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Investigation of the Hydrolysis of Perovskite Organometallic Halide CH₃NH₃PbI₃ in Humidity Environment

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Instability of emerging perovskite organometallic halide in humidity environment is the biggest obstacle for its potential applications in solar energy harvest and electroluminescent display. Understanding the detailed decay mechanism of these materials in moisture is a critical step towards the final appropriate solutions. As a model study presented in this work, *in situ* synchrotron radiation x-ray diffraction was combined with microscopy and gravimetric analysis to study the degradation process of CH₃NH₃Pbl₃ in moisture, and the results reveal that: 1) intermediate monohydrated CH₃NH₃Pbl₃·H₂O is detected in the degradation process of CH₃NH₃Pbl₃ and the final decomposition products are Pbl₂ and aqueous CH₃NH₃I; 2) the aqueous CH₃NH₃I could hardly further decompose into volatile CH₃NH₂, HI or I₂; 3) the moisture disintegrate CH₃NH₃Pbl₃ and then alter the distribution of the decomposition products, which leads to an incompletely-reversible reaction of CH₃NH₃Pbl₃ hydrolysis and degrades the photoelectric properties. These findings further elucidate the picture of hydrolysis process of perovskite organometallic halide in humidity environment.

Nowadays, solar cells which use perovskite organometallic halide as light absorption layer have aroused a vast concern all over the world, due to the merits of high efficiency, low-cost and simple synthesis process of the perovskite materials $^{1-12}$. In 2009, power conversion efficiency (PCE) of 3.81% was firstly demonstrated in perovskite solar cell with spin-coated CH₃NH₃PbI₃ on FTO¹. Six years later, PCE as high as ~20% has been acquired through continuous efforts in controlling the formation of the perovskite layer and choosing appropriate material for other layers $^{2-7}$. The quickly enhanced PCE seems signal a new era of perovskite solar cells.

Unfortunately, the instability of organometallic halide perovskite in humidity environment is a tough problem, which hinders its practical application in solar cells and electroluminescent display. Therefore, it is urgent to make clear the decay mechanism of this easily air-slaked material, which is fundamentally meaningful and is also a critical step for pursuing more appropriate solutions. As a model system of perovskite organometallic halide, CH₃NH₃PbI₃ has been intensively studied recently, including the instability problem in moisture^{13–20}. For instance, in 2014, Niu and Frost *et al* proposed a set of degradation equations¹⁶ and a possible decomposition pathway¹⁷, respectively. Thereafter, more experimental evidences were reported by Yang¹⁸, Christians¹⁹ and Leguy²⁰ *et al*. Yang and co-workers utilized *in situ* grazing incidence X-ray diffraction to monitor the phase evolution of CH₃NH₃PbI₃ in water vapor, where an intermediate phase was found and supposed to be (CH₃NH₃)₄PbI₆ • 2H₂O¹⁸. This intermediate phase was also discovered by Christians *et al*¹⁹. Moreover, Leguy *et al* reported a more systematic work performed with time-resolved XRD and ellipsometry, in which two different hydrated crystalline phases of CH₃NH₃PbI₃, i.e., CH₃NH₃PbI₃ • H₂O and (CH₃NH₃)₄PbI₆ • 2H₂O were detected and a suite of convincing degradation equations were provided²⁰. However, despite all these, more detailed questions should be answered, like 'what are the real final decomposition products?' and 'what is the function of moisture in the degradation process?'.

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Figure 1. Schematic diagram of the RH control device and the diffraction geometry in the in-situ XRD experiment.

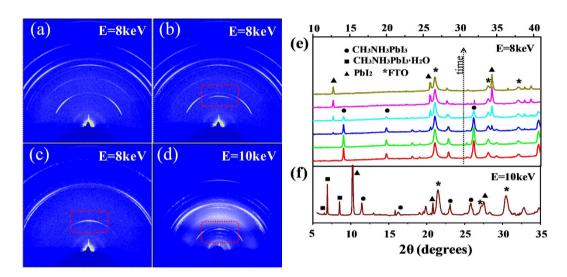


Figure 2. *In situ* **XRD patterns.** (**a-d**) Typical diffraction patterns of spin-coated CH₃NH₃PbI₃/FTO in degradation process and (**e-f**) the corresponding integral curves obtained by using Fit2D program.

