Supporting Information

Grain Transformation and Degradation Mechanism of Formamidinium and Cesium Lead Iodide Perovskite under Humidity and Light

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MATERIALS

The materials used are formamidinium iodide (FAI, Greatcell Solar), lead iodide (PbI_2 , 99%, Sigma-Aldrich), cesium iodide (CsI , 99.999%, Sigma-Aldrich), dimethylformamide (DMF, ACP Chemicals), dimethyl sulfoxide (DMSO, ACP Chemicals), chlorobenzene (Sigma-Aldrich), and indium tin oxide coated glass substrates (ITO, $1 \times 1 \text{ cm}^2$, Lumtec).

SAMPLE PREPARATION

$\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ / ITO / Glass

The precursor solution was made by dissolving FAI (196.0 mg, 1.14 mmol; 173.4 mg, 1.0 mmol; or 144.3 mg, 0.85 mmol for $x = 0.95, 0.85, 0.70$ respectively), CsI (15.6 mg, 0.06 mmol; 47.8 mg, 0.18 mmol; 93.6 mg, 0.36 mmol for $1 - x = 0.05, 0.15, 0.30$ respectively) and PbI_2 (553 mg, 1.2 mmol) in a solvent mixture of DMF and DMSO (4:1 v/v, 1 mL). This mixture was sonicated at 40°C for 1 h to ensure all the solute has dissolved. ITO coated glass was cleaned by sonicating in acetone (5 min, Sigma-Aldrich), isopropanol (2×5 min, Sigma-Aldrich), rinsed with isopropanol (2 mL, Sigma-Aldrich) and dried with dry air. The precursor solution was spin coated (Static dispense, Chemat Technology KW-4A) onto the cleaned ITO/glass substrate inside a nitrogen filled glove box accelerated from 0 to 2000 rpm, held at 2000 rpm for 10 s, then 6000 rpm for 60 s. After 20 s of spinning at 6000 rpm, chlorobenzene (300 μL) was added dropwise onto the spinning substrate. The color changed from clear yellow to clear brown. The perovskite/ITO/glass was then thermal annealed on a hot plate (Sci-Basics MHS-800) at 150°C for 10 min inside the glove box. The color changed from faint to dark brown. The samples were kept under nitrogen and shielded from light exposure until the start of the experiments. ITO/glass was chosen as the substrate a) to enhance the PTIR signal since ITO is highly reflective at this wavelength and b) because it is a commonly used substrate for device fabrication.

EXPERIMENTAL SETUP

Setup for Humidity and Light Exposure

Exposure of perovskites to light and different relative humidity levels were done directly in the enclosed AFM/PTIR instrument (Bruker Inspire™). The sample structure is $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ / ITO / glass without any additional encapsulation. The relative humidity (RH) and temperature was measured with Extech RH520. Low humidity was produced by flowing dry air into the chamber. High humidity was produced by first flowing dry air through three consecutive bubblers filled with deionized water heated to 70° C then into the AFM/PTIR chamber. During the AFM and PTIR measurements, the chamber was kept at $\text{RH} < 20\%$, 23 °C, and in the dark to prevent additional degradation. The temperature was kept constant at 23 °C measured in the chamber for all the degradation studies and AFM/PTIR measurements. An LED (Thorlabs MWWHL3) was used as the light source for the photodegradation. Light is focused directly onto the perovskite side normal to the sample surface. The intensity is 10 mW/cm² at the sample stage measured with a thermal sensor (Ophir Photonics 3A-QUAD with Vega power meter) with the spectra shown in Figure 1 in the main text (measured with Ocean Optics HR2000+CG-UV-NIR spectrometer with OceanView software). No additional filter was applied to the light source.

CHARACTERIZATION

Atomics force microscopy (AFM)

AFM height images were acquired using a Bruker Inspire™ in tapping mode using a platinum/iridium-coated tip (NanoWorld Arrow-NCpt, force constant = 42 N/m, resonance frequency = 285 kHz, tip radius < 25 nm). The data were recorded using the NanoScope v9.40 software package.

