Electronic Supplementary Information:

Photodecomposition and thermal decomposition in methylammonium halide lead perovskites and inferred design principles to increase photovoltaic device stability

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S1. Sample preparation

Powdered Samples

Lead (II) iodide (PbI₂, 99.9%) was purchased from Tokyo Chemical Industry Co., Ltd, lead (II) bromide (PbBr₂, 99.999%) was purchased from Sigma-Aldrich, methylammonium iodide (MAI) and methylammonium bromide (MABr) were purchased from Dyesol Limited. All chemicals were used as received without any further purification. Hybrid perovskites in powdered polycrystalline material form were obtained mimicking the procedure to deposit perovskite thin films on substrates. Briefly, 1 mL of DMF (Wako Pure Chemical Industries) solution (~1 M) containing desired stoichiometric precursor quantities to synthesize MAPbBr₃ or MAPbI₃ was poured on a 10 cm in diameter mortar kept at 100 °C inside of fume hood. Precursor solution is slowly spread on the mortar surface helped by the pestle. DMF solvent evaporates in 1-2 minutes remaining a solid crystalline material on the mortar that is carefully collected. Perovskite phase purity proof, absence of PbX₂ peaks and crystalline parameters are checked from powder XRD measurements, see Figure S1.

Thin-film samples for XRD and XPS degradation studies

FTO glasses (14 Ω /sq, Opvtech.) were cleaned by sequential sonication in deionized water, ethanol, acetone, and UV-Ozone treated before use. PbI₂, PbBr₂, MAPbI₃ and MAPbBr₃ precursor DMF solutions (~1 M) were spin-coated on the substrates and annealed at 100 °C for 5 min. XPS and XRD analysis of these thin-films is reported in Sections 8 and 9, respectively.



Figure S1. XRD powder diffraction of MAPbI₃ and MAPbBr₃ powdered polycrystalline samples.

S2. General procedure for sample degradation experiments

Powdered Samples

Typically, fresh samples of PbI₂ (~180 mg) are loaded in the sample holder located inside the chamber, Figure S2a. Once high vacuum level is reached ($<10^{-6}$ Torr), the pressure gauge and MS spectrometer are switched on. The temperature of the sample under dark conditions and high vacuum conditions was observed to be slightly high (30-35 °C) due to unavoidable e-ionization (radiative heating) of MS. Light power pulses of white, red, and blue LEDs are programmed using an Autolab PGSTAT204 potentiostat including the LEDs and the LED driver box accessory (Metrohm AG). Simulated sun-light is obtained using a 150 W short-arc Xe lamp from Solar Simulator (PEC-L01, Peccell Technologies Inc.). Light pulses in the solar simulator were computer controlled remotely by a homemade program and actuator. Both light power delivered by solar simulator and LEDs were calibrated using a calibrated silicon photodiode accounting quartz window and distance between light source and sample holder (see section S5 for light power calibration details). Mass spectrometer traces were recorded using a quadrupole mass spectrometer (1-300 amu) equipped with an electron multiplier detector (RGA300, SRS Stanford Research Systems). Conventional Faraday cup detector in this mass spectrometer was not reliable to detect diiodine traces at nearly room temperature. MS raw signals were calibrated using sensitivity factors calculated following the procedure explained in section S6.

Thin-film Samples

Thin-film samples (see section S1 for sample preparation) were loaded in the same vacuum chamber described in Figure S2a where the MS experiments were conducted. A Portable Solar Simulator (PEC-L01) was mounted on top of the vacuum chamber allowing the light exposure on the samples through a quartz glass view port. The samples were exposed to solar simulator light (~0.55 Sun) at vacuum of ~10⁻⁶ Torr during 4 h. Thin films were analyzed by XPS and XRD before and after degradation experiments, see sections S7-9.

S3. PbI₂ degradation under illumination/dark conditions.

Powdered samples and thin-films were prepared according to section S1. Degradation procedures follows section S2. Section S5 provides further details of light sources power calibration and emission wavelengths. Section S6 provides further details of relevant gas species sensitivity factors determinated using the electron photomultiplier detector in the MS equipment.

Control experiment of PbI₂ decomposition as a function of LED power.

Programmed sequential increase in light power is applied to the sample with a total of 12 sequential pulses for each of white, red, and blue LED light source, Figure S2c-e. The relationship between maximum partial pressure measured vs. photon flux applied in each pulse is shown in Figure S2b for white and blue LEDs, respectively. It can be observed that diiodine MS signal exceeds the detection threshold during white LED illumination at Pulse no. 8 (~2.2 10^{17} photon s⁻¹ cm⁻²), but it exceeds the threshold during blue LED illumination at a lower photon flux at Pulse no. 5 with ~1.4 10^{17} photon s⁻¹ cm⁻² blue photons. This different behavior can be explained based on the fact that white LED light illumination consists of a mixture of photons with two wavelengths (450nm and 550 nm) and 550 nm photons in white LED cannot produce I₂. As photon flux on the sample is sequentially increased, the rate of diiodine release is observed to increase for blue and white LED illumination (Figure S2b). Main difference between blue and white LEDs illumination pulses experiment is that the I₂ release rate vs. applied photon trace is displaced to the right for white LED experiments. This is explained by the fact that white LED flux contains less quantity of high energy photons above the PbI_2 band gap that are able to generate I_2 .

