Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Curing of Degraded $MAPbI_3$ Perovskite Films

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Experimental Detail

Materials

Methylammoninum iodide (MAI) powders were synthesized by reacting an aqueous solution of hydroiodic acid (57 wt%, Aldrich) with methylamine (33 wt % in methanol) stirring in an ice bath for 2 h. The mixture was dried at 65 °C using a rotary evaporator. The obtained precipitant was washed three times with diethyl ether and dried at 60 °C for 24 h. Commercial powder of PbI_2 and DMF solvent were used as received from Sigma-Aldrich.

Preparation of $MAPbI_3$ film

$MAPbI_3$ ($CH_3NH_3PbI_3$) perovskite film samples were prepared via the drop casting method. The mixture of PbI_2 and MAI with a molar ratio of 1:1 was first dissolved in N, N-Dimethylformamide (DMF) to form a 25 wt % solution. MAPbI3 perovskite films on the glass substrate were prepared by evaporating the DMF solution at 70°C under reduced pressure (12.7 torr) on time scales of 45 min and 90 min. The spin coated sample was prepared via spin-coating the 1M solution of PbI_2 in DMF at 7000 rpm for 30s. After drying, it was immersed into the 1M MAI in isopropanol (IPA) solution for 5 min. The film was then thermally annealed at 100°C for 15min.

Recovery of degraded $MAPbI_3$ film

The recovery experiment of the degraded perovskite thin film coated on the glass substrate was performed to demonstrate the reversibility of the phase degradation process. In a glove box with the humidity controller, the relative humidity level was maintained at 60 ± 5%. The samples were exposed to this atmosphere in the container for 14 days. And then the degraded samples were recovered by irradiation using X-ray (I= 6000 W/cm^2), UV light (λ=390 nm, I ≈ 7.56 mW/cm^2) and electron beam exposure (15keV). The recovered samples were placed in a sealed container with a humidity of 25 ± 5% for further recovery of the perovskite phase.

Materials Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex instrument using the Cu K_α beam (λ= 1.54 Å), with a fast rate of 4.5min/scan (scan step: 0.1°, duration time: 0.5s) for X-ray recovery and regular speed at 25 min/scan (scan step: 0.1°, duration time: 3s) for the XRD measurement of recovered films by other techniques. SEM images and EDX spectra were acquired on a Phenom ProX.

1. Calculated XRD data

The XRD data for $MAPbI_3$ were calculated using MDI Jade 6.5 software. The parameters used for the calculation of the XRD data of the cubic phase of $MAPbI_3$ are ρ=4.1643g/cm^3, V=247.2Å^3, $Pm\bar{3}m$, Z = 1, cell constant: a=6.276 Å and α=90°.

Table S1. Calculated XRD data of cubic phase of $MAPbI_3$

d(Å)	(h k l)	2-Theta	p
6.276	(1 0 0)	14.1	6
4.4378	(1 1 0)	19.991	12
3.6235	(1 1 1)	24.547	8
3.138	(2 0 0)	28.419	6
2.8067	(2 1 0)	31.858	24
2.5622	(2 1 1)	34.992	24
2.2189	(2 2 0)	40.626	12
2.092	(2 2 1)	43.21	30
1.9846	(3 1 0)	45.675	24
1.8923	(3 1 1)	48.041	24
1.8117	(2 2 2)	50.322	8
1.7406	(3 2 0)	52.53	24
1.6773	(3 2 1)	54.675	48
1.569	(4 0 0)	58.804	6

The parameters used for the tetragonal phase of $MAPbI_3$ are ρ=4.1264g/cm^3, V=997.9Å^3, I4/mcm, Z=4, cell constant: a=8.8743Å, b=8.8743Å, c=12.6708, and $\alpha=\beta=\gamma$=90°:

Table S2. Calculated XRD data of tetragonal phase of $MAPbI_3$

d(Å)	(h k l)	2-Theta	p	2.0939	(4 0 2)	43.168	8
6.3354	(0 0 2)	13.967	2	2.0917	(3 3 0)	43.216	4
6.2751	(1 1 0)	14.102	4	2.0015	(1 1 6)	45.269	8
4.4583	(1 1 2)	19.898	8	1.9862	(3 3 2)	45.636	8
4.4372	(2 0 0)	19.994	4	1.9844	(4 2 0)	45.682	8
3.7873	(2 1 1)	23.47	16	1.9177	(4 1 3)	47.365	16
3.6344	(2 0 2)	24.472	8	1.9068	(2 0 6)	47.651	8
3.1677	(0 0 4)	28.147	2	1.8936	(4 2 2)	48.004	16
3.1375	(2 2 0)	28.423	4	1.8172	(4 0 4)	50.16	8
2.8922	(2 1 3)	30.892	16	1.7656	(3 2 5)	51.733	16
2.8278	(1 1 4)	31.613	8	1.7577	(4 3 1)	51.982	16
2.8116	(2 2 2)	31.8	8	1.7519	(2 2 6)	52.166	8
2.8063	(3 1 0)	31.862	8	1.7455	(3 3 4)	52.373	8
2.5781	(2 0 4)	34.768	8	1.7404	(5 1 0)	52.538	8
2.5658	(3 1 2)	34.94	16	1.6874	(3 1 6)	54.322	16
2.4161	(3 2 1)	37.182	16	1.6816	(4 2 4)	54.523	16
2.2292	(2 2 4)	40.43	8	1.6782	(5 1 2)	54.643	16
2.2186	(4 0 0)	40.632	4	1.6469	(2 1 7)	55.772	16
2.1359	(2 1 5)	42.279	16	1.6405	(4 1 5)	56.009	16
2.1266	(3 2 3)	42.473	16	1.6363	(4 3 3)	56.167	16
2.1219	(4 1 1)	42.57	16	1.6342	(5 2 1)	56.246	16
2.1118	(0 0 6)	42.784	2	1.5839	(0 0 8)	58.2	2
2.1006	(3 1 4)	43.025	16	1.5688	(4 4 0)	58.814	4

