

Article

Compositional and Morphological Changes in Water-Induced Early-Stage Degradation in Lead Halide Perovskites

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Abstract: With tremendous improvements in lead halide perovskite-based optoelectronic devices ranging from photovoltaics to light-emitting diodes, the instability problem stands as the primary challenge in their development. Among all factors, water is considered as one of the major culprits to the degradation of halide perovskite materials. For example, CH₃NH₃PbI₃ (MAPbI₃) and CH(NH₂)₂PbI₃ (FAPbI₃) decompose into PbI₂ in days under ambient conditions. However, the intermediate changes of this degradation process are still not fully understood, especially the changes in early stage. Here we perform an in-situ investigation of the early-stage MAPbI₃ and FAPbI₃ degradation under high water vapor pressure. By probing the surface and bulk of perovskite samples using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and XRD, our findings clearly show that PbI₂ formation surprisingly initiates below the top surface or at grain boundaries, thus offering no protection as a water-blocking layer on surface or grain boundaries to slow down the degradation process. Meanwhile, significant morphological changes are observed in both samples after water vapor exposure. In comparison, the integrity of MAPbI₃ film degrades much faster than the FAPbI₃ film against water vapor. Pinholes and large voids are found in MAPbI₃ film while only small number of pinholes can be found in FAPbI₃ film. However, the FAPbI₃ film suffers from its phase instability, showing a fast α -to- δ phase transition. Our results highlight the importance of the compositional and morphological changes in the early stage degradation in perovskite materials.

Keywords: halide perovskite; degradation; water; PbI₂ formation; morphology

1. Introduction

Halide perovskite materials with excellent optoelectronic properties show extensive potential in applications including photovoltaics [1], photodetectors [2], light-emitting diodes, and so on [3]. However, the inherent instability prevents these materials from long-term usage in devices [4]. The two widely used perovskite materials, methylammonium lead triiodide (MAPbI₃) and formamidinium lead triiodide (FAPbI₃), are susceptible to degradation by multiple factors, including water, oxygen, UV light, electrical field, and heating [4,5]. Synergistic degradation by the combination of multiple factors were also seen. Recent reports found the degradation process is greatly accelerated when perovskite is exposed to water, oxygen, and light together [6,7]. However, the excess water is still considered as the one of the major culprits causing the degradation of perovskite materials. Without any protection,



both MAPbI₃ and FAPbI₃ films cannot last more than a few days in ambient air, quickly decomposed into PbI₂ [8].

Based on these observations, two general strategies are proposed to improve device stability. The first strategy is to prevent perovskite layers from making any contact with water. Methods associated with this strategy include encapsulation [9,10] and surface passivation [11]. The second strategy is to enhance the durability of perovskite against water. Methods associated with this strategy include organic and inorganic doping [12–14] and film quality improvement [15]. These efforts successfully extend the lifetime of PSCs to thousands of hours, but still far from fulfilling commercialization requirements [4]. To further extend the lifetime of perovskite materials, new strategy based on thorough understanding of perovskite degradation is needed.

It is clear that MAPbI₃ and FAPbI₃ decompose into PbI₂ at the end, but there are still uncertainties in the process of the degradation. For example, many studies suggest an indirect degradation pathway with sequential formation of two hydrated intermediates, monohydrate (CH₃NH₃PbI₃·H₂O) and dihydrate ((CH₃NH₃)₄PbI₆·2H₂O), during ingress of water [16]. The monohydrate forms first and is reversible, while dihydrate forms only after monohydrate. Prolonged exposure dihydrate with water leads to final decomposition [17]. However, this indirect pathway may not be always valid. Direct PbI₂ formation without steps of monohydrate and dihydrate formation was shown in some rigorous studies, raising doubts on the validity of the indirect degradation pathway. Schlipf et al. reported an earlier PbI₂ formation than the appearance of monohydrate in their in-situ XRD measurements [18]. Recent near ambient pressure X-ray photoelectron spectroscopy (NAPXPS) study also claimed the surface of a perovskite thin film prepared by thermal deposition quickly decomposed into PbI₂ at only 30% of relative humidity level [19]. Therefore, a direct degradation pathway leading to PbI₂ may exist, causing premature deterioration of device performance.