On the other hand, the monoiodine MS signal can be detected at lower photon flux than the diiodine MS signal. Monoiodine can be detected already at Pulse no. 1 and 4 for blue and white LED, respectively (Figure S2b). The most interesting distinctive feature observed comparing monoiodine and diiodine signals is that the two monoiodine MS signals using blue and white LED converges asymptotically as a higher photon flux is applied (Figure S2b). In Figure S2b, the expected quantity of monoiodine fragmentation inside MS during white LED experiment is indicated by a red line. However, monoiodine observed experimentally is higher than expected and it could be a signature of thermal evaporation of PbI₂. Note that monoiodine (127 amu) detected by MS can be ascribed to the fragmentation pattern of I₂ during the MS measurement. In fact, according to the NIST database,¹ the fragmentation pattern for I₂ corresponds to a molecular peak of 254 amu with 100% intensity followed by a peak for the monoiodine fragment (127 amu) with a peak intensity of 52.5%. Figure S13a describes the fragmentation pattern of I₂. Section S6 describes the diiodine/monoiodine calibration procedure for these MS measurements using this electron multiplier detector.

Control experiment of PbI₂ decomposition in dark as a function of sample temperature

To decouple the effect of temperature during illumination tests, an experiment using artificial sun light pulses from a Xe lamp from a solar simulator and heating interval events in dark conditions is carried out. This experiment consists of two parts, 1) pulses of 3 min of duration using constant power Xe lamp illumination (55.2 mW cm⁻²) alternating with 1 min duration rest intervals in dark conditions and 2) long heating interval in dark conditions until the sample reaches high temperatures close to that obtained with light pulses, see Figure S2f-h.

As seen before during white and blue LED light illumination experiments (Figure S2c-e), there is an appreciable level of I_2 gas release only under Xe lamp illumination conditions. On the other hand, during the sample heating in dark conditions, no release of I_2 gas is observed. However, the monoiodine trace can still be observed when the sample is heated above 70 °C. In view of these results, it is concluded that the release of I_2 during controlled degradation of PbI₂ only takes place during light irradiation using photons with energy greater than the PbI₂ band gap (2.34 eV, 530 nm).² On the other hand, under dark and heating conditions, the most plausible origin of monoiodine excess detected would be resulted from thermally evaporated under high vacuum conditions PbI₂ molecular entities or PbI₂ clusters being monoiodine a fragment observed by MS. Under dark conditions and moderate temperatures (~70 °C) in high vacuum conditions (~10⁻⁶ Torr), PbI₂ evaporation takes place:

$$PbI_2(s) \xrightarrow{\Delta} n PbI_2(g)$$
 (1)

This process described by Eq. 1 is followed by electron ionization inside MS inducing subsequent $PbI_2(g)$ molecules or clusters fragmentation:

$$nPbI_2(g) \xrightarrow{e^-} nI^- + nPbI^+ \tag{2}$$

Therefore under dark and heating conditions, only monoiodine fragment is detected by the MS equipment. [PbI] mass fragment can not be observed because it is out of the detection range of the MS equipment (1-300 amu).



Figure S2. a) Schematic drawing of the experimental setup for controlled PbI₂ and perovskite degradation experiments. H: electrical heater, T: thermocouple, P: crystal / cold cathode pressure gauge, MS: quadrupole mass spectrometer, top quartz window and Xe lamp or LED light sources with controlled on/off intervals. All components were housed inside a vacuum chamber with a base pressure of 5×10^{-8} Torr. A pin hole (2 mm diameter) in an aluminum foil shield separated the sample holder and the ionizer filament in the MS avoiding direct illumination of the sample by the filament. Experiments were performed initially at ~35°C. Experimental setup scheme for calibration purposes differed slightly, see Figure S10. b) Experimental partial pressure peak maxima measured for di- and monoiodine MS traces vs. photon flux in each interval for white (open square white symbol) and blued LEDs (solid square blue symbol). Numbered labels correspond to the pulse numbers shown in panels (d) and (e). Extracted points correspond to only