Crystal structure parameters used for $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ [1] are ρ=3.035g/cm^3, V=1239.59Å^3, monoclinic $P2_1/n$, Z = 2, cell constant: a=10.3937 Å, b=11.3055Å, c=10.5519 Å and β=91.298°:

Table S3. Calculated XRD data of $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$

d(Å)	(h k l)	2-Theta	p	2.9533	(3 2 0)	30.237	4
7.7129	(0 1 1)	11.463	4	2.9515	(-1 3 2)	30.256	4
7.6505	(1 1 0)	11.557	4	2.9409	(-2 3 1)	30.368	4
7.4881	(-1 0 1)	11.809	2	2.9305	(1 3 2)	30.479	4
7.3204	(1 0 1)	12.08	2	2.9201	(2 3 1)	30.589	4
6.2429	(-1 1 1)	14.175	4	2.8845	(-1 2 3)	30.977	4
6.1447	(1 1 1)	14.403	4	2.8584	(-3 2 1)	31.267	4
5.6528	(0 2 0)	15.664	2	2.8552	(1 2 3)	31.303	4
5.2746	(0 0 2)	16.795	2	2.8483	(-2 1 3)	31.38	4
5.1955	(2 0 0)	17.052	2	2.8325	(-3 1 2)	31.56	4
4.9825	(0 2 1)	17.787	4	2.8298	(3 2 1)	31.59	4
4.9656	(1 2 0)	17.848	4	2.8264	(0 4 0)	31.63	2
4.78	(0 1 2)	18.547	4	2.7927	(2 1 3)	32.022	4
4.7209	(2 1 0)	18.781	4	2.7778	(3 1 2)	32.198	4
4.5116	(-1 2 1)	19.661	4	2.7301	(0 4 1)	32.777	4
4.4741	(1 2 1)	19.827	4	2.7273	(1 4 0)	32.811	4
4.3768	(-1 1 2)	20.273	4	2.6561	(-2 3 2)	33.717	4
4.3425	(-2 1 1)	20.434	4	2.6443	(-1 4 1)	33.872	4
4.3091	(1 1 2)	20.595	4	2.6373	(0 0 4)	33.964	2
4.2764	(2 1 1)	20.754	4	2.6367	(1 4 1)	33.972	4
3.8565	(0 2 2)	23.043	4	2.6256	(2 3 2)	34.12	4
3.8252	(2 2 0)	23.234	4	2.6106	(-2 2 3)	34.323	4
3.7441	(-2 0 2)	23.745	2	2.5984	(-3 2 2)	34.488	4
3.6602	(2 0 2)	24.297	2	2.5978	(4 0 0)	34.497	2
3.6352	(-1 2 2)	24.467	4	2.571	(0 3 3)	34.868	4
3.6155	(-2 2 1)	24.602	4	2.5683	(0 1 4)	34.905	4
3.5961	(1 2 2)	24.737	4	2.5675	(2 2 3)	34.916	4
3.577	(2 2 1)	24.871	4	2.5559	(3 2 2)	35.08	4
3.5542	(-2 1 2)	25.033	4	2.5502	(3 3 0)	35.162	4
3.5489	(0 3 1)	25.072	4	2.5318	(4 1 0)	35.425	4
3.5427	(1 3 0)	25.116	4	2.5062	(-1 1 4)	35.799	4
3.4823	(2 1 2)	25.559	4	2.5054	(-1 3 3)	35.811	4
3.3662	(-1 3 1)	26.456	4	2.496	(-3 0 3)	35.95	2
3.3577	(0 1 3)	26.524	4	2.4913	(0 4 2)	36.021	4
3.354	(-1 0 3)	26.554	2	2.4883	(-3 3 1)	36.066	4
3.3506	(1 3 1)	26.582	4	2.4861	(1 3 3)	36.098	4
3.3132	(-3 0 1)	26.888	2	2.4828	(2 4 0)	36.149	4
3.3117	(3 1 0)	26.899	4	2.4806	(1 1 4)	36.181	4
3.3082	(1 0 3)	26.929	2	2.4743	(-4 1 1)	36.277	4
3.269	(3 0 1)	27.258	2	2.4694	(3 3 1)	36.352	4
3.2155	(-1 1 3)	27.72	4	2.4496	(4 1 1)	36.655	4
3.1794	(-3 1 1)	28.041	4	2.4401	(3 0 3)	36.803	2
3.175	(1 1 3)	28.081	4	2.4374	(-3 1 3)	36.846	4
3.1403	(3 1 1)	28.398	4	2.4285	(-1 4 2)	36.985	4
3.1215	(-2 2 2)	28.573	4	2.4226	(-2 4 1)	37.079	4
3.0724	(2 2 2)	29.039	4	2.4167	(1 4 2)	37.172	4
3.0663	(0 3 2)	29.098	4	2.4109	(2 4 1)	37.265	4
3.0505	(2 3 0)	29.252	4	2.39	(0 2 4)	37.604	4
2.9858	(0 2 3)	29.9	4	2.3852	(3 1 3)	37.682	4

Crystal structure parameters used for $CH_3NH_3PbI_3 \cdot H_2O$ [2] are ρ= 4.0258 g/cm^3, V= 526.3Å^3, monoclinic $P2_1/m$, Z = 2, cell constant: a= 10.3939Å, b= 4.6419Å, c= 11.1181Å and β= 101.161°:

