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ABSTRACT

We performed *in situ* x-ray diffraction (XRD) experiments on an inorganic–organic hybrid perovskite, CH₃NH₃PbI₃ (MAPbI₃), during its interaction with moisture to understand the degradation mechanism. Although the degradation of inorganic–organic hybrid perovskite is an important factor hampering their development as solar cell materials, understanding of the degradation process is currently limited. The moisture-induced degradation mechanism was revealed by the temperature dependence of the *in situ* XRD pattern sequences and first-principles calculations based on the nudged elastic band method. The combination of experimental and computational data suggests that the MAPbI₃ crystal spontaneously changes into the MAPbI₃ mono-hydrate crystal once water molecules activated with an energy of more than ~0.6 eV penetrate the (100) outer surface of the MAPbI₃ lattice. These findings have important implications for the development of more robust inorganic–organic hybrid perovskites as light absorbing layers in solar cells and other applications.

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Intensive effort has been directed at the application of inorganic–organic hybrid perovskite materials as light-absorbing layers in solar cells because of their utility in fabricating inexpensive and flexible devices as well as their extremely high power-conversion efficiencies. Studies on inorganic–organic hybrid perovskite materials in this field have been reported after an inorganic–organic hybrid perovskite material was applied as a light-absorbing layer of a solar cell in 2009.¹ Since then, power-conversion^{2–7} efficiencies for these materials have increased up to more than 25%,⁸ making them competitive with inorganic solar cells in terms of power-conversion efficiencies. Notably, these promising inorganic–organic hybrid perovskite materials are highly sensitive to moisture.^{9–21} However, understanding the degradation mechanism of inorganic–organic hybrid perovskite materials has proven to be challenging. In this study, we report *in situ* x-ray diffraction (XRD) measurements and first-principles calculations for the most representative among the class of inorganic–organic hybrid perovskite materials, CH₃NH₃PbI₃ (MAPbI₃), during its interaction with moisture. Comparing the temperature dependence of the *in situ*

XRD measurements with the theoretical calculation results allows us to gain an understanding of its degradation mechanism. Previously, we reported the degradation processes of MAPbI₃ using *in situ* XRD measurements.²² We have revealed the number of collisions required between the MAPbI₃ lattice and water molecules to induce the degradation reaction. In the present study, we determined the activation energy of the degradation process of MAPbI₃ caused by interaction with water molecules from the temperature dependence of the *in situ* XRD measurements. Further, we clarify the degradation mechanism using a combination of experimental and theoretical methods.

The degradation of MAPbI₃ is known to proceed via the following chemical reactions:^{23–27}

The chemical reactions in Eqs. (1) and (2) are reversible processes, and that in Eq. (3) is irreversible. The direct degradation of MAPbI₃ into PbI₂ can also occur via a catalytic reaction with water molecules.²⁸ The rate constants for each of the chemical reactions can be expressed as follows:

$$N_1 = N_0 \exp\left(-\frac{t}{\tau_1}\right), \quad (4)$$

$$N_2 = N_0 \left[-\frac{\tau_2}{\tau_2 - \tau_1} \exp\left(-\frac{t}{\tau_1}\right) + \frac{\tau_2}{\tau_2 - \tau_1} \exp\left(-\frac{t}{\tau_2}\right) \right], \quad (5)$$

$$N_3 = \frac{1}{4} N_0 \left[\frac{\tau_1}{\tau_2 - \tau_1} \exp\left(-\frac{t}{\tau_1}\right) - \frac{\tau_2}{\tau_2 - \tau_1} \exp\left(-\frac{t}{\tau_2}\right) + 1 \right] (\tau_3 \approx +\infty), \quad (6)$$