those where the partial pressures in panels (d) and (e) are above background. Continuous red line represents the hypothetically expected quantity of monodione observed by fragmentation inside the MS using white LED. c) Temperature recorded in the sample holder in the dark (grey area) and under illumination using three different LEDs (white, red, or blue) with increasing light power during 12 pulses of 60 sec of illumination followed by 60 sec of darkness. MS signals are calibrated with m/z values corresponding to partial pressure recorded simultaneously by MS for d) mono- and e) dijodine. Power delivered for each LED in each light pulse can be found in Section S5. f) Temperature recorded in the sample holder under dark (grey area) and illumination conditions (white area) using Xe lamp illumination pulses (3 min illumination and 1 min dark, 4 cycles) at constant light power of 55.2 mW cm⁻². After ~3000 s, heating in dark is carried out using an heating element mounted on the sample holder. g) mono- and h) dijodine calibrated m/z traces. i) Plane view (1, -2, 0) of a layered PbI₂ supercell in P-3m1 trigonal space group.³ Each $(PbI_2)_n$ layer showed in the figure depicts a step during the release of I₂ and generation of Pb⁽⁰⁾ by the two exciton mechanism.⁴ Step 1, left layer) Photons with higher energy than PbI₂ band gap (2.34 eV, 530 nm) arrive to the PbI₂ surface forming excitons. Two closely generated excitons can be separated if holes oxidize iodide anion and electrons reduce Pb²⁺ center. Step 2, middle layer) Generated iodine atoms are close enough to form I₂. Step 3, right layer) I₂ molecule is released from PbI₂ surface leaving two anion vacancies.

Determination of non-volatile products of photodecomposition on thin-films of PbI₂ using XRD and XPS analysis.

See section S7. Determination of non-volatile products of photodecomposition on thin-films of PbI₂, MAPbI₃ and MAPbBr₃ on FTO substrate samples using XRD and XPS analysis.

Recovery of PbI₂ thin-film from degraded Pb⁰ containing films using I₂.

Degraded PbI₂ thin-film containing Pb⁰ can be recovered back after exposure to I₂ gas in a closed glass bottle at room temperature and dark conditions. After few seconds it can be observed that the gray material observed in degraded film disappears forming again an orange-yellowish film on the top of the substrate. This I₂ exposure is hold during 4 h to counteract the 4h duration photodecomposition procedure. XPS measurement are carried out to check the remaining Pb⁰ content in the PbI₂ sample, see Figure S3, where it can be observed that there is no Pb⁰ traces remaining in the sample. The I/Pb ratio in the restored film is 1.62, which is close to that of pristine PbI₂ thin-film (I/Pb ~ 1.8, section S7) considering experimental uncertainties.



Figure S3. XPS spectra (Al-K α = 1486.6 eV) of a) Pb 4f and b) I 3d core levels of a recovered PbI₂ film after I₂ exposure.

Similar output can be observed by XRD diffraction where it can be observed that the $\sim 31^{\circ} 2\theta$ diffraction peak belonging to cubic Pb⁰ phase have completely disappeared, Figure S4a.



Figure S4. a) XRD diffraction patterns ($10^{\circ} - 55^{\circ} 2\theta$ degrees) collected at room temperature under ambient conditions for recovered thin-film samples of PbI₂ from degraded PbI₂/Pb⁰ films. Measured data (black dots), calculated diffraction pattern (top red line), difference pattern (bottom black line), and expected peak positions are shown. b) Comparison of the (001) diffraction peak in PbI₂ phase in pristine PbI₂ thin-film (blue) and recovered PbI₂ thin-film after I₂ exposure (green).

A comparison of the (001) diffraction peak in PbI₂ phase in pristine PbI₂ thin-film and recovered PbI₂ thin-film after I₂ exposure is shown in Figure S4b. According to the Rietveld refinement, recovered PbI₂ has larger crystalline domains (96 ± 6 nm) than pristine PbI₂ film (71 ± 3 nm). On the other hand, microstrain is larger in recovered film (0.0046 ± 0.0003 %) than in pristine film (0.0027 ± 0.0003 %).

Recovery of MAPbI₃ perovskite from degraded samples containing PbI_2 by using CH_3NH_2 is not demonstrated experimentally here because there is enough literature supporting that MAPbI₃ can be synthesized using PbI_2 thin-films and CH_3NH_2/HI gases sequentially or simultaneously not needing explicit synthesis of the methylammonium iodide salt.⁵

S4. Activation Energy calculation from MS traces

Activation energy for the reaction releasing diiodine is calculated using a modified constant initial rate method over all pulses generated during illumination runs. The reaction releasing diiodine from PbI₂ is

$$PbI_2 \rightarrow Pb^{(0)} + I_2 \tag{1}$$

The dependence of the reaction rate on the reactant concentration is isolated considering a large excess of PbI_2 surface ready to react at initial time so that their concentration remains essentially constant. Furthermore, only the raising temperature branch side of the pulse is considered for calculations. It simplifies the rate law because this constant and large excess concentration may be combined with the rate constant yielding a single effective rate constant as

 $\nu = k[PbI_2]_0^n = k_{eff} \tag{2}$

Initial reaction rate can be expressed in terms of reagent or product as for example

$$\nu = -\frac{d[PbI_2]}{dt} = \frac{d[I_2]}{dt} = k_{eff}$$
 (3)

where

$$k_{eff} = C e^{\frac{-E_a}{RT}} \tag{4}$$

Here C is a lumped constant including pre-exponential kinetic term and constant initial concentration, E_a is activation energy and RT is the gas constant and temperature. Substituting (4) in eq. (3) and taking natural logarithm in both sides, a linearized form can be obtained for eq. 3,

$$\ln(\frac{d[I_2]}{dt}) = -\frac{E_a}{RT} + \ln(C)$$
(5)

Equation 5 can be used to obtain graphically the slope E_a/R from all experimental pulses recorded using MS mass traces as partial pressures of I_2 , see Figure S5.