Photothermal induced resonance (PTIR)

The reader is referred to reference 1 for an in-depth description of the Peak Force IR technique.¹

PTIR images were obtained with a customized Bruker Inspire™ microscope operating in a Peak Force quantitative nanomechanical mapping (QNM) mode with the same tip as in AFM height imaging. It operates as follows. In Peak Force QNM mode, the sample stage moves sinusoidally

toward the AFM tip at 2 kHz, contacting and deflecting it periodically. The tip deflection is recorded as a function of time to produce deflection curves. The sinusoidal motion of the sample stage is extracted as an electric signal and input into a custom-built circuit that converts it to a frequency halved transistor-transistor logic (TTL) waveform (1 kHz), which is used to trigger the quantum cascade laser (QCL, DRS Daylight Solutions MIRcat-QT™) in pulsed mode at 1 kHz and 500 μ W. The laser emits only when the tip is in contact with the sample, as obtained by manually adjusting the phase delay of the triggering TTL wave. The laser output signal and the deflection curves are collected with a data acquisition card (National Instruments PCI-5122) and processed with a LabView program.

When collecting images in the PTIR mode, the fast Fourier transform (FFT) sum of the oscillation amplitude is output through a I/O device (National Instruments PCI-6115) and a BNC connector block (National Instruments BNC-2110) which is routed to the Bruker NanoScope V controller and the image displayed with the NanoScope software v9.40. In the spectra mode, the AFM tip is paused on a specific XY spatial position on the sample. A LabView program is used to record the FFT sum and subsequently change the laser wavenumber. PTIR spectra are generated by plotting the FFT sum as a function of the wavenumber.

To reduce imaging artifacts, the PTIR images at 1712 cm^{-1} have been normalized by dividing the images by the 1800 cm^{-1} image intensity. Furthermore, the trace and retrace PTIR image is overlapped and the maximum is taken. The trace and retrace image overlaps on the flat area but is only mismatched at the grain boundary where a large change in height present. With a large height change, the PTIR channel does not track the surface properly, but this only happens in either the trace or the retrace channel. Therefore, by taking the maximum from the trace and retrace channel, the artifact from the grain edge can be reduced.

X-ray diffraction (XRD)

X-ray diffraction (XRD) was collected with Phillips PW1830 HT generator, PW1050 goniometer, PW3710 control electronics with a X-Pert software using Cu K α radiation source at a resolution of $2\theta = 0.2^\circ$. The samples were prepared in the same way as described above.

Ultraviolet-visible absorption spectroscopy (UV-VIS)

UV-Vis absorption spectra were collected using a Perkin Elmer Lambda 25 spectrophotometer.

Photoluminescence (PL)

Photoluminescence measurements were performed using a Horiba Fluorolog instrument. by illuminating the samples with a monochromatized Xe lamp (peak wavelength at 600 nm). The excitation and emission slit width is 14 nm and 5 nm, respectively.

Time of flight secondary ion mass spectrometry (TOF-SIMS)

TOF-SIMS V static SIMS spectra were obtained using an ION-TOF GmbH TOF-SIMS instrument. For the analysis with the primary beam, Bi^{3++} was used with 60 keV.

X-ray photoelectron spectroscopy (XPS)

XPS spectra were collected using a K-Alpha x-ray photoelectron spectrometer (Thermo Fisher Scientific) excited with monochromatic Al $K\alpha$ (1486.6 eV) x-rays.

Attenuated total internal reflection – Fourier transform infrared spectroscopy (ATR-FTIR)

Far-field Fourier Transform infrared (FTIR) spectra were collected using a Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer in ATR mode at 4 cm^{-1} resolution.

PTIR VS. FOURIER TRANSFORM IR SPECTROSCOPY (FTIR)

Figure S1. PTIR and FTIR spectra showing the formamidine C=N absorption band at 1712 cm^{-1} . The intensity was offset for easier comparison

ADHESION VS. RH%

Figure S2. Adhesion increases as RH% increases.

The adhesion was measured in the same setup as PTIR, but without emission from the mid-IR laser. The increase in adhesion as RH increases indicates the presence of water adsorbed on the surface of the perovskites. Measurements were taken in the order of 18, 65, 85, 22 RH% to control for possible AFM tip contamination that can also increase the adhesion.

LOW HUMIDITY UNDER LIGHT

Figure S3. (top) PTIR at 1712 cm^{-1} ($2 \times 2\text{ }\mu\text{m}^2$) and AFM images ($10 \times 10\text{ }\mu\text{m}^2$) at RH = 20% under light. The white squares in the AFM images show where the PTIR images were taken. (bottom) XRD: RH < 20 % under light.