Meanwhile, it is also uncertain the role of PbI₂ in degradation. Excessive PbI₂ appeared beneficial to the device performance, though it may affect the long-term photostability [20,21]. Previous studies usually assumed the PbI₂ is formed from the surface, their data usually suggest a linear degradation speed, implying no water-blocking effect from PbI₂ layer on surface [22]. Studies using in-vivo XRD measurements confirmed PbI₂ formation in sample but was unable to determine whether PbI₂ is on the top of surface or not [8,23]. PbI₂ layer was observed by surface sensitive techniques such as XPS, but in these studies, perovskite films were usually measured after complete decomposition and missed the critical PbI₂ formation period [22,24].

Another uncertainty is the effect of morphological change in the early stage of degradation. Morphology is considered as one of the important factors that affects the performance and lifetime of devices. Interestingly, it can be beneficial if a small fraction of water is introduced during fabrication [25]. Improved performance and lifetime are witnessed in these devices. These improvements are believed to be due to increased grain size as well as trap passivation [26,27]. Morphological change may be detrimental if grains are grown too large and cause film disintegration. However, the process at which the film loses its integrity is largely ignored. Previous studies focused on non-morphological changes such as trap passivation and grain boundary variation at early degradation stage [17,28]. Others studied much later degradation stage, when the perovskite is completely reverted to PbI₂ [8,29]. Therefore, the morphology evolution in degradation needs further investigation.

Here we report a study focusing on the critical changes in the early stage of MAPbI₃ and FAPbI₃ degradation in a precise and controlled condition. Multiple experimental techniques are applied to study water-induced compositional and morphological evolutions under high water vapor pressure at room temperature. Surprisingly, the surface of degraded samples remained stoichiometric to the pristine phase while PbI₂ is found in bulk. This finding excludes the possibility of self-passivation by PbI₂ and supports the coexistence of both degradation pathways under high water partial pressure condition. Meanwhile, prominent morphological changes such as pinholes and large voids are observed in MAPbI₃ sample, revealing loss of film integrity initiated in the early stage degradation. In comparison, FAPbI₃ film remains largely intact with much less pinholes, indicating a much slower

morphology evolution. However, the FAPbI₃ sample suffers from water-induced phase change. XRD data show the dominant δ phase in the degraded FAPbI₃ sample, indicating a fast α to δ phase transition in the early stage of the degradation. Our results successfully clarify compositional and morphological changes in the early-stage degradation of perovskite thin films.

2. Materials and Methods

The MAPbI₃ sample and FAPbI₃ sample are prepared by standard solution preparation methods with anti-solvent treatment. All organic cation salts were purchased from Dyesol (Queanbeyan, Australia) while lead iodide was bought from Acros Organics (Geel, Belgium). MAPbI₃ and FAPbI₃ perovskite solutions were prepared by mixing precursors in stoichiometric ratio (1 M concentration) in anhydrous dimethylformamide (DMF from Sigma Aldrich, St. Louis, MO, USA). The perovskite thin films were spun-coated on cleaned indium-tin-oxide (ITO) substrates at 5000 rpm for 12 s. The anti-solvent treatment was performed by dripping 100 μ L toluene on the spinning substrates 9 s prior to the end of spinning. Subsequently, MAPbI₃ samples were annealed at 100 °C for 30 min while FAPbI₃ samples were annealed at 160 °C for 10 min. Prepared samples were transferred from glovebox to XPS system through an air-tight container to minimize contact with external atmosphere. XPS measurements were conducted in-situ before and after water vapor dosing in the high-pressure gas cell. SEM and XRD were ex-situ measured before and after water vapor dosing in near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) system.

The film crystallinity was measured using Bruker D8 discover X-ray diffractometer (Billerica, MA, USA) with Cu K α radiation (λ = 1.54 Å). The morphology is measured by JEOL FESEM 6700 (Akishima, Japan). The surface composition was measured by PREVAC NAP-XPS system (Rogow, Poland) with monochromatic Al K α X-ray source (hv = 1486.7 eV).