Table S4. Calculated XRD data of $CH_3NH_3PbI_3 \cdot H_2O$

d(nm)	(h k l)	2-Theta	p	0.23823	(4 0 1)	37.729	2
0.82928	(-1 0 1)	10.659	2	0.23797	(-1 1 4)	37.772	4
0.68196	(1 0 1)	12.971	2	0.2375	(-3 1 3)	37.849	4
0.54539	(0 0 2)	16.239	2	0.23619	(-3 0 4)	38.068	2
0.52505	(-1 0 2)	16.872	2	0.23512	(0 1 4)	38.247	4
0.50987	(2 0 0)	17.378	2	0.23479	(2 1 3)	38.304	4
0.50056	(-2 0 1)	17.704	2	0.2321	(0 2 0)	38.766	2
0.44634	(1 0 2)	19.875	2	0.23096	(3 1 2)	38.964	4
0.431	(2 0 1)	20.59	2	0.23079	(-4 0 3)	38.994	2
0.42712	(0 1 1)	20.779	4	0.22851	(-2 1 4)	39.399	4
0.42248	(1 1 0)	21.01	4	0.22732	(3 0 3)	39.614	2
0.41464	(-2 0 2)	21.412	2	0.22701	(0 2 1)	39.67	4
0.40505	(-1 1 1)	21.925	4	0.22659	(-4 1 1)	39.746	4
0.38373	(1 1 1)	23.16	4	0.22631	(1 2 0)	39.799	4
0.36559	(-1 0 3)	24.326	2	0.22351	(-1 2 1)	40.319	4
0.36359	(0 0 3)	24.462	2	0.22345	(4 1 0)	40.329	4
0.35349	(0 1 2)	25.172	4	0.22317	(2 0 4)	40.383	2
0.34777	(-1 1 2)	25.593	4	0.22231	(-1 0 5)	40.545	2
0.34398	(-3 0 1)	25.88	2	0.22117	(1 1 4)	40.763	4
0.34325	(2 1 0)	25.936	4	0.2203	(-4 1 2)	40.932	4
0.34098	(2 0 2)	26.112	2	0.21972	(1 2 1)	41.045	4
0.34036	(-2 1 1)	26.16	4	0.21816	(0 0 5)	41.352	2
0.33991	(3 0 0)	26.195	2	0.21628	(-2 0 5)	41.728	2
0.32751	(-2 0 3)	27.206	2	0.2155	(4 0 2)	41.886	2
0.32325	(1 0 3)	27.571	2	0.21356	(0 2 2)	42.284	4
0.32173	(1 1 2)	27.704	4	0.21228	(-1 2 2)	42.552	4
0.31736	(-3 0 2)	28.094	2	0.21195	(4 1 1)	42.621	4
0.31585	(2 1 1)	28.231	4	0.21124	(2 2 0)	42.772	4
0.30923	(-2 1 2)	28.848	4	0.21056	(-2 2 1)	42.916	4
0.30803	(3 0 1)	28.963	2	0.21051	(-3 1 4)	42.928	4
0.28721	(-1 1 3)	31.114	4	0.20787	(-5 0 1)	43.499	2
0.28624	(0 1 3)	31.222	4	0.20732	(-4 0 4)	43.621	2
0.27717	(-1 0 4)	32.271	2	0.20666	(-4 1 3)	43.769	4
0.27643	(-3 0 3)	32.36	2	0.20592	(1 2 2)	43.934	4
0.27637	(-3 1 1)	32.367	4	0.20535	(1 0 5)	44.061	2
0.27481	(2 1 2)	32.556	4	0.20445	(-5 0 2)	44.266	2
0.27425	(3 1 0)	32.625	4	0.20435	(2 2 1)	44.289	4
0.2727	(0 0 4)	32.815	2	0.20416	(3 1 3)	44.333	4
0.27217	(2 0 3)	32.88	2	0.20395	(5 0 0)	44.381	2
0.26761	(-2 1 3)	33.457	4	0.20253	(-2 2 2)	44.709	4
0.26626	(3 0 2)	33.631	2	0.20225	(-3 0 5)	44.773	2
0.26527	(1 1 3)	33.761	4	0.20113	(2 1 4)	45.036	4
0.26252	(-2 0 4)	34.125	2	0.20051	(-1 1 5)	45.184	4
0.26198	(-3 1 2)	34.197	4	0.19744	(0 1 5)	45.926	4
0.25963	(-4 0 1)	34.517	2	0.19604	(-2 1 5)	46.271	4
0.25666	(3 1 1)	34.929	4	0.19594	(-1 2 3)	46.297	4
0.25493	(4 0 0)	35.174	2	0.19563	(0 2 3)	46.374	4
0.25157	(1 0 4)	35.66	2	0.19546	(4 1 2)	46.417	4
0.25028	(-4 0 2)	35.85	2	0.19507	(3 0 4)	46.516	2

2. XRD pattern of fresh, degraded and recovered perovskite $MAPbI_3$.

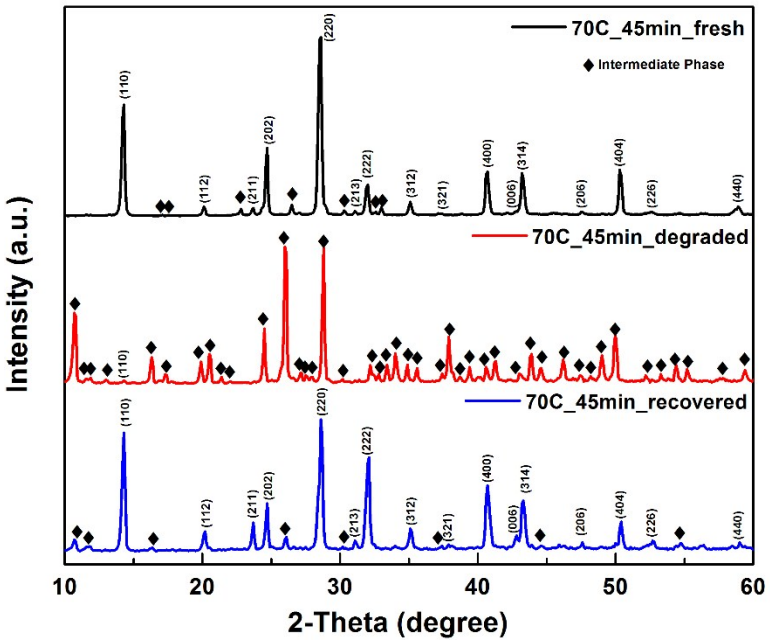

Figure S1. The XRD patterns of (A) fresh perovskite film, (B) degraded under humidity of 60% ± 5% for 14 days, (C) the film recovered from degraded phases. The intensity in all patterns is normalized for comparison.