Figure S5. Natural logarithm of the time derivative of the I_2 partial pressure measured by MS during blue LED pulses vs. inverse of the temperature (black dots). All data points from pulses are drawn but only midearly points for each pulse obey the constant and large excess reagent concentration assumption. A straight and common negative slope can be easily visualized and the slope is obtained graphically by freehand using the frontier data. Later or sooner points do not obey the approximation and deviates from eq. 3 being them not considered for the slope. Note that this method is still valid even using non-calibrated MS data traces.

S5. Light power calibration

Light power delivered by solar simulator and LEDs were calibrated using a calibrated silicon photodiode (FDS100, Thorlabs, Inc) with spectral response from 350 nm to over 1100 nm. Calibration measurement

accounts quartz viewport and distance from light source to sample holder. In principle the 2 mm thickness quart window shows > 90% of transmittance in the visible region, see Figure S6.



Figure S6. Transmittance spectrum from the quartz window used in the experimental setup.

Light emission wavelengths for LEDs and solar simulator used in this work were measured by a Konica Minolta CS-2000 spectroradiometer. Increasing LED power light pulses were measured using the silicon

photodiode (Figure S7a) and photon flux (Figure S7b) was calculated taking into consideration the before measured light emission wavelengths for LED (Figure S8) and solar simulator (Figure S9).



Figure S7. a) Sequentially increased LED light power pulses applied on samples and b) the corresponding photon flux for such pulses. For comparison purposes, yellow star is light power and photon flux for AM1.5G simulated sun.



Figure S8. Three different spectral irradiances and photon fluxes (pulses no. 1, 6 and 12) for blue, red and white LED and the AM1.5G standard for the ease of comparison. Note that log scale is used in y axis. It can be observed that even pulse no. 1 (lowest light power used in LED experiments) for blue and red LED is already higher in photon flux and spectral irradiance compared with AM1.5G standard.



Figure S9. Spectral irradiance from the AM1.5G standard (black) and PEC portable solar simulator (blue). Power illumination from the halogen lamp obtained from calibration taking in account distance source-sample and quartz window.

S6. Mass spectrometer detector calibration

Calibration of the quadrupole Mass Spectrometer using an electron multiplier detector (SRS Stanford Research Systems, RGA300) is carried out for partial pressure analysis of CH₃I, NH₃CH₂ and I₂ (diiodine) using direct comparison of the partial pressure analyzer output with a transfer standard pressure gauge.⁶ Figure S2a shows the setup used for measurement and Figure S10 the modified setup for calibration purposes.



Figure S10. Sketch drawing of the experimental setup for calibration purposes. P: crystal cold pressure gauge, MS: quadrupole mass spectrometer. A variable leak valve and glass sample container, for liquids and solid used as standard materials, is located in one side of the vacuum chamber.

Iodomethane and methylamine sensitivity factors

Iodomethane (CH₃I, reagent grade) was purchased from Wako Chemical Ltd., methylamine (NH₂CH₃) 40% water solution was purchased from Tokyo Chemical Industry Co., Ltd. Both reagents were used as received. A few milliliters liquid sample of CH₃I or CH₃NH₂ is loaded at atmospheric pressure inside the sample container which is connected to the leak valve. Vapor pressure at room temperature for pure CH₃I liquid is obtained from NIST webpage and the vapor pressure of the NH₂CH₃ water solution from Romero et al work.⁷ Because the small aperture delivered by a precision variable leak valve (MDC Vac. Prods., LLC.), the pressure and temperature in the glass vessel is considered constant through the experiment. Then, five different valve aperture positions are maintained during ~ 1 minute meanwhile partial pressure is recorded for CH₃I (142 m/z peak) and CH₃NH₂ (31 m/z peak) using the electron multiplier detector and total pressure measured by the crystal/cold cathode pressure gauge (model CC-10, Tokyo Instruments, P symbol in Figure S10). Pressure increments vs partial pressure increments from MS are plotted and linear fitting is carried out to obtain the calibration factor, see Figure S11. There is a linear relation between the partial pressure and the corresponding MS signals of the gases. Deviations from linearity in sensitivity factors (A) calculations are to be expected above 10⁻⁵ Torr due to space charge effects in the ionizer and ion-neutral scattering interactions in the filter. MS sensitivity involves measuring the MS signals over several orders of magnitude of partial pressure to determine the range over which a linear relationship exists. The sensitivity factor for CH₃I and CH₃NH₂ is calculated as the slope of the MS signal vs. partial pressure measure by external gauge over the linear range.