$$N_4 = 3N_3 (\tau_3 \approx +\infty), \quad (7)$$

where t is the time and N_1 , N_2 , N_3 , and N_4 are the numbers of MAPbI₃, MAPbI₃ mono-hydrate, MAPbI₃ di-hydrate, and PbI₂ molecules, respectively. The time constants, τ_1 , τ_2 , and τ_3 , correspond to the chemical reactions in Eqs. (1), (2), and (3), respectively. As we did not observe the chemical reaction in Eq. (3) in this study, we can assume that $\tau_3 \approx +\infty$. The creation of mono-hydrate MAPbI₃ [Eq. (1)] is the most important for the loss of power-conversion efficiency. Our previous study²² reported that the rate constant (τ_1) of the chemical reaction in Eq. (1) was 18 min at a temperature of 26 °C and that multiple collisions ($1/\eta = 1.8 \times 10^9$, where η is the collision yield) between the water molecules and crystalline MAPbI₃ are required to degrade the material. The collision yield (η) was calculated from the collision frequency, molecules per unit area of a wall ($F = 3.6 \times 10^{23}$ molecules cm⁻² s⁻¹), the degradation rate constant of the surface (τ_{surface}), and the number of molecules per unit area ($N = 2.4 \times 10^{14}$ molecules cm⁻²) using the following equation:

$$F\tau_{\text{surface}}\eta = N, \quad (8)$$

where τ_{surface} was calculated from the rate constant τ_1 using the following expression:

$$\exp\left(-\frac{\tau_{\text{surface}}}{\tau_1}\right) = \frac{l}{d}, \quad (9)$$

where d and l are the sample thickness and surface layer thickness ($l = 0.6$ nm), respectively, of MAPbI₃.

We equipped the chamber with a heater and a thermocouple for *in situ* XRD measurements to investigate the temperature dependence of the XRD patterns. The experimental details are described in the [supplementary material](#) (methods and supplementary Fig. 1). Briefly, a vacuum-compatible chamber for *in situ* XRD was placed at the sample position of an x-ray diffractometer (SmartLab, Rigaku). Cu K_α x-rays were diffracted out-of-plane at the MAPbI₃ thin film sample. MAPbI₃ thin films were fabricated via a two-step deposition method in an Ar atmosphere with residual water vapor (<10 ppm).^{29–31} A solution of PbI₂ (1.0 mol L⁻¹ in *N,N*-dimethylformamide) was spin-coated along with a solution of MAI (0.24 mol L⁻¹ in isopropyl alcohol) onto a glass substrate (1.8 × 1.8 cm²) at a rotation rate of 2000 rpm. All the chemicals were purchased from Tokyo Chemical Industry Co. Ltd. The sample films were annealed on a hot plate at a temperature of 100 °C to remove residual solvent. The sample thickness (d) was measured to be 580 nm (supplementary Fig. 2). We placed the sample film inside the

vacuum-compatible chamber, introduced 40 mg of liquid water into the chamber, and evacuated the chamber with a rotary pump to fill the chamber with water vapor. The temperature of the vacuum chamber was controlled using the heater and thermocouple during the experiments. *In situ* XRD patterns were obtained from the sample substrate as it interacted with the water vapor.

Figure 1(a) shows the XRD patterns of the sample film without interaction with water molecules and after interaction with water molecules (at 5, 25, and 90 min) at a temperature of 30 °C. The time evolution of the XRD patterns is presented in more detail (over a range of 5–300 min) in supplementary Figs. 3 and 4. Peaks that can be assigned to MAPbI₃, MAPbI₃ mono-hydrate, MAPbI₃ di-hydrate, and PbI₂ crystals are apparent [Fig. 1(b)].^{32–36} The MAPbI₃ crystals in the sample film before its interaction with moisture are highly oriented to the (110) plane. The time dependencies of the XRD peak intensities corresponding to the (110) plane of MAPbI₃, the (100) plane of MAPbI₃ mono-hydrate, the (011) plane of MAPbI₃ di-hydrate, and the (001) plane of PbI₂ are shown in Fig. 1(c). Simulated XRD patterns were calculated using the kinematic theory-based software packages, CrystalMaker[®] and CrystalDiffract[®]. The MAPbI₃ (110) plane peak intensity exponentially decreases, due to the chemical reaction in Eq. (1), and the rate constant (τ_1) of the same reaction is calculated to be 13 min at a temperature of 30 °C, i.e., faster than the value (18 min) at 26 °C. The number of collisions ($1/\eta$) between water molecules and the MAPbI₃ sample, which induce the degradation [Eq. (1)] at 30 °C, is calculated to be 1.3×10^9 using Eqs. (8) and (9).

