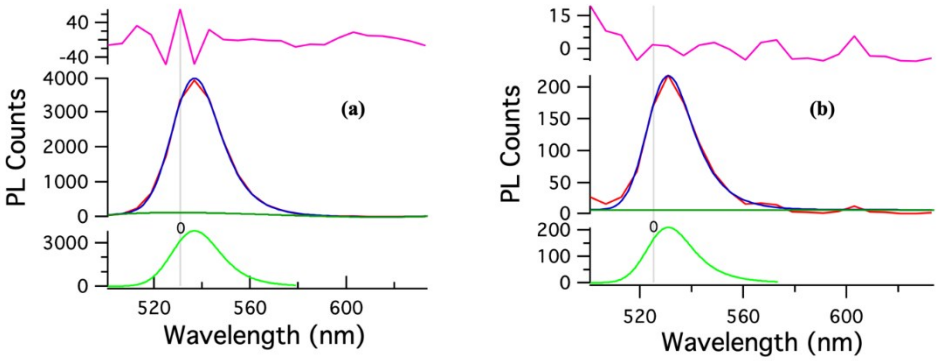

Fig. S1.3 PL spectra obtained from the ion exposed surface (a) low dose area (1×10^{11} I/cm^2) (b) high dose area (1×10^{12} I/cm^2)) of 12.5MeV I^{7+} and are fitted with expmodGauss function; where blue = fitted curve, green = peak1 and pink = residue after curve fitting

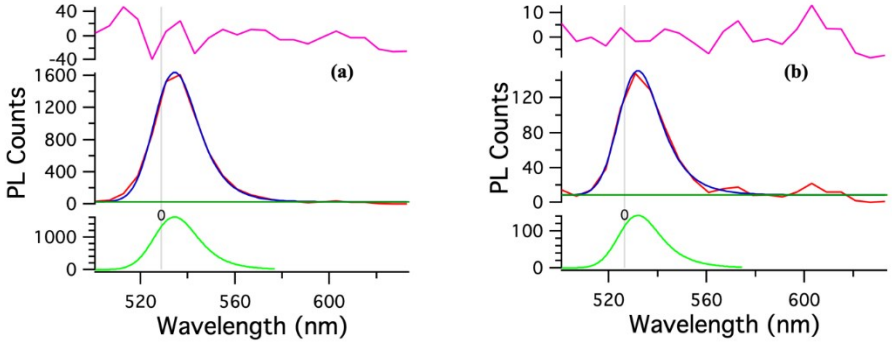

Fig. S1.4 PL spectra obtained from the ion exposed surface (a) low dose area (1×10^{11} Br/cm^2) (b) high dose area (1×10^{12} Br/cm^2)) of 12.5MeV Br^{5+} and are fitted with expmodGauss function; where blue = fitted curve, green = peak1 and pink = residue after curve fitting

Table S2. The peak position and FHWM of PL peaks for patterned surfaces (both pristine crystal and areas irradiated with ion beam), obtained from fitting of all spectra with Voigt function, and background with log-polynomial function

Ion irradiation conditions	Peak position (nm)	FWHM (nm)
No exposure	533.7	21.547
1×10^{11} I/cm^2	535.14	20.318
1×10^{12} I/cm^2	530.94	21.188
1×10^{11} Br/cm^2	534.37	22.158
1×10^{12} Br/cm^2	531.91	20.587