HIGH HUMIDITY IN THE DARK

Figure S4. (top) PTIR at 1712 cm^{-1} ($2 \times 2\text{ }\mu\text{m}^2$) and AFM images ($10 \times 10\text{ }\mu\text{m}^2$) at RH = 85% in the dark. The white squares show where the PTIR images were taken. (bottom) XRD: 80% RH in the dark.

DEGRADATION AT EXTENDED TIMES

80 % relative humidity, dark

20 - 40 % relative humidity illuminated

Figure S5. (top) exposure to 80% RH in the dark. (bottom) exposure to 20-40% RH illuminated.

When the perovskite is illuminated at 40% RH, depressions also formed, but only after 21 h, in contrast to 6 h when exposed to 80% RH in the main text. After 56 h, the sample is exposed to 20% RH and light, and the depressions do not grow in size from 56 – 154 h. From Figure S5, light and 20% RH also does not lead to the formation of depressions for 50 h. When exposed to 80% RH in the dark, no formation of depressions or needles were noticed. However, some large grains formed from 85 – 104 h. We conclude that the depression is only formed when illuminated and this process is accelerated by higher RH.

AFM ROUGHNESS AND PTIR INTENSITY VS. TIME

Figure S6. $20 \times 20 \mu\text{m}^2$ AFM images. The white squares indicate where the AFM images in Figure S7 are taken from.

Figure S7 Complete set of AFM and PTIR images from Figure 3, including a zoomed in image in the fresh sample.

PTIR OF NEEDLES AND DEPRESSIONS

Figure S8. PTIR spectra of needles and depressions.

PTIR spectra on needles and depressions shows that they do not contain any FAI, suggesting that the FAI formed from decomposition was volatile. A peak is still present at 1712 cm^{-1} for depressions, possibly due to the remaining perovskite that is yet to be converted to PbI_2 and FAI. In contrast, the needles do not show any absorption at 1712 cm^{-1} . Note that both $\delta\text{-FAPbI}_3$, and $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ shows a peak at 1712 cm^{-1} due to the formamidinium moiety. These spectra have been normalized by dividing to spectra measured on the substrate.

TOF-SIMS OF THE DEPRESSIONS

Figure S9. a) TOF-SIMS Pb^+ map. The square and the arrow indicate the same area shown in Figure 4a. b) AFM topography showing the depressions.

POTENTIAL SOURCES OF ERROR FOR AFM AND PTIR DEGRADATION STUDIES

Although AFM and PTIR are typically branded as “non-destructive” analytical techniques, we found that under certain conditions the setup can cause additional degradation of the perovskites. In the following section, we explain why the degradations observed are not due to instrumental artifacts.

Potential degradation from AFM mechanical motion

PTIR uses the Peak Force quantitative nanomechanical mapping mode in which the AFM tip is deflected until a certain setpoint by the sample in contact, and inevitably a pressure is applied to the sample by the tip. We have noticed that using Peak Force setpoint larger than 40 nN and a tip radius of ~20 nm, changes in the AFM morphology can be seen. It has been shown that pressure can induce degradation to perovskites.² However, when exposed to light or water alone (Figure S3 and S4) AFM morphology and roughness do not change. The same deflection setpoint and applied pressure were used in the high humidity and light experiment, thus no degradation comes from the AFM tip.

Potential laser induced degradation

The red laser in the AFM head and the mid-IR laser used for the PTIR absorption may cause additional degradation, for example, photoinduced degradation or heating from the mid-IR laser. To minimize the potential source degradation mentioned above, in-situ experiments were not carried out. Instead, in ex-situ experiment, the perovskites were exposed to light and/or high humidity in the absence of the mid-IR laser, the AFM deflection laser and pressure applied from the AFM. The effect of these instrumental factors is present only when the sample is imaged. During this time, the AFM chamber is kept at < 20% RH, where we show from Figure S3 that no degradation occurs.

Indium ion leaching from the ITO substrate

Indium ions have been reported to migrate from the ITO substrate to the perovskite layer.³ In Figure S10 below, we show with x-ray photoelectron spectroscopy (XPS) that no indium ion was observed in the perovskite layer, where two peaks at 454 and 446 eV would be present otherwise.³

Figure S10. XPS at indium 3d region.

PTIR AT A NON-ABSORBING WAVELENGTH

Figure S11. AFM and PTIR images at 1800 cm^{-1} at the same area shown in Figure 3 in the main text. All the images are $4 \times 4\text{ }\mu\text{m}^2$. Area marked by the dotted white line indicate areas where no absorption was observed at 1712 cm^{-1} in Figure 3.