3. Recovery of spin-coated samples

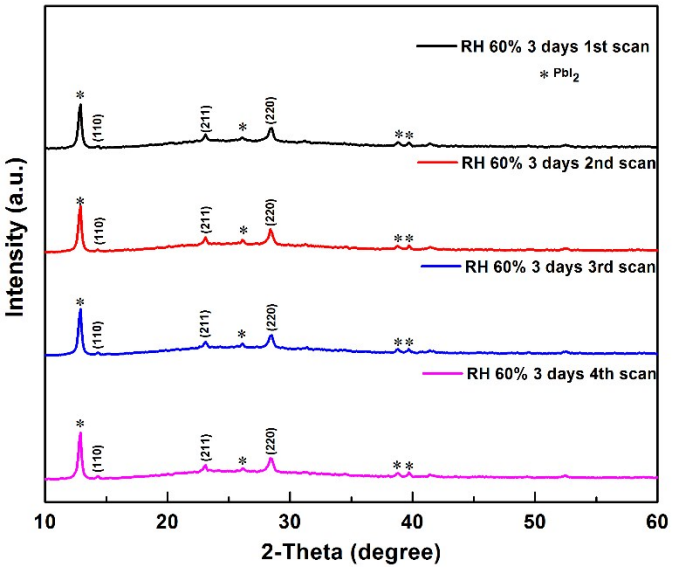

Figure S2. The XRD patterns of spin-coated perovskite films degraded under humidity of 60% for 3 days, after 4 scans of X-ray irradiation (50min, 12.5min/scan), no obvious recovery was observed through X-ray treatment. Labeled peaks in the sample belonging to the tetragonal perovskite.

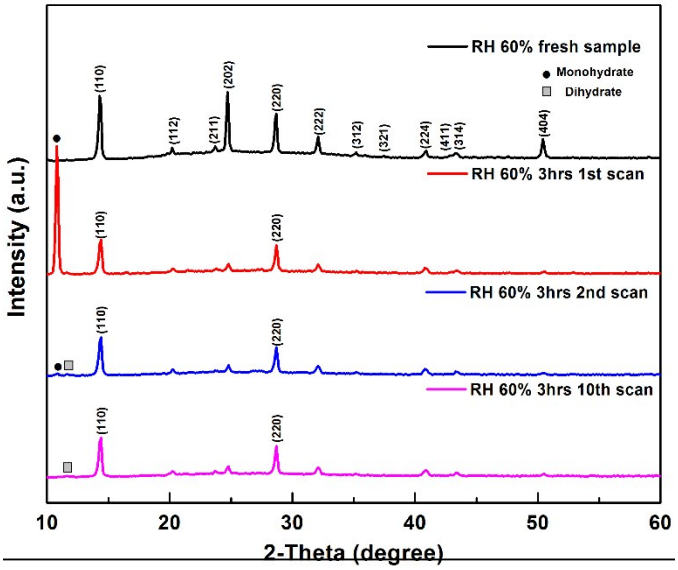

Figure S3. The XRD patterns of spin-coated perovskite films degraded under controlled humidity of 60% for 3 hrs. Major recovery occurred during the first scan of 5 min X-ray exposure. However, the observed recovery should be mainly due to the low humidity level 25% during XRD measurement. After 10 consecutive X-ray irradiation scans (4.5min/scan), no further recovery was observed. The labeled peaks belong to the tetragonal perovskite phase.

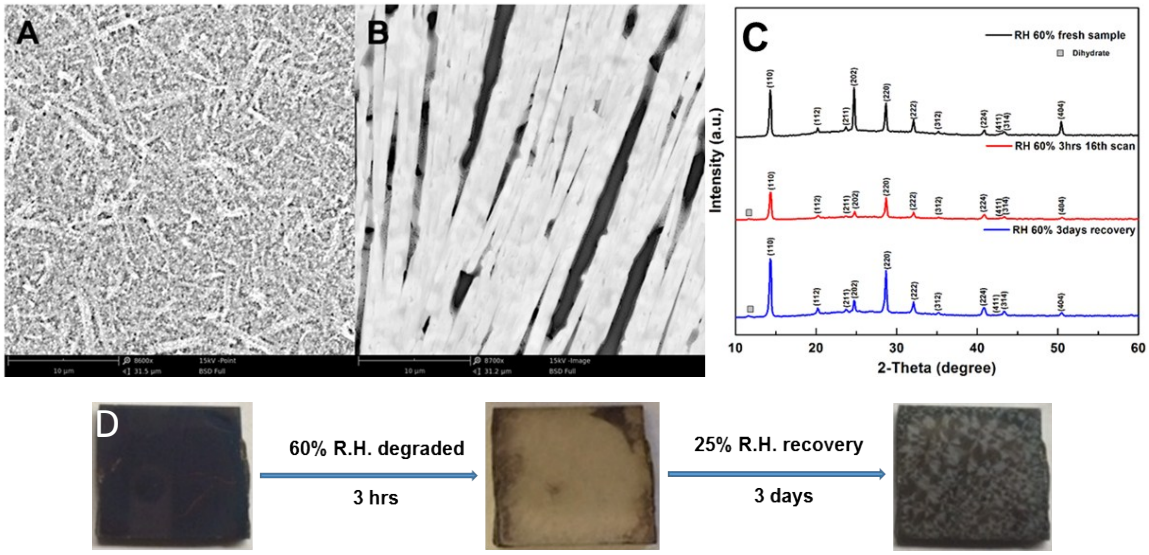

Figure S4. The SEM images of (A) fresh spin-coated perovskite film and (B) film recovered for 3 days from degradation (humidity of 60% for 3 hrs). (C) The XRD patterns of fresh spin-coated perovskite film, the degraded film (3 hrs under R.H. 60%) after 16 scans of X-ray irradiation (72min, 4.5min/scan), and film recovered 3 days under R.H. of 25%. Labeled peaks in the sample belong to the tetragonal perovskite phase. (D) Photographs of perovskite films from fresh to recovered stage.