Figure S11. MS signal vs. partial pressure measure by external gauge for a) CH₃I and b) CH₃NH₂. Sensitivity factor are 0.126 and 0.031, respectively.

Monoiodine/ Diiodine sensitivity factors

Sensitivity factor calculation for the diiodine/monoiodine pair follows a procedure slightly different from above procedures for CH₃I and CH₃NH₂ because of the high vapor pressure of solid iodine and fast recrystallization of iodine vapors in contact with cold surfaces. Such fast recrystallization does not permit to use the external glass container. High vapor pressure of solid iodine impedes direct sample holder loading and reaching simultaneously the working pressure for the MS equipment. Iodine pellets (I₂, reagent grade) was purchased from Wako Chemical Ltd and used without further purification process. A few milligrams of iodine pellets were encapsulated in glass tube leaving a small orifice (0.1 mm or less) on the top of the glass capsule. The glass capsule is loaded in the sample holder equipped with heating element inside the vacuum chamber. Vacuum pump is started and the chamber reach an equilibrium pressure of $\sim 1 \times 10^{-4}$ Torr at room T as measured from the external pressure gauge. In such a moment, the heating element is powered up accelerating the evaporation of solid I₂. Pressure raises until reach a maximum followed by a pressure decay indicating the material is exhausted. MS equipment and detector are switched on at the moment that a safe pressure for the MS operation is reached. Decay in partial pressure signals for diiodine and monoiodine together with decay in total external pressure are measured and sensitivity factors are calculated from these pressure decays. An educated guess implies that the total measured pressure belongs to I_2 gas and sensitivity factor is calculated taking the ratio of the time derivative of the MS signal and total pressures traces. Monoiodine sensitivity factor is obtained considering that diiodine fragmentation pattern from NIST database indicates a 52.5 % MS intensity signal for monoiodine compared to the 100% intensity for I₂ molecular MS peak (Figure S13a). Sensitivity factors calculated for di-, and monoiodine from pressure decays are shown in Figure S12.



Figure S12. Sensitivity factor calculated using MS signal and total pressure measured by an external pressure gauge for a) diiodine and b) monoiodine.

Selected MS fragmentation pattern for molecules in this work

Fragmentation patterns m/z peaks retrieved from NIST MS library data¹ for compounds mentioned in the main manuscript are shown in Figure S13.



Figure S13. Experimental fragmentation pattern of a) diiodine, b) dibromine, c) hydrogen bromide, d) methylamine, e) methane iodide, f) methane bromide and g) dimethylformamide (DMF).



Figure S14. Extracted CH₃I/CH₃NH₂ ratio released during MAPbI₃ controlled degradation The ratio represents after taking into account calibrated MS traces.

S7. Summary results on determination of non-volatile products of photodecomposition on thin-films of PbI₂, MAPbI₃ and MAPbBr₃ on FTO substrate samples using XRD and XPS analysis.

Photodecomposition tests were carried out in ~200 mg of powdered samples to obtain a measurable quantity of volatile compounds to be detected by MS. Because photodecomposition is mainly produced at the sample surface, it is extremely difficult to check what non-volatile products from photodecomposition remains after degradation procedure on the top of such powdered samples. Therefore, thin-films of PbI₂, MAPbI₃ and MAPbBr₃ on FTO substrates were prepared to check the remaining photodecomposition products after a 4 h under Xe lamp illumination test (0.55 Sun) inside the same vacuum chamber used for above MS experiments. Chemical compositions of such thin-films were analyzed before and after illumination test using X-ray photoelectron spectroscopy (XPS, Section S8) and X-ray diffraction (XRD, Section 9) measuresments, see Figure S15. Sections S8 and S9 provides further details on XPS and XRD measurements and analysis.

XPS and XRD measurements clearly confirm formation of metallic Pb⁰ for all PbI₂, MAPbI₃ and MAPbBr₃ on FTO substrate samples after photodecomposition, see Figure S15. It was observed that the freshly prepared PbI₂ film showed a characteristic yellow color. However, it gradually turned to a dark grey color after light exposure. Concurrent to Pb⁰ formation, XPS measurements showed a reduction of iodine content in the thin-film sample, which is consistent with the releases of I₂ based on MS measurements. The atomic ratio of Pb^{2+} : Pb^0 : I of the fresh PbI_2 film was 1 : 0 : 1.8, which is in good agreement with expected nominal ratio (1:0:2); whereas the ratio for the degraded PbI₂ film became 0.75: 0.25: 1.0. Such significant increase in Pb⁰ and decrease in I content after light illumination indicate that PbI₂ is decomposed to metallic-Pb accompanied by the release of I₂ (see section S8 for experimental details and XPS results). MAPbI₃ and MAPbBr₃ samples also confirmed Pb⁰ formation, but in these cases, it was also accompanied by PbI₂ and PbBr₂ formation how later observed by XRD, see Table S1 and Figure S15. XPS is a surface sensitive technique, and typically measures a few nanometers of the thin-film surface. On the other hand, XRD measurements carried out in the same degraded thin-films confirm the bulk formation of cubic Pb⁰ for all samples and PbX_2 phase for perovskite films (see section S9 for experimental details and XRD results). However, XRD measurements only take into consideration crystalline material formed. Accounting such differences between XPS and XRD techniques, the mismatch between the chemical compositions obtained can be understood. However, we note that both techniques corroborate the formation Pb⁰ even the quantity trend observed for all samples.