At 1800 cm^{-1} , no absorption is expected for FA. The large change in PTIR intensity in Figure 3 on the FAPbI_3 grains was not observed here. In addition, the area outlined by the white dotted line represent the inorganic decomposition product, where at 1712 cm^{-1} a large contrast was observed between the needle and the surrounding grains. Furthermore, the PTIR intensity are much lower at 1800 cm^{-1} since it is not at an absorption peak. The darker regions present at 1800 cm^{-1} are due to the AFM tip temporarily losing contact with the surface where a large height change occurs (also in Figure 3) and at the same time limited by the maximum Peak Force setpoint that can be used without damaging the sample. For this reason, analysis of the grain boundary should be done with caution and is not discussed in this manuscript.

AFM ROUGHNESS AND PTIR INTENSITY VS. TIME

Figure S12. (left) Average root mean square roughness in the AFM morphology from Figure S7 and two other samples (blue), Figure S3a (orange) and S4a (black). (right) PTIR intensity over time with the same color label.

AFM and PTIR measurements were performed on three different areas in two different samples. The uncertainty between the three areas in the AFM roughness and PTIR intensity plot (blue dots) is due to the local compositional differences in the $4 \times 4 \mu\text{m}^2$ imaged. This is especially clear after many hours of light and humidity exposure since the location where the holes and needles form are randomly distributed.

CRYSTAL SIZE CHANGE AND DEGRADATION KINETICS

Figure S13. (a-c) Area percent of different areas taken from AFM topography images. (d-f) volume during the first step of the degradation with the JMAK fit. (g) AFM topography showing the locations where the particular samples are taken at. Light blue: large grains, dark blue: needles, white: depressions.

To quantify the growth and decay of different materials, we look at how the areas change using the AFM topography images. Figure S13g illustrates where the areas are taken for grains (light blue), needles (dark blue) and depressions (white) for 8, 13, 17, and 28 h. The depressions are identified by the lowered AFM topography formed at 5 h which has a distinct structure from the otherwise homogenous film with uniform thickness. The needles are elongated large grains (versus other part of the film) formed also at 5 h. The percent area is determined using the ratio of each material's area versus the total outlined area at 0 h. A similar process was done with each time step and the areas plotted versus time (Figure S13a-c). In Figure S13a, the blue points correspond to the conversion of small grains to large grains, and the orange points correspond to the decomposition of the large grains as the organics evaporate. Note that in the later degradation times, the total fractional areas do not add to one. This is due to the numerous gaps between the grains created as the large grains shrink which are not considered in the analysis.

With this simple analysis, we are able to illustrate the two-step degradation process that plateaus at 11 – 13 h (gray dashed line). For the grains (Figure S13a), the plateau onset at 11 h occurs at the point where the large grains of δ -FAPbI₃ formed. In δ -CsPbI₃ (Figure S13b), needles formation plateaus at around 11 h, after which the area increases very gradually. In the depressions (Figure S13c), the slowing of the growth at this time period probably corresponds to when the depressions have completed the conversion to PbI₂. In addition, we found that the growth of needles and growth of depressions are very different at after 13 h. In PbI₂, a second sigmoidal function was clearly observable after 11 h, possibly due to the photodecomposition of PbI₂ to Pb and I₂. In contrast, with CsPbI₃, the growth after 11 h, is much slower than PbI₂ possibly due to the slow conversion CsPbI₃ to CsI and PbI₂.

The above is a very crude analysis of the degradation. For example, at later times, numerous degradation pathways are happening simultaneously, and film thickness changes may induce errors in determining the material's areas.

Modeling with JMAK equation

The solid-state decomposition can be modeled using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation. For a more complete description and derivation, please refer to references (⁴⁻⁸). Fitting to this crystal growth model allows the determination of the reaction rate constant and the order of growth:

$$\alpha(t) = \frac{V(t)}{V(t_{end})} = 1 - e^{-kt^n}$$

In the equation above, $V(t_{end})$ is the volume of the crystal after the growth has plateaued, $V(t)$ is volume of the crystal at time t , k is the temperature dependent rate constant and n is the Avrami exponent. By plotting the volume ratio of the crystals, $V(t)/V(t_{end})$, versus t , and fitting to the Avrami equation, the rate and the order of crystal growth can be determined. The volume $V(t)$ of the different materials was determined using the AFM images from Figure S7 as follows. The volume of the needle was determined by multiplying the area by the film thickness (689 nm), by assuming that the film and needle thickness is the same and does not change at this time (See Figure S14). The volume of the depression was measured by summing the height at each particular point in the depression over the whole depression. The volume of FAI was determined by subtracting the depression volume from the total volume (638 nm $\times$ depression area). The end volume, $V(t_{end})$ is defined as the $V(t)$ when the growth has plateaued. In the second step of the degradation (> 11 h), film thickness decreased, thus fitting was not done due to additional complications to volume changes when the grains decompose.