4. Fluorescence lifetime imaging and time correlated single photon counting measurement

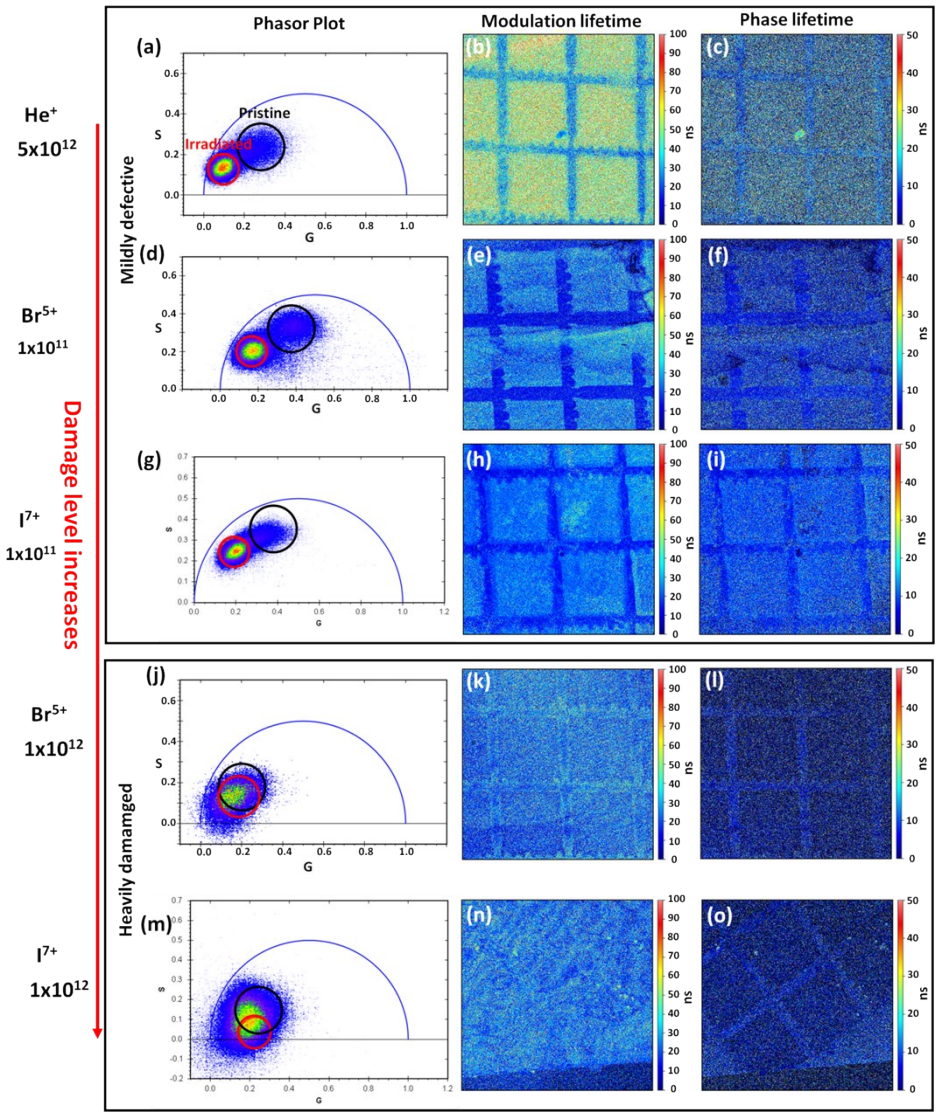

Fig. S2.1 FLIM imaging: Phasor plot, modulation lifetime map, phase lifetime map of samples patterned with six different conditions in the order that surface defect density increases from top row to bottom row.

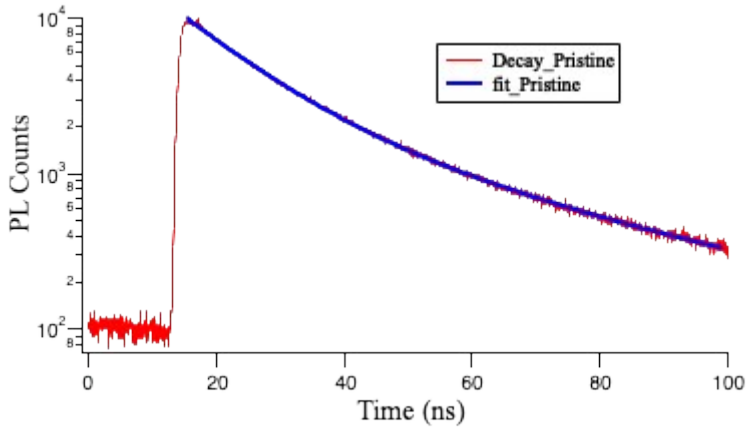

Fig. S2.2 TCSPC decay curve measured on a pristine $MAPbBr_3$ single crystal and its fitted plot.