Table S1. XPS and XRD based chemical compositions determination for non-volatile products in degraded thin-film samples of PbI_2 and $MAPbX_3$ (X = I, Br).

		XPS	(mol/mol)		XRD	(mol/mol)
Sample*	$Pb^{2+} 4f$	$Pb^0 4f$	X 3d	MAPbX ₃	PbX ₂	Pb ⁰
PbI ₂	0.75	0.25	1	-	0.34	0.66
MAPbI ₃	0.82	0.18	1.6	0.27	0.30	0.43
MAPbBr ₃	0.85	0.15	1.3	0.32	0.38	0.30

* Atomic ratios of $Pb^{2+} 4f/I 3d$ of the fresh PbI_2 , MAPbI₃ and MAPbBr₃ film were 1/1.8, 1/3.1 and 1/1.27, respectively, based on XPS. No traces of Pb^0 or PbX_2 in pristine (before degradation) thin films were observed by XRD, see Section 9 for further details in XRD analysis.



Figure S15. XPS spectra (Al-K_{α} = 1486.6 eV) of Pb 4f core level of PbI₂, MAPbI₃ and MAPbBr₃ film samples as a), e) and i) before and b), f) and j) after light exposure (55.2 mW/cm²) for 4 h under vacuum. Before light illumination, for the fresh PbI₂ and MAPbX₃ sample XPS spectrum of Pb 4f core electronic level showed the doublet peaks corresponding to spin-orbit splitting of Pb 4f_{7/2} and 4f_{5/2} at 138.3 eV and 143.1 eV, respectively. After light illumination, the degraded sample showed significantly lower intensity for the Pb 4f core levels, and new doublet peaks appeared at 137.0 eV and 141.9 eV corresponding to metallic-Pb.⁸ XRD diffractograms for the corresponding thin-films are c), g) and k) before and d), h) and l) after 4 h light exposure. Crystal phases used for quantification were ICSD-68819 for PbI₂, ICSD-96501 for the cubic F m -3 m Pb⁰ phase, ICSD-238610 for tetragonal MAPbI₃ and ICSD-252415 for cubic MAPbBr₃.

S8. Further details on XPS measurements and analysis in thin-films.

The surface electronic properties of PbI₂, MAPbI₃ and MAPbBr₃ were characterized by XPS (Kratos AXIS ULTRA HAS, monochromated Al-K α = 1486.6 eV) in order to observe effect of the light exposure in vacuum on the surface chemical compositions. The binding energy (BE) was calibrated by measuring the Fermi edge (E_F = 0 eV) and Au-4f_{7/2} (84.0 eV) on a clean Au surface. Freshly prepared samples were first analyzed by XPS. The BE scale of PbI₂ spectra was calibrated using the adventitious carbon peak (C 1s) at ~285 eV as reference.^{9,10} In our samples, residual amounts of adventitious carbon would be unavoidable due to air exposure prior to the XPS measurements. In addition, C 1s signal originating from residual solvents may be also expected. Great care was taken in order to minimize X-ray exposure time when acquiring PbI₂, MAPbI₃, and MAPbBr₃ samples. X-ray induced sample damage was monitored by taking five consecutive scans and comparing these spectra. Acquisition time for each scan varied from 20 to 70 s depending on the core level regions. The five scans were averaged to a single spectrum if no significant changes were observed.

Peak fittings and standard deviation calculations were performed with CasaXPS 2.3.16. Shirley function was used to simulate the background signal due to inelastic scattering processes.¹¹ Raw XPS spectra of the Pb 4f, I 3d (for PbI₂ and MAPbI₃), Br 3d (for MAPbBr₃), C 1s, and N 1s (for MAPbI₃ and MAPbBr₃) were fitted with Gaussian-Lorentzian (G-L) functions. Peak positions, full width at half maximum (FWHM), and the relative spectral areas were extracted from fitted curves. The intensity ratios between the $4f_{7/2}$ and $4f_{5/2}$ (Pb) and $3d_{5/2}$ and $3d_{3/2}$ (I and Br) doublets due to spin-orbit coupling were 1.33 and 1.50 (± 3% error), respectively. The concentration of the different elements (metallic-Pb, I, Br, C and N) relative to Pb²⁺ was estimated from the fitted areas after normalization with the atomic sensitivity factors (ASF).¹²⁻¹⁴