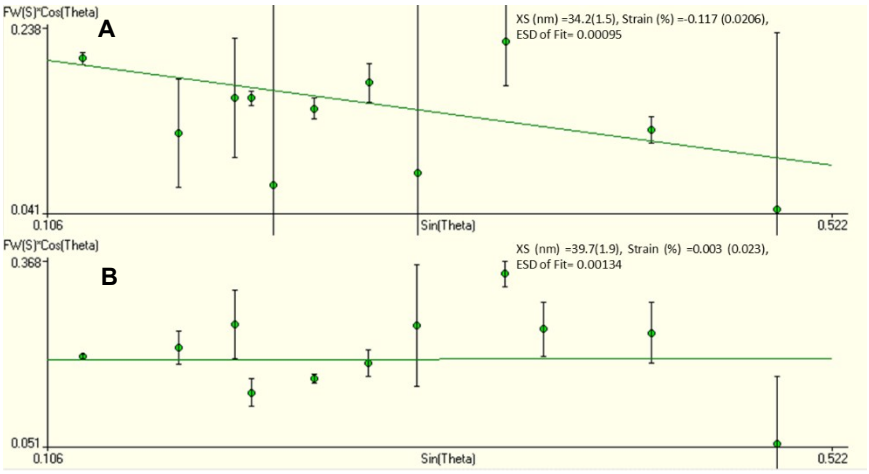

Figure S5. Williamson-Hall plots of the size and strain of (A) fresh spin-coated perovskite film and (B) film recovered 3 days after degradation (60% humidity for 3 hrs). According to the equation $\beta_{hkl}\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta$, where β_{hkl} is the specimen broadening, θ is the peak position, K is the shape factor of the average crystallite, λ is wavelength of Cu kα radiation, D is crystalline size and ε is the microstrain.

4. Recovery by UV-irradiation

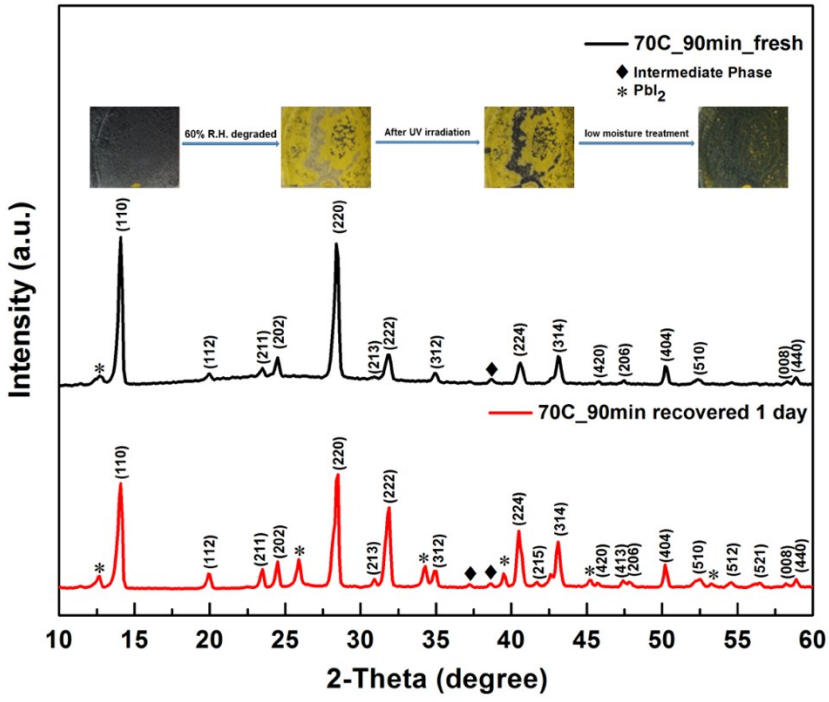

Figure S6. XRD patterns of a fresh perovskite film prepared at 70°C for 90 min and recovered after 15 minutes UV irradiation and low humidity exposure. The inset shows photographs of

perovskite film sintered at 70°C for 90 min, degraded under 60 ± 5% humidity for 14 days, after 15 minutes UV irradiation and then stored 1 day at 25 ±5% humidity.

5. SEM images and EDX spectrum

The SEM images and EDX spectrum of the fresh sample are shown in Fig. S7:

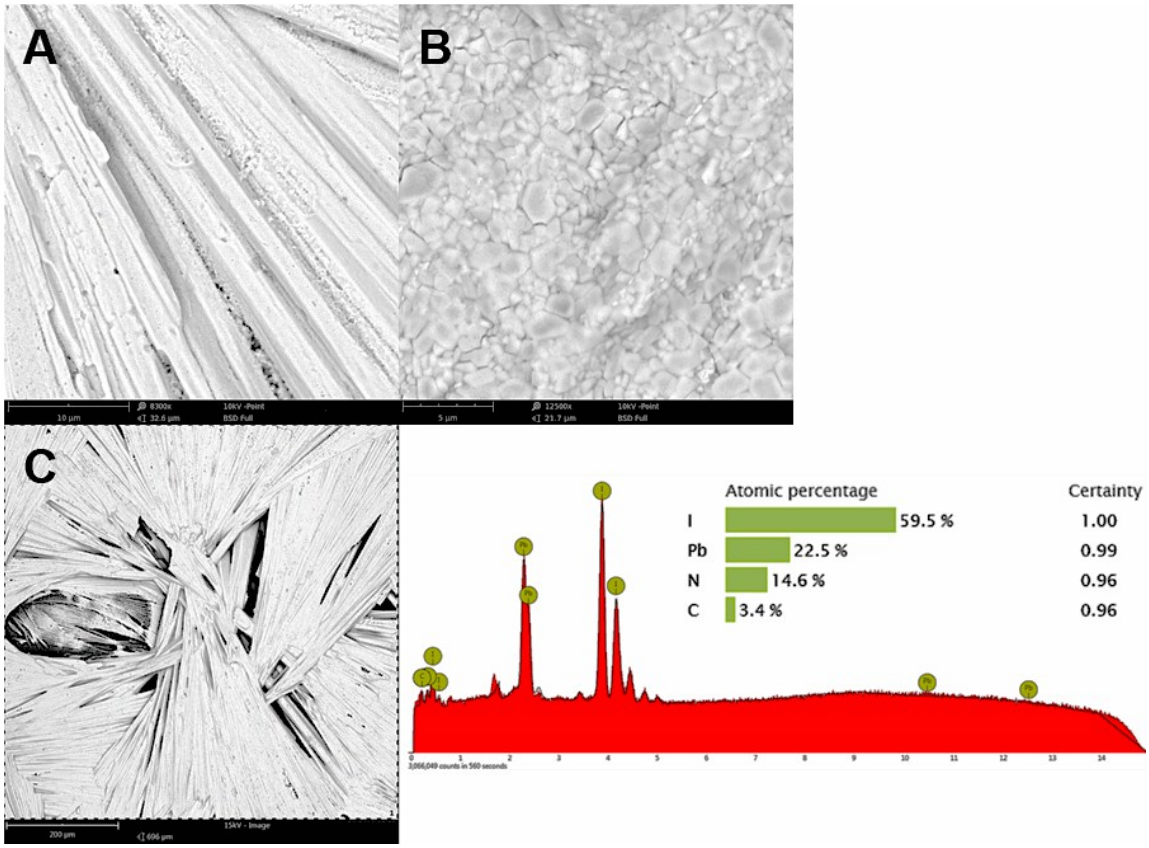

Figure S7. The SEM images and EDX spectrum of the fresh sample prepared at 70°C for 45min under vacuum, A) at 8300x magnification, acquired from the center part; B) at 12500x magnification, acquired from the edge part; C) EDX spectrum acquired by overview scanning of the region in image C with a scale bar 200µm. The fan-shaped morphology formed in the drop-casted sample prepared under vacuum.

The SEM images and EDX spectrum of the X-ray recovered sample are shown in Fig.S8:

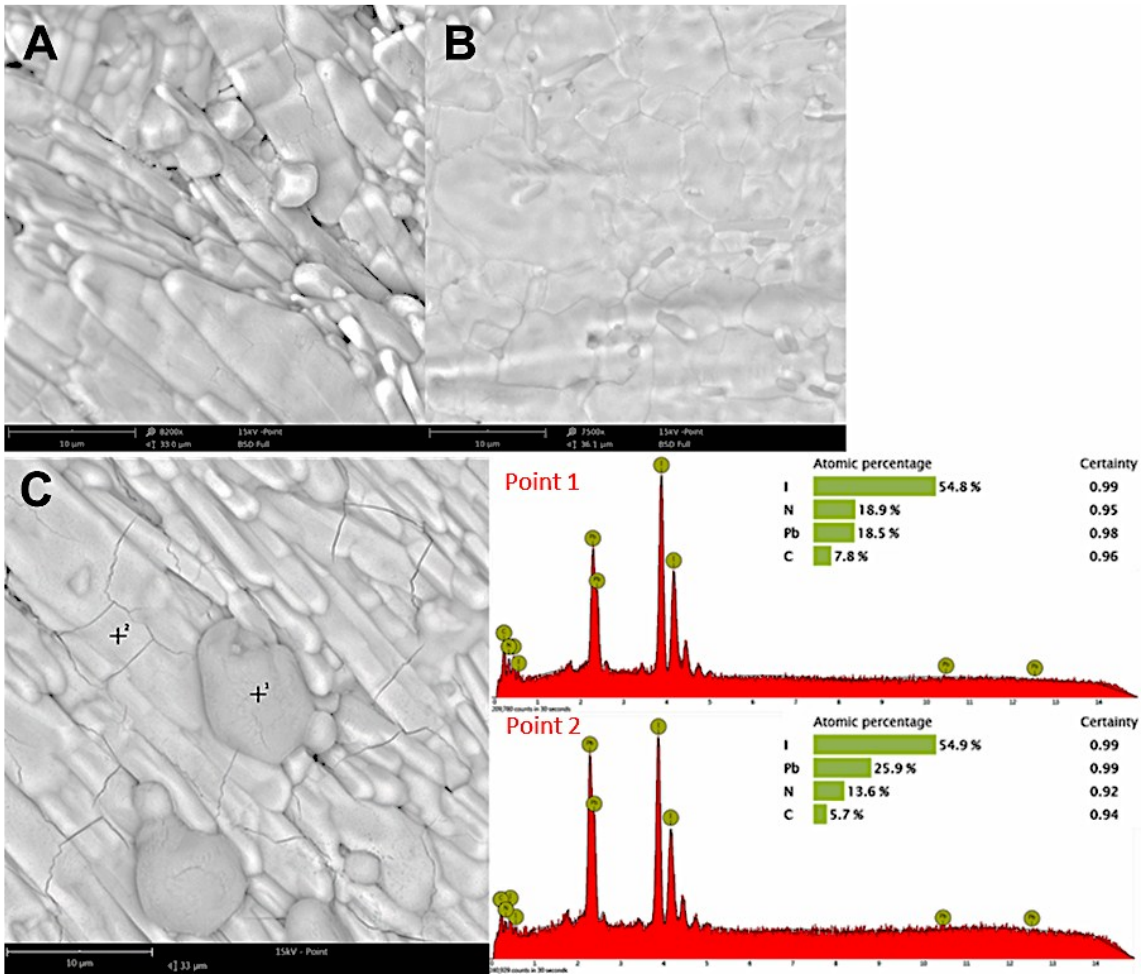

Figure S8. The SEM images and EDX spectrum of the X-ray recovered sample, A) at 8200x magnification, acquired from the center part; B) at 7500x magnification, acquired from the edge part; C) EDX spectrum acquired at point 1 and point 2 in image C with a scale bar 10µm, indicating the formation of stoichiometric perovskite grains nucleated from the PbI_2 rich bulk body.