To address these issues, here, we carefully studied the degradation process of typical perovskite organometallic halide $CH_3NH_3PbI_3$ in moisture. Using *in-situ* synchrotron XRD experiment, four distinct states have been revealed and in which monohydrated $CH_3NH_3PbI_3 \cdot H_2O$ and one decomposition product PbI_2 are found. Another decomposition product, CH_3NH_3I , is confirmed through a solid-liquid separation experiment and it was demonstrated to be difficult for aqueous CH_3NH_3I to transform to volatile matter through a gravimetric analysis. The microscopy analysis reveals that the reaction of $CH_3NH_3PbI_3$ with water vapor is not a completely reversible one, because the moisture alters the distribution of decomposition products and thus partially separates PbI_2 and CH_3NH_3I .

Results and Discussion

In situ synchrotron radiation XRD experiment. Figure 1 is the schematic of the experiment setup, in which $CH_3NH_3PbI_3/FTO$ film was placed in a homemade sample cell at the diffractometer center. The relative humidity (RH) in the cell was controlled by tuning the flow rate of nitrogen gas and the temperature of the heater. The RH value was real-time monitored by a commercial hygrometer and which was regulated to about 80% during the whole experiment. To confine the moisture, the cell was sealed with kapton film which will not block the incident and diffractive x-ray beam passing through.

Figure 2 shows the typical diffraction patterns selected from the large set of data collected during the *in situ* synchrotron radiation XRD experiment, which indicates the degradation process of spin-coated CH₃NH₃PbI₃/FTO in moisture.

Figure 2a-c are three typical patterns taken during one test (X-ray photon energy E=8keV) with a time sequence of $a \rightarrow b \rightarrow c$, and the corresponding integrated curves are presented in Fig. 2e among those belong to the time-serial data set. Figure 2a is the diffraction pattern of the as-grown $CH_3NH_3PbI_3/FTO$ without water vapor around the sample, which reveals that the film is polycrystalline with preferred orientation along the normal direction. As shown in Fig. 2b, with the time increasing in a relative humidity of $80 \pm 5\%$, the diffraction peaks of perovskite $CH_3NH_3PbI_3$ gradually decrease due to degradation and the reflections belonging to PbI_2 (PDF#07-0235) become more and more intense. Figure 2c shows that the final decomposition product is composed mainly by PbI_2 . However, according to the law of conservation of elements, at least another decomposition product should be there. Since no obvious peaks from other phases appear in this pattern, that product is believed

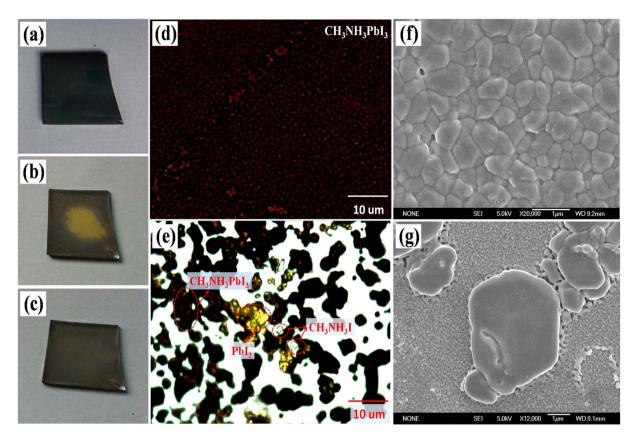


Figure 3. Microscopy images of CH₃NH₃PbI₃/FTO film before and after decaying. (a) Photographs of the as-grown CH₃NH₃PbI₃/FTO film and (b,c) the decayed CH₃NH₃PbI₃ films after taken out from the moisture. (d) Optical micrographs of the as-grown CH₃NH₃PbI₃/FTO film and (e) the decayed CH₃NH₃PbI₃ film. (f) SEM images of the as-grown CH₃NH₃PbI₃/FTO film and (g) the decayed CH₃NH₃PbI₃ film.

to be volatilized or dissolved in water. As described in detail in the following part, the product is proved to be aqueous CH_3NH_3I .