3. Results and Discussion

To investigate the degradation on the perovskite surface, it is important to control the hydration level precisely. Many previous works used ambient condition with different relative humidity (RH) values to probe the degradation process [23,30,31]. However, RH is not an absolute unit and can largely vary due to temperature change. Therefore, RH value is not an accurate parameter to measure the content of water. Furthermore, gases in the air such as oxygen may also have implications on the perovskite degradation, making the process more complicated [28,32]. Here we use the gas cell inside a NAPXPS system to study the interaction of perovskite samples to water vapor. The in-situ environment excludes any other external factors and the measured water partial pressure is more accurate than RH value.

 $MAPbI_3$ and $FAPbI_3$ samples are exposed to 23 mbar of water vapor pressure in NAPXPS cells separately for two times with 1 h each. The water vapor partial pressure is about 80% RH for the measured cell temperature of 23 °C. The lower exposure pressure at 18 mbar or below shows no distinguished changes. Extending the exposure time to 6 h resulted in further decreased XPS intensities as well as I/Pb, N/Pb, and C/Pb ratios. Therefore, we only discuss the 2 h exposure in detail. To monitor potential surface composition changes, XPS high-resolution spectra from MAPbI₃ and FAPbI₃ before and after water vapor exposure were acquired (Figure 1). It should be highlighted that measurements were done at an ultrahigh vacuum condition after the system was fully recovered from water exposure. Therefore, signals from monohydrate and dihyrate are not expected. For MAPbI₃, the spectra of I $3d_{5/2}$, Pb 4*f*, and N 1*s* contain single peaks at 619.6, 138.8, and 402.7 eV, respectively. All of them originated from MAPbI₃ [33]. In the spectrum of C 1s, two peaks at 286.7 and 285.5 eV can be distinguished. The higher binding energy peak (C1) is from C–N bonding in MA cation. The lower binding energy peak (C2) is attributed to the adventitious carbon and it is not related to perovskite itself. The binding energies of carbon peaks are consistent with previous reports [33,34]. After water vapor exposure, peak intensities of I 3d_{5/2}, Pb 4f, N 1s, and C1 gradually decrease. Only the C2 peak shows a slight increase. Meanwhile, the peak position remains unchanged. The drop in peak intensities are also

observed for the FAPbI₃ sample (Figure 1e–g). However, the magnitude of the drop is smaller. The relative intensities of different elements are summarized in Figure 2. These intensities in FAPbI₃ drop about 10% to 20%, while in MAPbI₃, the intensities drop more than 30% for iodine and close to 50% for nitrogen. To clarify if this decrease is related to the decomposition, the normalized atomic ratios between iodine, lead, nitrogen, and C1 are compared, as listed in Table 1. For MAPbI₃, the I/Pb ratio is 3.1 in the pristine sample, indicating a slightly iodine rich on the surface. After the first and second water vapor exposure, this ratio further increased to 3.5 and 3.7, respectively. Meanwhile, the N/Pb ratio and C/Pb ratio are also maintained above 1, indicating no sign of organic cation deficiency at surface. Therefore, the atomic ratio change of Pb/I only suggests enrichment of organic cations or deficiency of lead atoms. None of these changes support PbI2 formation. For FAPbI3, the composition change is even smaller. The I/Pb ratio is between 3.1–3.6 and N/Pb ratio is between 2.1–2.2. The C/Pb ratio is slightly lower than 1, but no systematic decrease after water vapor exposure was observed. From the atomic ratio data, it can be concluded that there is no sign of PbI₂ formation. It appears to contradict a previous NAPXPS study, in which the perovskite surface is completely decomposed at 9 mbar of water partial pressure [19]. This contradiction can be justified by the difference in sample fabrication. Unlike the solution process method, the perovskite films prepared by vacuum deposition usually have smaller domain sizes and poorer crystalline quality. A lower-quality film may result in much faster degradation. Instead, our results are consistent with studies using solution-processed perovskite samples, where no significant surface degradation were reported [24,35].