The SEM images and EDX spectrum of the E-beam recovered sample are shown in Fig.S9:

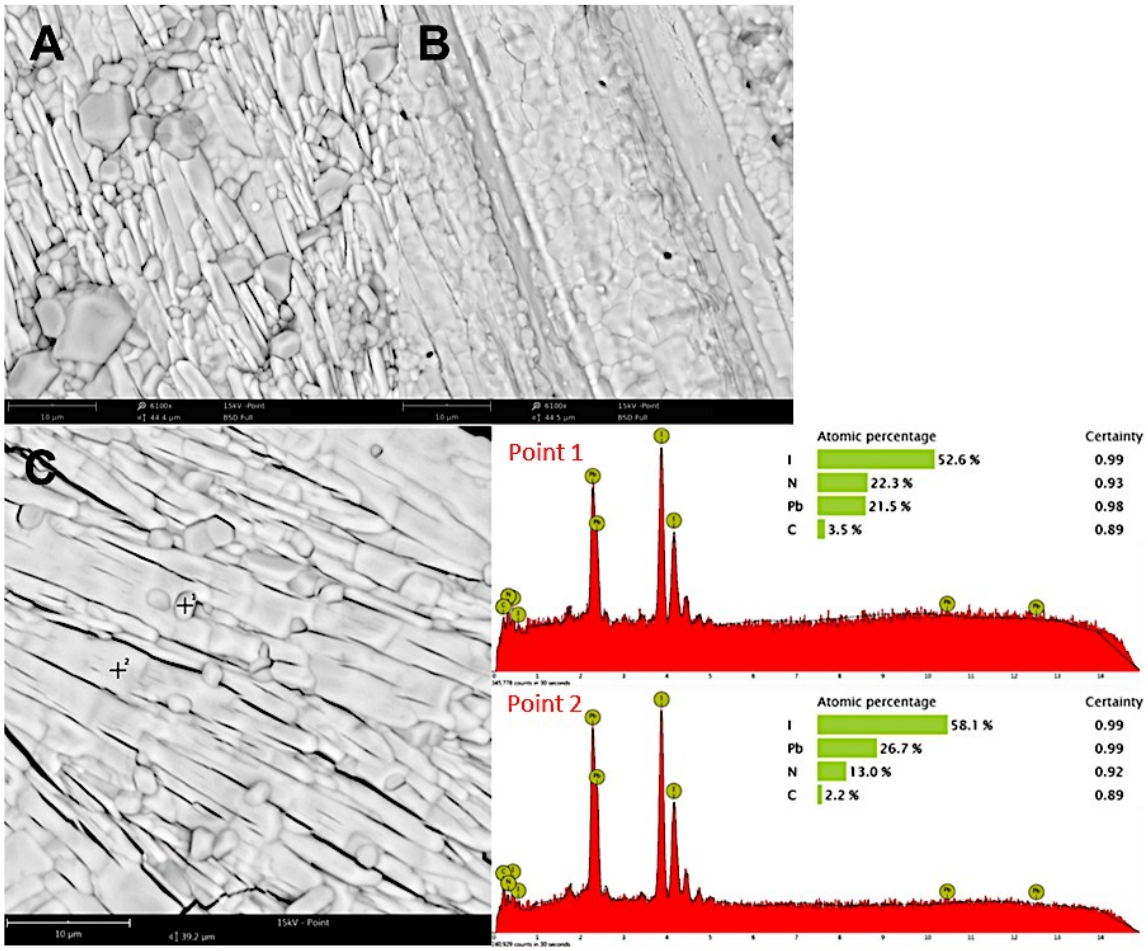

Figure S9. The SEM images and EDX spectrum of the E-beam recovered sample, A) at 6100x magnification, acquired from the center part; B) at 6100x magnification, acquired from the edge part; C) EDX spectrum acquired at point 1 and point 2 in image C with a scale bar 10µm, indicating the formation of stoichiometric perovskite grains nucleated from the MAI rich bulk body.

The SEM images and EDX spectrum of the low moisture recovered sample are shown in Fig.S10:

