

Supporting Information

In situ and real-time ToF-SIMS analysis of light-induced chemical changes in perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Experimental Section

Characterization of as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ film.

Figure S1-S4

Table S1

Experimental Section

Materials. N, N-dimethylformamide (DMF, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, >99.5%) was purchased from Shanghai MaterWin New Materials Co., Ltd. (China). Lead diiodide (PbI_2 , >99.999%) was obtained from Sigma-Aldrich (Shanghai, China). The F-doped tin oxide (FTO) glass was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. (China). All chemicals were of analytical grade. Ultrapure water (resistivity = $18.2 \text{ M}\Omega\cdot\text{cm}$) produced from a Milli-Q apparatus was used throughout the experiments.

Synthesis of Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. To obtain a uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite precursor, $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were mixed at a 1:1 molar ratio and dissolved in DMF (40% w/w) under vigorous magnetic stirring for 12 h at $60 \text{ }^\circ\text{C}$. The reaction was conducted under argon atmosphere in glove box. The as-prepared precursor was then spin-coated on the FTO glass and annealed at $100 \text{ }^\circ\text{C}$ for 10 min.¹ Thus, the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ sample was obtained and used for subsequent experiments.

Characterizations. SEM characterizations of the samples were performed on a scanning electron microscope (Hitachi, S-4800) at 15 kV, equipped with an OXFORD INCA EDS analyzer. XRD spectra were obtained on a Bruker D8 FOCUS X-ray diffraction in the range of $10^\circ\text{--}80^\circ$. UV-vis spectra were carried out on a CRAY 500 Ultraviolet-obviously-near-infrared spectrophotometer. ToF-SIMS analysis was carried out with a ToF-SIMS V instrument (IONTOF GmbH, Muenster, Germany)

equipped with a 30 keV Bi⁺ ion gun and a white light source with known power of 4 W (power density: 55 mW/cm²). The power of lasers was detected by LE-CPW power meter series (LEOPTICS, Shenzhen, China). The irradiation intensity on the sample of each laser (blue laser, 470 nm; green laser, 532 nm and red laser, 635nm) was about 10 mW/cm². 80 mW/cm² simulated visible light was produced by Xenon lamp after filtrate the UV light (<400 nm) and IR light (>780 nm).

Characterization of as-prepared CH₃NH₃PbI₃ film.

The CH₃NH₃PbI₃ sample prepared by spin-coating on FTO substrate and annealing at 100°C was characterized by SEM, XRD, EDS, ToF-SIMS and UV-vis spectrum (Figure S1, ESI). The surface morphology of CH₃NH₃PbI₃ sample was investigated by SEM. In Figure S1A, the surface of CH₃NH₃PbI₃ sample showed uniform morphology with an averages grain sizes of 100-200 nm, demonstrating that well-crystallized CH₃NH₃PbI₃ was synthesized.² The crystal structure and composition of CH₃NH₃PbI₃ sample was characterized by XRD. As shown in Figure S1B, diffraction peaks at 14.26°, 20.16°, 23.62°, 24.64°, 28.60°, 32.00°, 35.14°, 40.80° and 43.06° were detected in CH₃NH₃PbI₃ corresponding to the (110), (112), (211), (202), (220), (310), (312), (224) and (314) planes of the tetragonal perovskite structure, respectively. Other stronger diffraction peaks marked with asterisks were originated from FTO substrates. No other impurity peaks can be seen, indicating highly ordered perovskite crystal structure of the CH₃NH₃PbI₃

samples.³ EDS analysis was applied to determine the elemental composition of the as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Figure S1C). The EDS spectrum showed the peaks of C, N, Pb and I elements. The atomic ratio of Pb and I was about 3:1 which was in good agreement with the molecular formula. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ sample was further analysed by ToF-SIMS spectrum (Figure S1D). Dominant peaks were seen at m/z 126.9, 157.9, 253.8, 285.8, 380.7, 461.8, 588.7 and 796.7, corresponding to I^- , CNH_5I^- , I_2^- , CNH_6I_2^- , I_3^- , PbI_2^- , PbI_3^- and Pb_2I_3^- , respectively.⁴ These peaks were selected as characteristic secondary ions of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and were further used to study the subsequent light-induced chemical changes. The UV-vis spectrum of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was shown in Figure S1E to explain the different optical absorption at the UV-vis wave band.⁵ The wavelength positions of three laser systems used in subsequent study were labelled with dashed lines of corresponding colors. The optical absorption intensities are blue laser > green laser > red laser.