5. Electron beam energy loss along the depth in $MAPbBr_3$

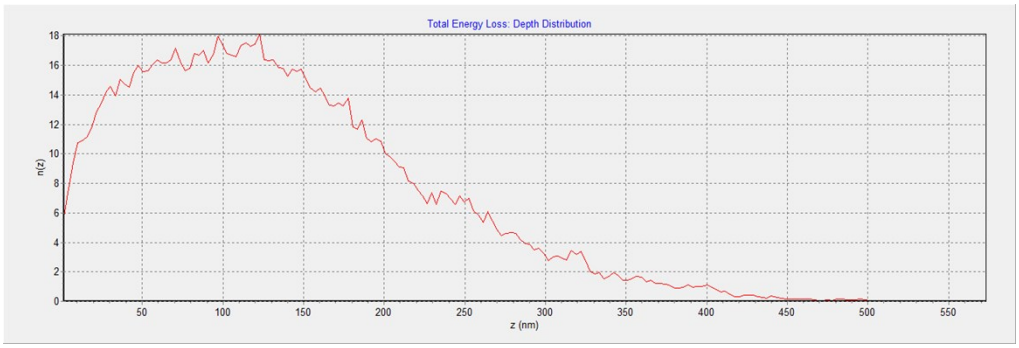

Fig. S3 The calculated depth distribution of energy loss for 5kV electrons incident on $MAPbBr_3$

6. Composition analysis of heavily damaged $MAPbBr_3$

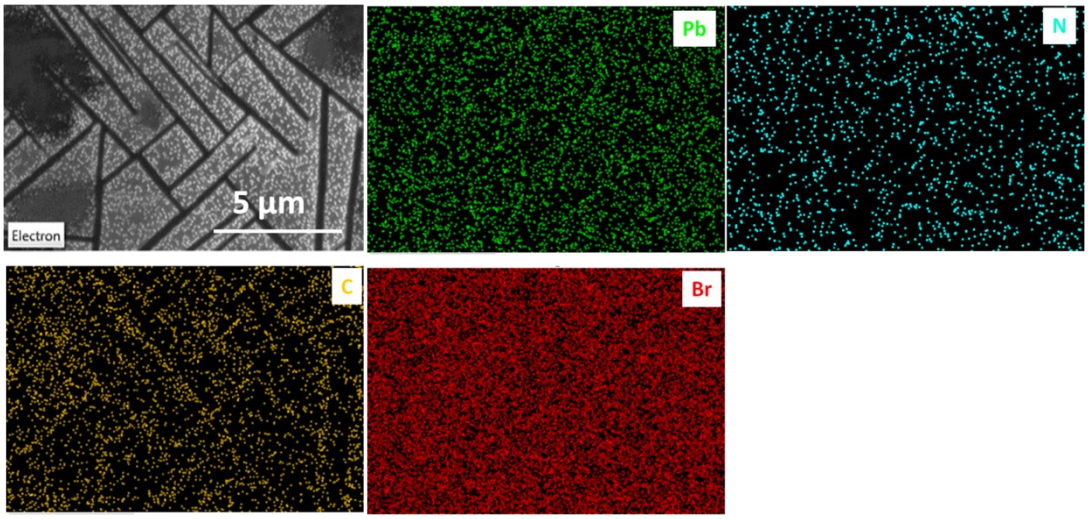

Fig. S4.1 SEM image of an irradiated region on heavily damaged crystal by high dose Br^{5+}, and corresponding elemental maps of C, N, Pb, Br by EDS.

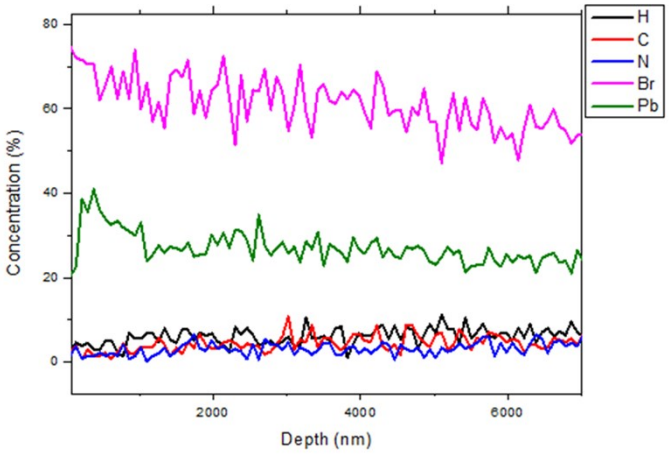

Fig. S4.2 ERDA measurements of the elemental distribution along the depth with accumulated dose equal to heavily damaged crystal by high dose I^{7+}.