	k	$k^{1/n}$	n
δ_o -CsPbI ₃	$4.74 \times 10^{-3} \text{ min}^{-n}$	0.114 min^{-1}	2.47
PbI ₂	$2.33 \times 10^{-4} \text{ min}^{-n}$	0.123 min^{-1}	3.99
FAI	$1.40 \times 10^{-4} \text{ min}^{-n}$	0.123 min^{-1}	4.24

The obtained k and n were plotted in the table above, in addition, $k^{1/n}$ is listed to show the common growth unit of inverse time. The Avrami exponent, n , depends on the dimensionality of the growth or the crystal shape. For example, $n = 4, 3, 2$ correspond to 3-dimension growth, 2-dimension disk-like growth, and 1-dimension needle like growth, respectively. Please refer to references (4-8) for a more detailed mathematical description of the Avrami exponent. For PbI₂ and FAI, $n = 3.99$ and 4.24 respectively, suggesting a uniform growth in all three dimensions with $n \sim 4$. For CsPbI₃, $n = 2.47$, suggesting a growth mainly in one dimension (needle-like) but also growth in the second dimension which widens the needles.

CHANGE IN FILM THICKNESS WHEN EXPOSED TO LIGHT AND 85% RH

Figure S14. Film thickness versus time under light and 85% relative humidity. AFM topography showing the morphology during the height change. The scale bar is 5 μm .

The film thickness was determined by scratching the sample and using the AFM to measure the height change of the film edge. From the AFM images (Figure S14 inset), we can see that the thickness decrease occurs when the $\delta\text{-FAPbI}_3$ decomposes and needles form. Only a single step degradation was observed in contrast to the two steps change in AFM roughness vs. time (Figure S12) since no change in the film thickness was observed for during phase separation and holes formation.

Note that degradation may occur faster at the edge since it is more exposed to water vapor. Therefore the decrease in height occurs at 5 – 10 h in contrast to 15 – 32 h in the main text.

PTIR SPECTRA AT DIFFERENT LOCATIONS AT DIFFERENT DEGRADATION STEPS

Figure S15. PTIR spectra on two different grains at different time steps during the degradation. PTIR of formamidinium iodide (FAI) was included for reference.

PHOTOS OF THE DEGRADATION

Figure S16. Photos of the sample after different time periods of exposure to light and 85% RH. The wafer is 1 $\times$ 1 cm^2 .

XPS SPECTRA OF THE DEGRADATION

Figure S17. XPS spectra of Pb 4f, C 1s, and O 1s regions.

The Pb 4f peaks at 138 and 143 eV shifted to lower binding energy, but the Pb 4f peaks that correspond to Pb^0 at 136 and 141 eV⁹ was not observed. The C 1s peak at 285 eV correspond to adventitious carbon.^{10,11} The peak at 286.5 eV is from the FA cation^{10,11}, which is only present at the 0 h sample but not after 24 h of decomposition. A new C 1s peak at 289 eV has been attributed to CO_3 from PbCO_3 .^{10,11} The O 1s peak at 532 eV increased in intensity with a clear shoulder at 530 eV.^{10,11} These results above suggest that oxygen containing lead salts such as PbO , Pb(OH)_2 and PbCO_3 were formed from the decomposition of PbI_2 under humid air and light.

DEGRADATION AT VARIOUS FORMAMIDINIUM AND CESIUM COMPOSITION.

Figure S18. AFM topography images of varying FA and Cs composition. All images are $10 \times 10 \mu\text{m}^2$. The images were collected at the same area during the degradation for each composition. The data for $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ is the same as Fig. S7, placed here for comparison. Depressions were also observed in $\text{FA}_{0.70}\text{Cs}_{0.30}\text{PbI}_3$ but was not captured in the $10 \times 10 \mu\text{m}^2$ images shown here.

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