Figure 1. Cont.



Figure 1. High-resolution spectra of I $3d_{5/2}$, N 1*s*, Pb 4*f* and C 1*s* obtained from MAPbI₃ (**a**–**d**) and FAPbI₃ (**e**–**h**) samples before and after water vapor exposure to different periods, respectively.



Figure 2. The relative intensities change after different water vapor exposure period. (**a**) Elemental intensity changes of MAPbI₃ sample. (**b**) Elemental intensity changes of FAPbI₃ sample.

Table 1. Atomic ratio of different elements obtained by XPS from MAPbI₃ and FAPbI₃ before and after water vapor exposure.

Exposure Time	MAPbI ₃			FAPbI ₃		
	I/Pb	N/Pb	C/Pb	I/Pb	N/Pb	C/Pb
0 h	3.1	1.6	1.5	3.1	2.2	0.8
1 h	3.5	1.0	1.5	3.6	2.1	0.7
2 h	3.7	1.5	2.4	3.3	2.1	0.9

Since there is no trace of PbI₂ formation on the surface, the decrease in intensities is probably due to reduced film coverage. This is supported by the observation in XPS wide scans (Figure 3). After water vapor exposure, new peaks originated from In 3*d* and O 1*s*, indicating the partial exposure of ITO substrates. This is clear evidence that large voids form in MAPbI₃ thin film. The In 3*d* signal is much stronger in the MAPbI₃ sample, suggesting greater film area shrinkage. Therefore, it can be

concluded that though the surface composition barely changes, the film coverage greatly reduced. Large voids compromise the device integrity and is probably the determining factor to device lifetime.



Figure 3. XPS wide scans obtained from MAPbI₃ and FAPbI₃ samples before and after water vapor exposure. (a) MAPbI₃ sample; (b) FAPbI₃ sample.

Besides surface sensitive XPS measurements, XRD is used as a complementary technique to evaluate the changes in the bulk. In Figure 4, the XRD spectra of MAPbI₃ and FAPbI₃ are shown before and after water vapor exposure. The spectra of both pristine samples only contain peaks from perovskite itself. No PbI₂ peak at 12.7° is observed [36]. After water vapor exposure, a small PbI₂ peak is observed in both samples. Since there is no trace of PbI₂ formation on surface, the signal must come from the site below the very top surface. It appears counterintuitive that PbI₂ formation starts from the bulk instead of surface. One probable explanation is due to the fast diffusion of water molecules and organic cations [37,38]. The water diffusion into the bulk may cause decomposition both inside and on the surface. However, when volatile organic cation escapes via the surface, it may partially compensate the loss of cations at the surface region, delaying PbI_2 formation on the surface. It is also possible that part of PbI₂ crystals formed along the grain boundaries without much exposure to the top surface. Without surface PbI₂ formation, it may be beneficial to keep the interface unchanged, but it also means that slowing down the degradation by PbI₂ passivation will not occur. In the FAPbI₃ sample, the diffraction peak (001) at 13.8° disappeared and a peak at 11.8° emerged. Other high-order peaks also emerged at new two theta degrees. This change is consistent with the α -to- δ phase transition observed in FAPbI₃ previously [35]. Therefore, FAPbI₃ is more sensitive to water-induced phase change.



Figure 4. XRD data of MAPbI₃ and FAPbI₃ sample before and after water vapor exposure. PbI₂ spectra are shown as a reference. Peaks marked with * is from indium-tin-oxide (ITO) substrate. (**a**) XRD spectra of the MAPbI₃ sample before and after water exposure. (**b**) XRD spectra of the FAPbI₃ sample before and after water exposure.