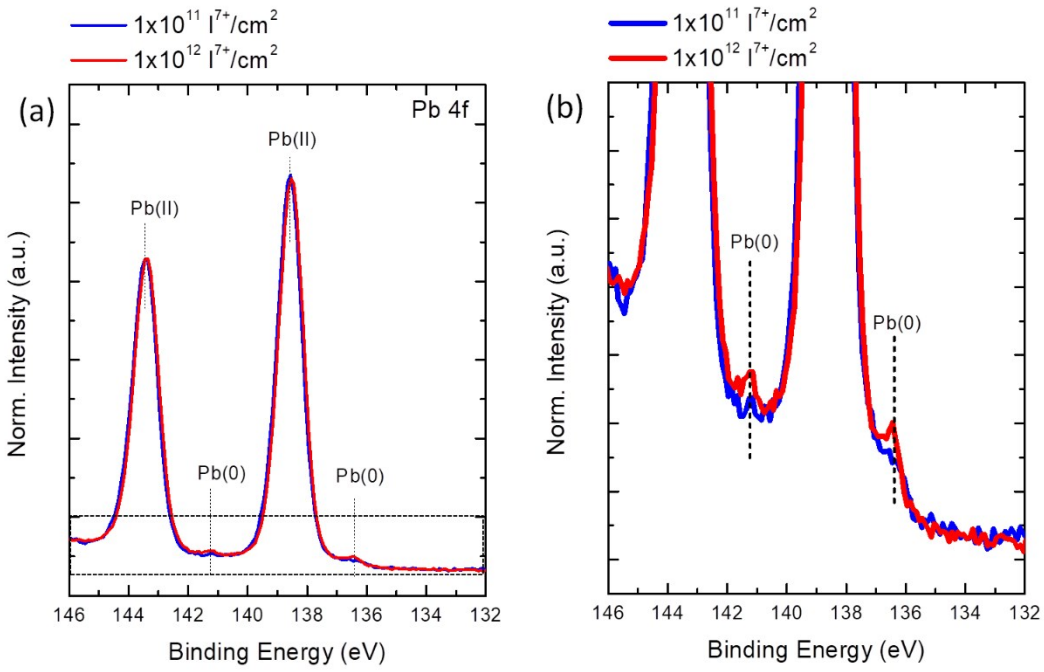

Fig. S4.3 (a) XPS spectra of the crystal surfaces patterned by $1x10^{11}$ I^{7+}/cm^2 and $1x10^{12}$ I^{7+}/cm^2; (b) zoomed in of the spectra within the black dashed square of panel (a). Quantification results show that the Pb^0 is approx. 0.8% of the whole Pb content on the surface patterned by $1x10^{11}$ I^{7+}/cm^2, and instead it is approx. 1.7% of the total Pb content for $1x10^{12}$ I^{7+}/cm^2.