References

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Figure Captions:

Figure S1 SEM (A), XRD (B), EDS (C), ToF-SIMS (D) and UV-vis absorption (E) analysis of the synthesized perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ sample.

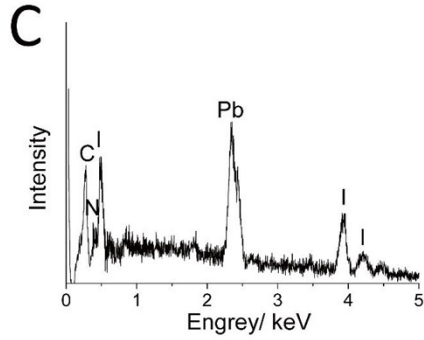
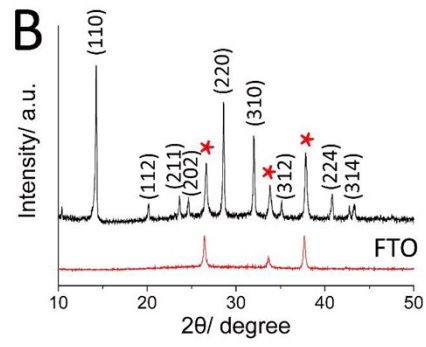
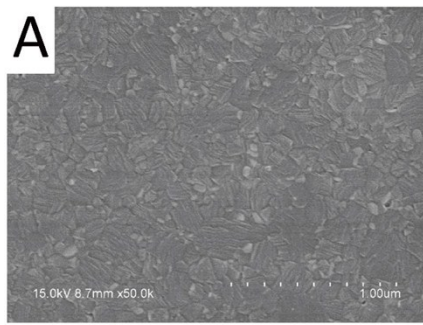
Figure S2 The intensity changes of selected secondary ions in $\text{CH}_3\text{NH}_3\text{PbI}_3$ film storing in air from 0 to 3 weeks (N=5).

Figure S3 ToF-SIMS time-resolved signal changes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ with 80 mW/cm^2 simulated visible light illuminate from 1500 s.

Figure S4 The time-resolved signal changes of I^- at the interface.

Table S1 The migration of iodine calculated by the intensity changes of some selected secondary ions from $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Figure S1



El	AN	Series	unn. C	norm. C	Atom. C	Error
			[wt.%]	[wt.%]	[at.%]	[wt.%]
I	53	L-series	38.23	57.82	33.45	2.2
Pb	82	M-series	21.56	32.61	11.56	1.0
C	6	K-series	3.67	5.56	33.97	0.8
N	7	K-series	2.65	4.01	21.02	0.7
Total:			66.12	100.00	100.00	

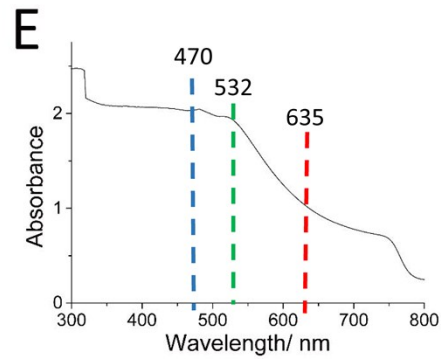
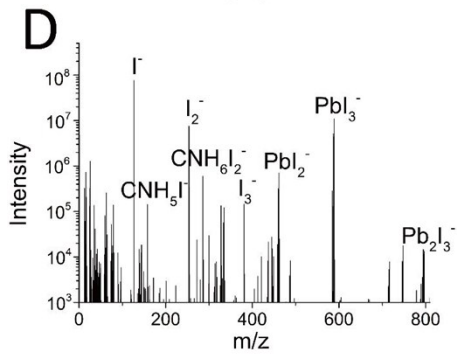