When we repeated the *in situ* XRD measurements, sometimes, we could fortunately detect a metastable phase during the degradation process. One of such patterns is presented in Fig. 2d and the integral curve is plotted in Fig. 2f. The peaks at 6.5° , 6.9° and 8.5° are ascribed to the (001), (110) and ($\overline{1}01$) reflections of the metastable monoclinic $CH_3NH_3PbI_3\cdot H_2O^{20}$. Please note that such intermediate phases were not obvious every time during our XRD experiments, because it is difficult to catch these time- and space-limited phases without enough diffraction intensity by using x-ray beam with sub-millimeter size. Of course, it is more possible to detect such hydrates if people delay the degradation process by decreasing the relative humidity around the sample.

Microscopy Analysis. During the *in situ* XRD experiment, the as-grown brown black CH₃NH₃PbI₃/FTO film (Fig. 3a) gradually becomes yellow (Fig. 3b) in the humidity environment. But, it is interesting that the surface of the film slowly turns yellow to light black (Fig. 3c) after we take the film out of the humidity condition, which seems should be attributed to the water evaporating from the sample.

This phenomenon combined with XRD results (data not show here) indicates the reaction between CH₃NH₃PbI₃ and water vapor is not fully reversible. We guess the underlying cause is that the water vapor not only decompose CH₃NH₃PbI₃ into PbI₂ and aqueous CH₃NH₃I, but also separates these products to some degree. To demonstrate this hypothesis, optic microscopy and scanning electron microscopy (SEM) were utilized to investigate the film morphology before and after the degradation.

Figure 3d is a typical optical micrograph of the as-grown spin-coated CH₃NH₃PbI₃/FTO film. The uniform brown black color indicates the film is homogeneous without obvious second phase. Similar distribution state is also revealed from the corresponding SEM image (Fig. 3f). For the film after the degradation, three types of grain with different color could be easily recognized from the optical micrograph Fig. 3e. The yellow particles are PbI₂, bright transparent grains should be CH₃NH₃I, and the brown black ones are the revived CH₃NH₃PbI₃. In addition, the distribution of these color grains were found in an obvious isolated and disorder manner in comparison with the initial CH₃NH₃PbI₃ film. The SEM image in Fig. 3g also clearly illustrates the rough morphology of the decayed CH₃NH₃PbI₃ film. The above microscopy analysis proves that the moisture indeed alters the distribution of decomposition products and thus makes the reverse reaction between CH₃NH₃PbI₃ and water insufficient.

Till now, the degradation process and decay mechanism may be expressed as follows:

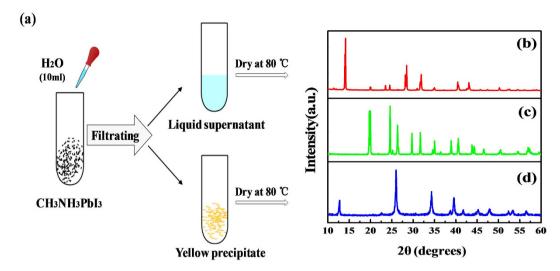


Figure 4. (a) Schematic diagram of solid-liquid separation experiment; XRD patterns of (b) CH3NH3PbI3 powder, (c) the resulting powder separated out from the liquid supernatant and (d) dried yellow precipitate.

$$CH_3NH_3PbI_3 + H_2O \leftrightarrow CH_3NH_3PbI_3 \cdot H_2O \tag{1}$$

$$CH_3NH_3PbI_3 \cdot H_2O \leftrightarrow PbI_2 + CH_3NH_3I + H_2O \tag{2}$$

Solid-Liquid Separation Methods and Gravimetric Analysis. As shown in the microscope images, the separation of PbI_2 and CH_3NH_3I in real space is the key step towards the irreversible reaction between $CH_3NH_3PbI_3$ and water. The cause of this separation is thought to be the different solubility of PbI_2 and CH_3NH_3I in water, which is verified by the following solid-liquid separation experiment.