PbI₂ thin-film XPS analysis

XPS spectra revealed formation of metallic-Pb (Pb⁰) in PbI₂ film after the photodegradation under vacuum condition. Pristine PbI₂ sample shows a typical yellow colored film (Eg ~2.3 eV), but it changed to a dark grey colored film after the light treatment. This color change under the light exposure is very likely due to the reduction of initial Pb²⁺ to Pb^{0.4} PbI₂ XPS spectrum of Pb 4f core electronic level for fresh sample showed doublet spin-orbit coupling signals of Pb (4f_{7/2} and 4f_{5/2}) at 138.3 eV and 143.1 eV (Figure S15a). On the other hand, degraded PbI₂ illustrated these peaks with less intensity, but also new doublet peaks at 137.0 eV and 141.9 eV (Figure S15b), which were assigned to Pb⁰. Meanwhile, doublet signals of I (3d_{3/2} and 3d_{5/2}) at 619.1 eV and 630.6 eV were observed in the fresh PbI₂ sample (Figure S16a). The peak heights, however, dramatically reduced after the photodegradation process. As release of I₂ gas was monitored in the MS degradation experiment, the loss of I observed in the XPS spectrum would be also due to escaped I₂ gas from the PbI₂ film. While C 1s signal at BE of 295 eV did not significantly change its intensity (Figure S16b). This C is adventitious carbon. Atomic ratio of Pb²⁺ : Pb⁰ : I for fresh film was 1 : 0 : 1.8, which agrees quite well with expected nominal ratio of 1 : 0 : 2. Whereas the ratio in degraded PbI₂ sample was 0.8 : 0.3 : 1 (Table S1 and Table S2). Significant increase in Pb⁰ and decrease in I after the light treatment indicate that PbI₂ is photodecomposed into Pb⁰ and I₂ gas.



Figure S16. XPS spectra (Al-K α = 1486.6 eV) of a) I 3d and b) C 1s core levels of a PbI₂ film deposited on FTO corresponding to fresh sample (0 h) and after light exposure (55.2 mW/cm²) under vacuum (4 h). 'X' denotes adventitious-carbon or solvent-related C-species.

MAPbI₃ thin-film XPS analysis

Photodegradation of MAPbI₃ perovskite implied reduction of Pb^{2+} to Pb^{0} as well as significant loss of I, C, and N.

Fresh MAPbI₃ sample showed sharp and high intensity doublet signals corresponding to spin-orbit splitting of Pb ($4f_{7/2}$ and $4f_{5/2}$) at 137.1 eV and 142.2 eV (Figure S15e); whereas the degraded sample had less intense peaks at the BEs. Additionally, new doublet peaks at 137.0 eV and 143.9 eV (Figure S15f) appeared in the degraded film. These findings suggest that Pb²⁺ was reduced to metallic Pb⁰. In addition, peak intensities of I $3d_{3/2}$ and $3d_{5/2}$ doublet peaks at 619.5 eV and 630.1 eV, respectively, decreased after the light treatment on MAPbI₃ film (Figure S17a). The mechanisms of the loss of I from MAPbI₃ is not as simple as the case of PbI₂, but XPS spectra illustrated also dramatic perovskite C and N intensity peaks (Figure S17b,c). Photodecomposition of MAPbI₃ to HI, CH₃NH₂, CH₃I, I₂ and NH₃ were recorded in our MS analysis (Figure 2 shown in the main text). This indicates that it might have been released as I₂, but also together with C as a form of CH₃I. The peak position of adventitious carbon was shifted towards higher BE compared to that in PbI₂ film. This is probably due to the overlap region with perovskite carbon peak and formation of unknown organic compound of polymeric nature in MAPbI₃.¹⁵

Atomic composition ratios of Pb^{2+} : Pb^0 : I : C_{PVSK} : N in fresh and degraded MAPbI₃ were 1 : 0 : 3.1 : 1.3 : 0.9 and 0.8 : 0.2 : 1.6 : 0.3 : 0.1, respectively (Table S1 and S2). The fresh sample had an expected nominal ratio of 1 : 0 : 3 : 1 : 1, while the degraded sample possessed appearance of Pb^0 and significant decrease of I, C_{PVSK} and N. Despite less amount of Pb^0 was observed in MAPbI₃ compared to PbI_2 , the loss of I was even more significant in MAPbI₃.



Figure S17. XPS spectra (Al-K α = 1486.6 eV) of I 3d, C 1s and N 1s core levels of a MAPbI₃ film deposited on FTO corresponding to fresh sample (0 h) and after light exposure (55.2 mW/cm²) under vacuum (4 h). 'X' denotes adventitious-carbon or solvent-related C-species. 'PVSK' denotes C in MAPbI₃ perovskite.

MAPbBr₃ thin-film XPS analysis

Degradation of MAPbBr₃ appeared to have the same trend as MAPbI₃. Effects of the light exposure in vacuum on MAPbBr₃ surface changes were monitored. XPS revealed the reduction of Pb^{2+} to Pb^{0} and decrease in Br, perovskite C and N signal intensities.