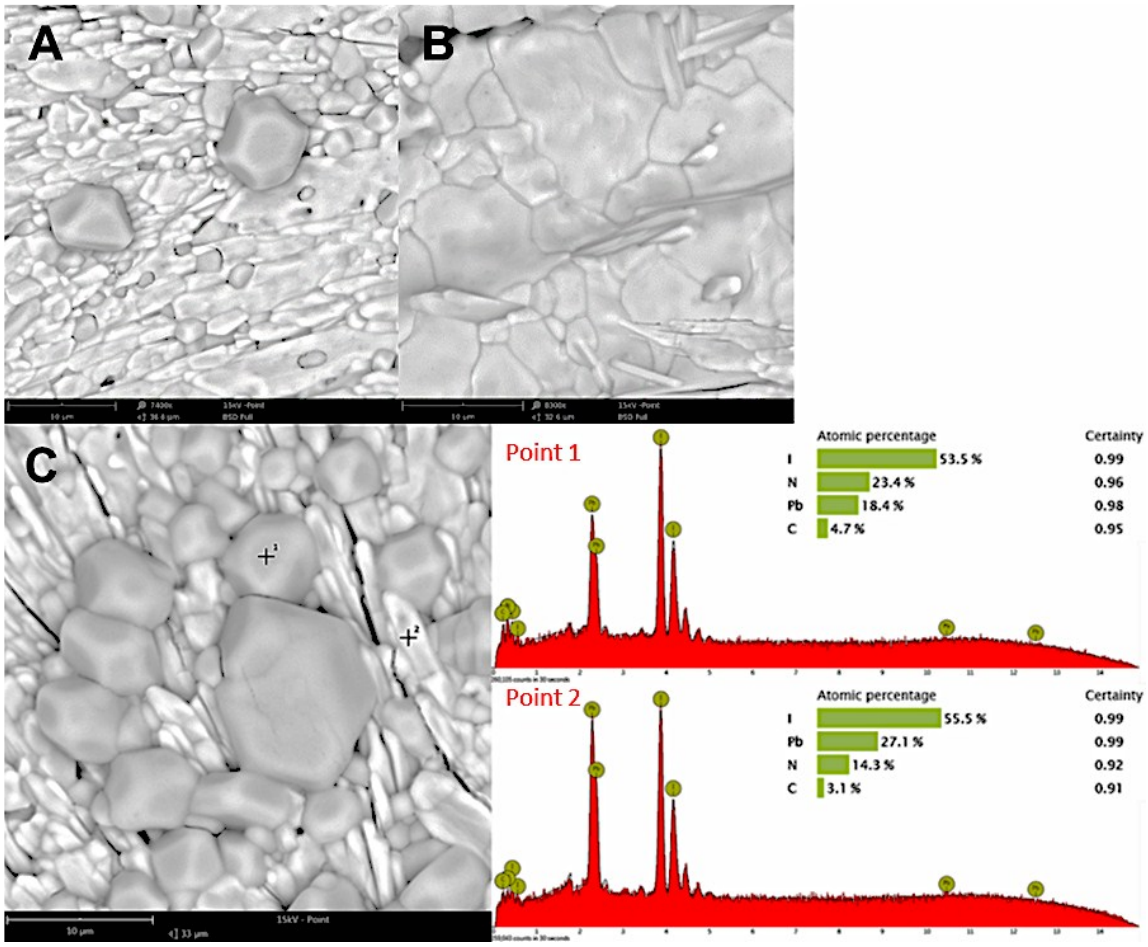

Figure S10. The SEM images and EDX spectrum of the low moisture recovered sample, A) at 7400x magnification, acquired from the center part; B) at 8300x magnification, acquired from the edge part; C) EDX spectrum acquired at point 1 and point 2 in image C with a scale bar 10µm, indicating the formation of MAI rich perovskite grains nucleated from the PbI_2 rich bulk body.

The SEM images and EDX spectrum of the heat recovered sample are shown in Fig.S11:

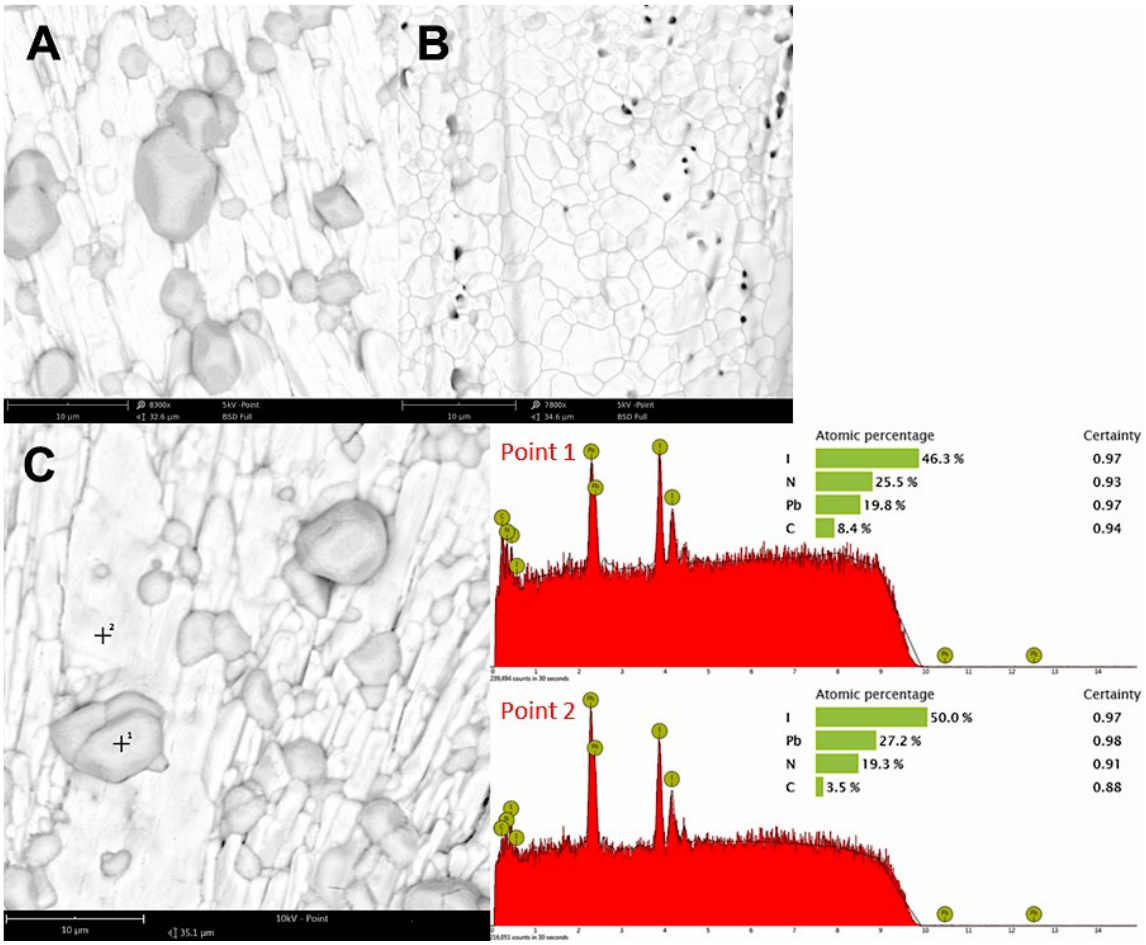

Figure S11. The SEM images and EDX spectrum of the heat recovered sample, A) at 8300x magnification, acquired from the center part; B) at 7800x magnification, acquired from the edge part; C) EDX spectrum acquired at point 1 and point 2 in image C with a scale bar 10µm, indicating the formation of MAI rich perovskite grains nucleated from the PbI_2 rich bulk body.