Here, $CH_3NH_3PbI_3$ powder is used as the research object to make things simple and clear. The steps of the experiment are schematically shown in Fig. 4a. First, $CH_3NH_3PbI_3$ powder (XRD pattern presented in Fig. 4b) was put in distilled water, and the black powder was found turned into yellow precipitate at once. Then, the liquid supernatant and the yellow precipitate were separated by centrifuging and filtrating. Both the liquid supernatant and yellow precipitate were dried at 80 $^{\circ}$ C in dark and the resulting powders were characterized by XRD (Fig. 4c,d), respectively.

From the XRD patterns, it is found that the soluble product of $CH_3NH_3PbI_3$ hydrolysis is CH_3NH_3I (PDF#10-0737) and the yellow precipitate is PbI_2 (PDF#07-0235). The difference in solubility of these two products is the major reason for separation.

Back to the aforementioned another question, i.e. 'what are the real final decomposition products of $CH_3NH_3PbI_3$ hydrolysis', previous studies mostly claim that the final rest product is PbI_2 while the aqueous CH_3NH_3I will volatilize as CH_3NH_2 , HI or I_2 in the condition of moisture and sunlight. Detailed information can be found in ref.16,17,21. Noted that $CH_3NH_3PbI_3/TiO_2/FTO$ hetero-structure was used in these studies, it could not exclude the interfacial effect²¹ in $CH_3NH_3PbI_3/TiO_2$ since TiO_2 is well-known photocatalytic material²². Therefore, another question emerged naturally is what the hydrolysis products of stand-alone $CH_3NH_3PbI_3$. Here, a high-precision gravimetric analysis has been carried out to investigate whether the aqueous CH_3NH_3I will further volatilize for $CH_3NH_3PbI_3$ powders, and the results are listed in Fig. 5. First, two sets of 0.621g $CH_3NH_3PbI_3$ powder and two sets of 0.320g CH_3NH_3I powder were put in test tubes separately, and then 5 ml distilled water was injected in each test tube. Next, one set of watered $CH_3NH_3PbI_3$ and one set of aqueous CH_3NH_3I were directly dried in dark, i.e. in the drying oven at $80\,^{\circ}C$ for a week, while the rest were dried in sunlight for the same time. Finally, all the dried powders were weighted using electronic balance with a precision of 0.01 mg.

The 1^{st} row in Fig. 5 reveals the color and weight change of $CH_3NH_3PbI_3$ powder in this experiment. Notice that the $CH_3NH_3PbI_3$ decayed in water changes back to black again either dried in dark or in sunlight, which confirm that the reaction between $CH_3NH_3PbI_3$ and water is almost reversible if the decomposition products are not separated. As shown by the weight values listed in the figure, the $CH_3NH_3PbI_3$ powder almost does not loss any weight either dried in dark or in sunlight, which indicates that no obvious volatile matter release during $CH_3NH_3PbI_3$ hydrolysis, i.e. it is hard for CH_3NH_3I to further separate. The conclusion was also verified by the control experiment performed on CH_3NH_3I powder, in which the results listed in the 2^{nd} row show that the CH_3NH_3I powder weight almost does not reduce in any cases. In the above measurements, no reflections from other phases were detected by XRD before and after gravimetric analysis (data not shown here). Please note that, the results and conclusion presented here are much different from that found in $CH_3NH_3PbI_3/TiO_2/FTO$ hetero-structure, indicating TiO_2 could influence the degradation process of $CH_3NH_3PbI_3$.