The XPS data suggest film coverage is reduced after water vapor exposure. To understand how severe the reduction in surface coverage is, the surface of both samples are ex-situ measured by SEM

(Figure 5). The pristine MAPbI₃ film is compact with no observable pinholes, while the FAPbI₃ film only contains a few. The FAPbI₃ film shows similar grain size with small bright grains on the surface. The formation of these bright grains is probably due to the annealing process to convert the film from δ phase to α phase. However, during annealing, grain recrystallization also occurs, leaving small grains scattered on the surface. This phenomenon was observed in the previous study as well [39]. After water vapor exposure, the number of pinholes is greatly increased on the MAPbI₃ surface. These pinholes are formed along the grain boundaries and do not affect remaining grains. Meanwhile, a grain-coarsening effect is observed. The average grain size has increased from about 0.13 to 0.23 μ m². All these observations can be attributed to water-induced recrystallization [26]. On the FAPbI₃ surface, the increase in pinholes is far less. Instead, needle-like crystals scatter on the surface, probably related to the δ phase of FAPbI₃ [40]. In summary, more pinholes are found on the MAPbI₃ surface, indicating a poorer morphology stability against water.



Figure 5. SEM images of MAPbI₃ and FAPbI₃ samples before and after water vapor exposure for 2 h. (a) Pristine MAPbI₃ sample; (b) MAPbI₃ sample after degradation; (c) pristine FAPbI₃ sample; (d) FAPbI₃ sample after degradation.

Except small pinholes, a much larger-scale reconstruction pattern is also observed on the MAPbI₃ surface (Figure 6). This reconstruction is not seen on the FAPbI₃ surface. The pattern has a spherulite-like feature with sub-millimeter scale. This pattern was shown in previous works, but its appearance was not discussed [17,41]. This spherulite-like pattern is highly symmetric, where each half assembles an alluvial fan. Inside the pattern, the film has been completely reconstructed, forming long crystals with fused boundary pointing towards the joint of two alluvial fans. Meanwhile, voids are seen between reconstructed patterns or between reconstruction pattern and nearby film. The symmetry of this pattern implies the film reconstruction initiates from the center and then spreads out. The formation of these reconstruction center could be due to either localized surface hydrophilic spots, which make water soaking easy or temporary, and localized humidity level variation, which may cause micro water drops formation on the surface, or both. Interestingly, the relative two-fold symmetric alluvial fan-like structure also indicates non-uniform diffusion on the surface. Along preferential water diffusion direction, adsorbed water diffuses much faster, allowing quick bilateral movement of water

to two opposite ends. At the direction perpendicular to the preferential diffusion direction, water diffuses much slower and does not spread out. It is possible that both monohydrate and dihydrate were formed during recrystallization. However, the film is always measured after water exposure and at ultrahigh vacuum condition. Therefore, from the morphology shown in SEM images, perovskite crystals reversed back from hydrates. The void created by this pattern is much larger than the pinholes formed at grain boundaries. Therefore, it poses a much more severe threat to integrity of devices, and may cause premature device failure. The SEM results are consistent with the XPS data in which nearly 30% and 10% of the film area disappeared after water exposure of MAPbI₃ and FAPbI₃, respectively.



Figure 6. Large-scale morphology changes on the MAPbI₃ sample after water exposure. (**a**) Spherulite-like pattern on the MAPbI₃ surface. (**b**) Zoomed image of the center of spherulite-like pattern.

4. Conclusions

In conclusion, we find the degradation of perovskite materials involves multiple changes. For MAPbI₃, the initial degradation is dominated by water-induced recrystallization, which causes drastic changes in film morphology. For FAPbI₃, the initial change mainly occurs due to the phase transition. For both perovskite films, we reveal the PbI₂ formation occurring in the bulk rather than on the surface, probably mainly at grain boundaries. Therefore, PbI₂ in the degraded film does not act as a water-blocking barrier to slow down the degradation process. The tendency of PbI₂ formation at grain boundaries rather than on the surface is also observed in non-stoichiometric sample with excess PbI₂ or stoichiometric samples degraded by heat. Therefore, it can be generally concluded that degradation process of perovskite film is not slowed by the emergence of PbI₂. Our results highlight the importance of the external water-blocking layer because PbI₂ does not form a continuous film on the surface. Also, a more robust device structure with self-supporting layers may have better resistance to morphology change at the earlier stage of degradation.

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