7. A calculation of the surface Frenkel defect density based on SRIM

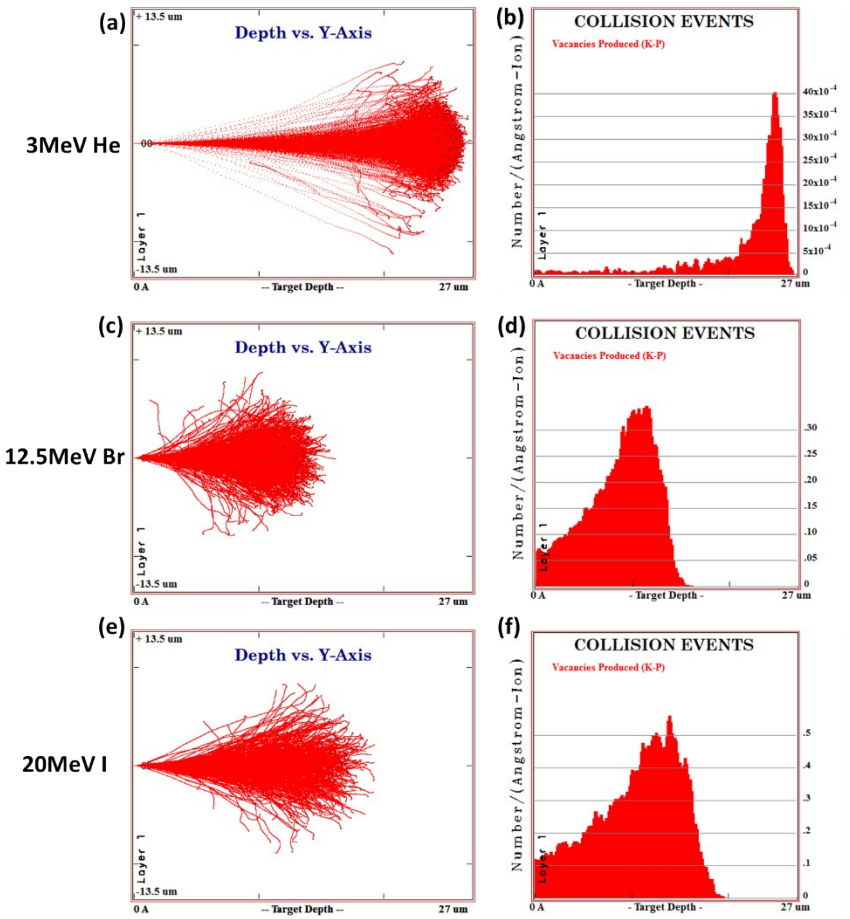

Fig. S5.1 The ion distribution and defect distribution in $MAPbBr_3$ calculated by SRIM[3] for a, b) 3MeV He^+, c, d) 12.5MeV Br^{5+}, e, f) 20MeV I^{7+}.

With the input of incident ion type, ion energy and target material, the vacancy number per Angstrom in depth per ion distribution along the depth is obtained, seen in Fig. S5.1.With its value at the surface (defined as D), the surface defect density (SDD) is calculated as $S^{DD}\ (vacancy/cm^3) = D \cdot ion\ dose \cdot 10^8$, where ion dose is in the unit of ion number/cm^2, and D is the vacancy number per Angstrom in depth per ion at the surface of $MAPbBr_3$. (Table S3**)**

Table S3. The ion type, ion dose, and calculated defect density at the surface of $MAPbBr_3$.

Ion type (mass)	Defect/Å/Ion at the surface	Dose (ions/cm^2)	Defect density at the surface (/cm^3)
He^+ (4)	0.0001	5×10^{11}	5×10^{15}
		5×10^{12}	5×10^{16}
Br^{5+} (79)	0.075	1×10^{11}	7.5×10^{17}
		1×10^{12}	7.5×10^{18}
I^{7+} (127)	0.15	1×10^{11}	1.5×10^{18}
		1×10^{12}	1.5×10^{19}

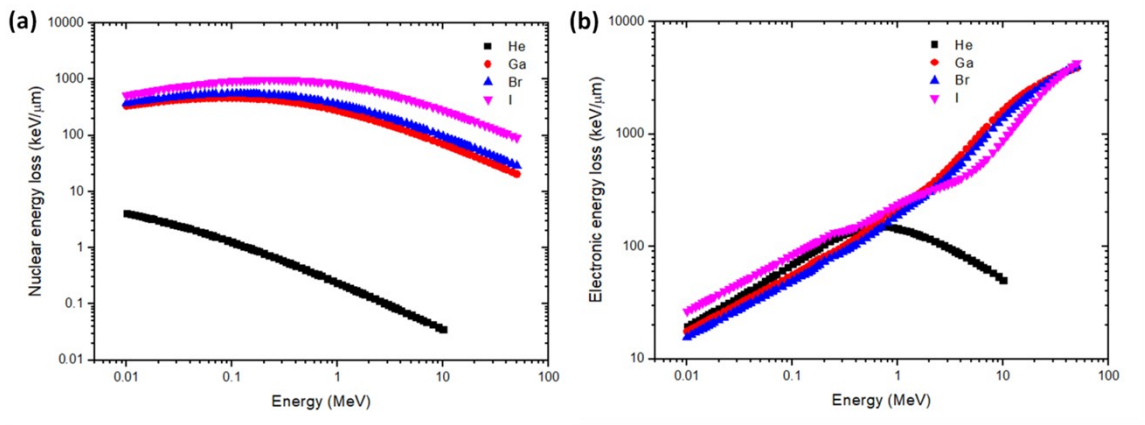

Fig. S5.2 The nuclear and electronic energy loss for He^{+}, Br^{5+}, I^{7+} in $MAPbBr_3$ calculated by SRIM[3].

References:

1. M. A. Digman, V. R. Caiolfa, M. Zamai and E. Gratton, *Biophysical Journal*, 2008, **94**, L14-L16.
2. J. R. Lakowicz, *Principles of fluorescence spectroscopy*, New York : Springer, 3rd ed.. edn., 2006.
3. J. F. Ziegler, M. D. Ziegler and J. P. Biersack, *Nucl. Instrum. Meth. B*, 2010, **268**, 1818-1823.