Now, it could be said that the above decay equations (1 and 2) are the major reaction for stand-alone CH₃NH₃PbI₃, and the electric transport layer (ETL) in perovskite solar cells may affect the stability of perovskite

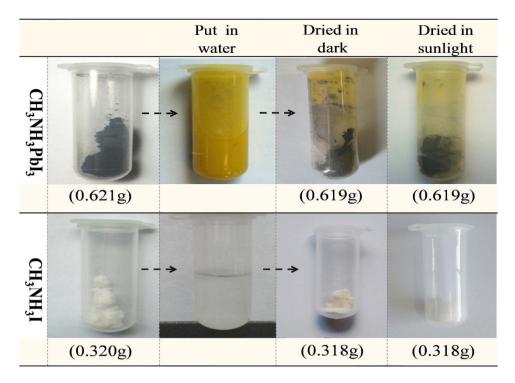


Figure 5. Color and weight change of CH₃NH₃PbI₃ (1st row) and CH₃NH₃I (2nd row) powder when dried in dark or sunlight.

organometallic hilides^{23–26}. Our findings in this paper further elucidate the picture of hydrolysis process of this perovskite material in humidity environment.

Conclusion

Based on *in situ* synchrotron radiation XRD, a reasonable decomposition pathway for $CH_3NH_3PbI_3$ materials in moisture is proposed and the intermediate monohydrated $CH_3NH_3PbI_3$ · H_2O is detected during the degradation process. Moreover, the function of moisture was further investigated via microscopy and gravimetric analysis. The results show that moisture not only decompose $CH_3NH_3PbI_3$ into PbI_2 and aqueous CH_3NH_3I but also altered their distribution, which result in poor connection between PbI_2 and CH_3NH_3I and thus leads to an incompletely-reversible reaction of $CH_3NH_3PbI_3$ hydrolysis. Furthermore, it is confirmed that the final products of $CH_3NH_3PbI_3$ hydrolysis are just PbI_2 and aqueous CH_3NH_3I , and CH_3NH_3I will hardly further decompose into volatile CH_3NH_2 , HI or I_2 for $CH_3NH_3PbI_3$ itself. The degradation process and decay mechanism of perovskite $CH_3NH_3PbI_3$ in moisture becomes clearer with this work, which is believed to be helpful to understand the instability problem in moisture of various perovskite organometallic halides and figure out the possible solutions according to their applications.

Methods

To prepare the $CH_3NH_3PbI_3$ specimens, equimolar CH_3NH_3I and PbI_2 (98%, Sinopharm) were mixed in γ -butyrolactone (97%, Sinopharm) at 60 °C overnight whilst being stirred. Then, the aqueous precursor was deposited on FTO glass by spin-coating at 2000 rpm for 40s. Finally, the specimens were annealed at 100 °C for 15 min on a preheated hot plate, and the obtained $CH_3NH_3PbI_3/FTO$ films were brown black²⁷.

In situ synchrotron radiation XRD was performed at the BL14B station of Shanghai Synchrotron Radiation Facility (SSRF), and the experimental setup is schematically shown in Fig. 1. The diffractive patterns were recorded by a two-dimension x-ray detector (charge coupled device, CCD) with 3072×3072 pixels. To monitor the reaction at real-time, the diffraction patterns were continuously recorded with 10 seconds per frame and 1 second between adjacent frames.

To investigate the CH₃NH₃PbI₃ film morphology before/after the reaction, microscopy analysis was performed by using optical microscope (OLYMPUS, BX51) and scanning electron microscope (SEM, JSM-6700F).

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Author Contributions

J.Z. and Z.L. designed the experiment. B.C. and W.Z. carried out synthesis of materials. J.Z., Z.L., Y.D., H.X. and C.G. performed the *in situ* XRD experiment and data analysis. Microscopy analysis and the rest experiment were performed by B.H., Y.Z., Y.Y. and L.L. The paper was written by J.Z and Z.L. All authors reviewed and commented on the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

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