MAPbBr₃ sample before the light treatment showed doublet spin-orbit coupling peaks of Pb $4f_{7/2}$ and $4f_{5/2}$ at 138.8 eV and 143.6 eV, respectively (Figure S15i). These peak intensities decreased followed by formation of new doublets at 136.5 eV and 141.4 eV after the photodegradation treatment (Figure S15j), which corresponded to the reduction of initial Pb²⁺ to Pb⁰. Doublet spin-orbit splitting of Br $3d_{3/2}$ and $3d_{5/2}$ at ~68.5 eV and 69.5 eV, respectively, were recorded in MAPbBr₃ film. Their peak intensities were apparently lower after the photodegradation (Figure S18a). XPS signals corresponding to perovskite C (Figure S18b) and N (Figure S18c) core-levels also reduced after the photodegradation process.

 Pb^{2+} : Pb^{0} : Br : C_{PVSK} : N atomic ratio of 1 : 0 : 2.7 : 1.1 : 0.9 was found in the fresh MAPbBr₃ film, which was sufficiently close enough to the expected ratio of 1 : 0 : 3 : 1 : 1. However, the ratio after the photodegradation in vacuum was 0.85 : 0.15 : 1.32 : 0.36 : 0.17. Thus, MAPbBr₃ also undergoes photodecomposition of Pb^{2+} to Pb^{0} .



Figure S18. XPS spectra (Al-K α = 1486.6 eV) of Br 3d and C 1s, N 1s core levels of a MAPbBr₃ film deposited on FTO corresponding to fresh sample (0 h) and after light exposure (55.2 mW/cm²) under vacuum (4 h). 'X' denotes adventitious-carbon or solvent-related C-species. 'PVSK' denotes C in MAPbI₃ perovskite.

	Pb ²⁺	Pb ⁰	Ι	Br	C _{PVSK}	Cx	Ν
PbI ₂ (fresh)	0.98 ± 0.01	0.02 ± 0.01	1.75 ± 0.02	-	-	0.39 ± 0.27	-
PbI ₂ (degraded)	0.75 ± 0.02	0.25 ± 0.01	1.01 ± 0.01	-	-	0.33 ± 0.30	-
MAPbI ₃ (fresh)	0.99 ± 0.04	0.01 ± 0.05	3.08 ± 0.10	-	1.34 ± 0.56	0.82 ± 0.31	0.89 ± 0.35
MAPbI ₃ (degraded)	0.82 ± 0.03	0.18 ± 0.02	1.60 ± 0.05	-	0.32 ± 0.24	1.35 ± 0.60	0.11 ± 0.25
MAPbBr ₃ (fresh)	0.99 ± 0.01	0.01 ± 0.01	-	2.66 ± 0.05	1.09 ± 0.45	0.24 ± 0.17	0.88 ± 0.24
MAPbBr ₃ (degraded)	0.85 ± 0.03	0.15 ± 0.01	-	1.32 ± 0.05	0.36 ± 0.17	0.86 ± 0.47	0.17 ± 0.18

Table S2. Composition ratio \pm standard deviation of PbI₂, MAPbI₃, and MAPbI₃ calculated from XPS spectra.

S9. Further details on XRD measurements and analysis thin-films.

Powder X-ray diffractograms were recorded in GIXRD mode (detector scan, omega= 0.5°) using a D8 Bruker Discover (Cu-K α 1 radiation) with 2 θ degrees varying from 10° to 55° using 0.5 s of acquisition time for every 0.02° 2 θ intervals. Quantitative analysis for all powder samples were obtained fitting the entire XRD pattern with MAUD 2.71 software package.¹⁶ Figure S19 shows XRD patterns of PbI₂, MAPbI₃, MAPbBr₃ and PbBr₂ before and after long term degradation tests (4 hours under 0.55 sun in vacuum conditions). Table S3 show percentage by weight (calculated molar percentage is shown in Table S1) obtained from refinements accounting the remaining corresponding lead halide derivatives and Pb⁰.

	Composition After Degradation		
Sample	MAPbX ₃	PbX_2	Pb^0
PbI ₂	-	53	47
MAPbI ₃	42	35	23
MAPbBr ₃	43	39	18
PbBr ₂	-	63	37

Table S3. Quantitative analysis of crystalline material observed by XRD (% w/w)



Figure S19. XRD diffraction patterns ($2\theta = 10^{\circ} - 55^{\circ}$) collected at room temperature under ambient conditions for pristine thin film samples of PbI₂, MAPbI₃, MAPbBr₃, and PbBr₂ on FTO substrate. Measured data (black dots), calculated diffraction pattern (top red line), difference pattern (bottom black line), and expected peak positions are shown. Crystal phases used for quantification were ICSD-68819 for PbI₂, ICSD-96501 for the cubic F m -3 m Pb⁰ phase, ICSD-238610 for tetragonal MAPbI₃ and ICSD-252415 for cubic MAPbBr₃.

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