Figure S2

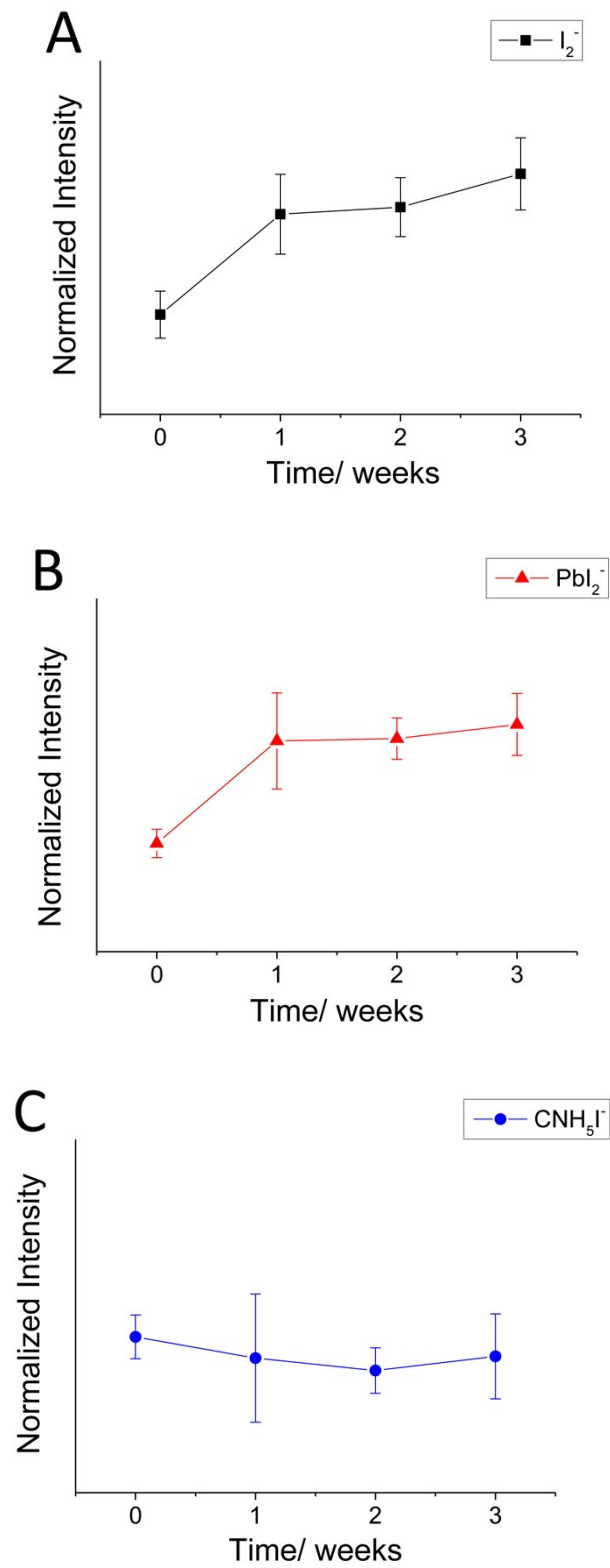


Figure S3

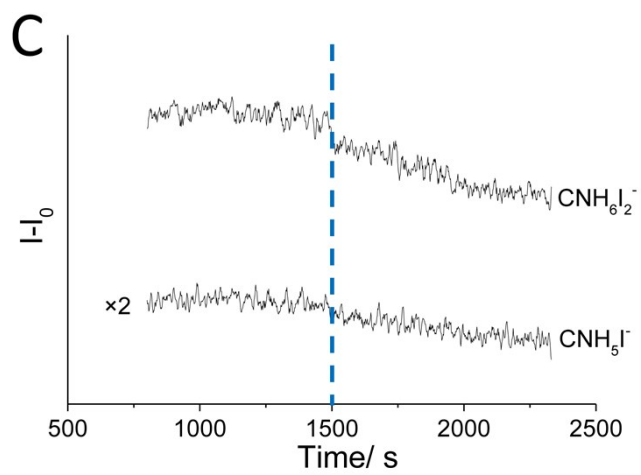
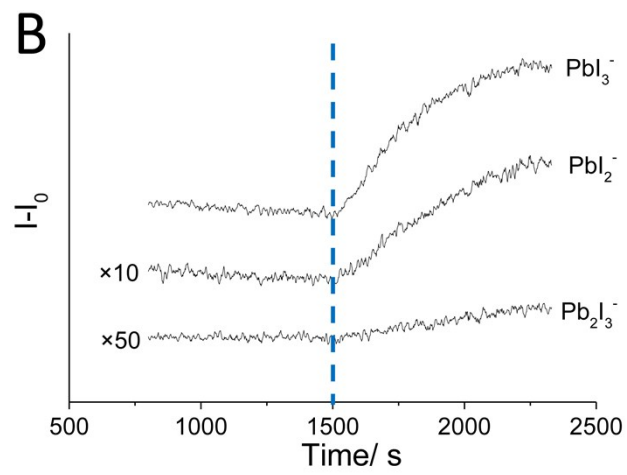
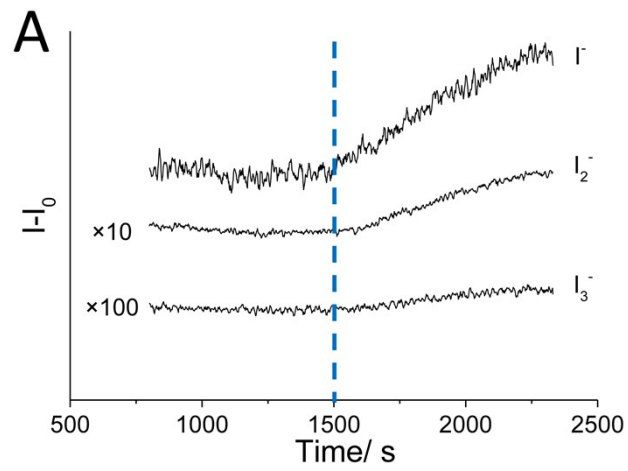


Figure S4

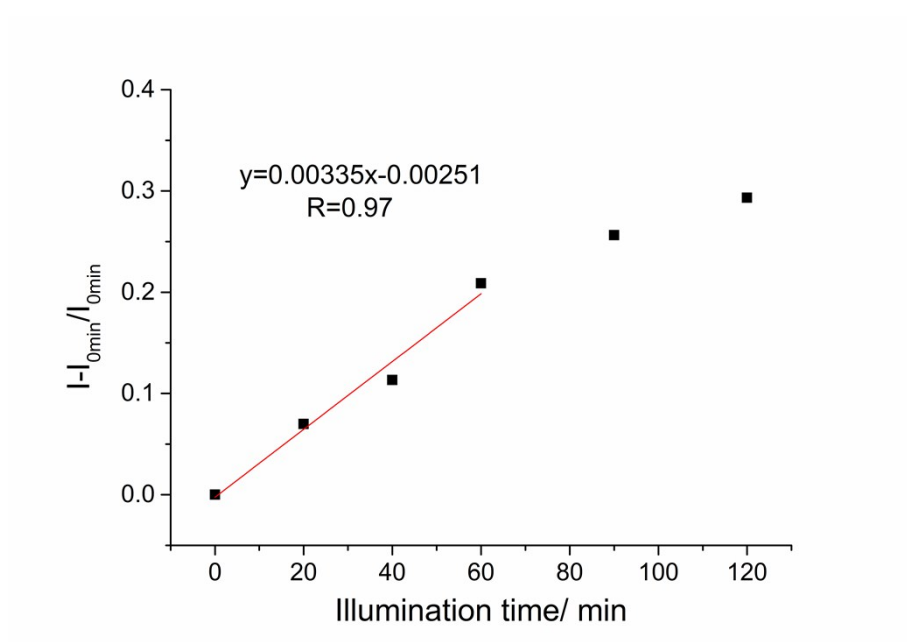


Table S1 The migration of iodine calculated by the intensity changes of some selected secondary ions from $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Secondary ions	I_1	I_2	$(\frac{I_1 - I_2}{I_1} \times 100\%)$
I^-	371092	353165	4.8%
I_2^-	25949	25924	4.0%
PbI_3^-	63495	62857	1.0%
PbI_2^-	3666	3501	4.5%
CNH_6I_2^-	2249	2016	10.4%
CNH_5I^-	501	449	10.4%

I_1 : The secondary intensities of ions at 1500 s.

I_2 : The secondary intensities of ions at 1600 s.