In this study, we assume that the reaction between the crystalline MAPbI₃ sample and H₂O molecules, i.e., the degradation induced by moisture [Eq. (1)], occurs when water molecules with energies higher than the reaction threshold energy (E_{th}) collide with the MAPbI₃ crystal. The energies of molecules in the gas phase follow a Maxwell-Boltzmann distribution, and hence, the proportion of higher-energy water molecules is greater at higher temperatures. The Maxwell-Boltzmann distributions $f(E)$ of water molecules at temperatures of 26 and 30 °C are shown in Fig. 2. The reaction threshold required to induce the degradation is obtained from the collision yield required to induce the degradation and the energy distribution, according to

$$\eta(T) = \frac{\int_{E_{\text{th}}}^{\infty} f(E) dE}{\int_0^{\infty} f(E) dE}, \quad (10)$$

where the collision yield (η) is a function of temperature (T). As determined according to the above discussion, the collision yields at 26 and 30 °C are 5.6×10^{-10} and 7.7×10^{-10} , respectively. According to the Maxwell-Boltzmann distribution and Eq. (10), the reaction threshold (E_{th}) at a temperature of 30 °C is 0.63 eV, which corresponds to the experimentally obtained value at a temperature of 26 °C. The rate constant (τ_1) as a function of temperature (T) can be simplified using Eqs. (8), (9), and (10) to

$$\tau_1(T) = \frac{N}{F\eta(T)\ln\left(\frac{d}{l}\right)}. \quad (11)$$

The collision frequency (F) is a function of temperature. However, the effects of temperature are negligible in the range of 23–35 °C, and

FIG. 1. (a) XRD patterns of the prepared MAPbI₃ sample before and during its interaction with water molecules alongside (b) the calculated XRD patterns of MAPbI₃ and MAPbI₃ mono-hydrate. (c) Time evolution of the XRD intensities of MAPbI₃, MAPbI₃ mono-hydrate, MAPbI₃ di-hydrate, and Pbl₂ during the interaction of the sample with water molecules.

hence, F can be approximated as a constant under these experimental conditions. The normalized XRD intensities of MAPbI₃ at $t = 30$ min within the temperature range of 23–35 °C are shown in Fig. 3. The calculated data shown in Fig. 3 are obtained from Eqs. (10) and (11) and the following equation:

$$I(T) = I_0 \exp\left(-\frac{30 \text{ (min)}}{\tau_1(T)}\right), \quad (12)$$

where $I(T)$ and I_0 are the XRD intensity at $t = 30$ min and the initial XRD intensity, respectively, and the reaction threshold (E_{th}) is fixed at

FIG. 2. Maxwell-Boltzmann distributions of water molecules at 26 and 30 °C. The inset, an enlarged view of the area demarcated by the blue dotted line, shows the energy threshold for the reaction of water molecules colliding with the MAPbI₃ crystal.

0.63 eV. The calculated curve agrees well with the experimental data. Thus, the threshold for the reaction of water molecules with the MAPbI₃ crystal is confirmed to be 0.63 eV at room temperature (23–35 °C). It should be noted that we could not obtain the normalized XRD intensity at a temperature above 35 °C because of the crystallization of MAPbI₃ and MAPbI₃ di-hydrate.

To understand the mechanism of the moisture-induced degradation of MAPbI₃, the process of the insertion of a water molecule within the MAPbI₃ lattice was investigated via first-principles theoretical calculations³⁷ based on density functional theory. We adopted a MAPbI₃ tetragonal slab as a model of the outer surface layers. Using the nudged elastic band method,³⁸ we investigated the water-insertion process on the (100) and (001) surfaces as shown in Figs. 4(a) and 4(b). Figures 4(c) and 4(d) show the insertion barrier potentials of the (001)

FIG. 3. Normalized XRD intensity of MAPbI₃ at $t = 30$ min over the temperature range of 23–35 °C. The red calculated line is obtained using Eqs. (10), (11), and (12).

FIG. 4. [(a) and (b)] Trajectory of water molecules in the MAPbI₃ tetragonal lattice ($2 \times 2 \times 1$ slab) from the (a) (001) and (b) (100) outer surfaces. [(c) and (d)] Barrier energy variation corresponding to the images of the inserted H₂O on the (c) (001) and (d) (100) surfaces. The red solid lines indicate fitted estimates of the energy barrier. In (a) and (b), the numbers (0–5) correspond to the positions of the water molecules in (c) and (d). We define the surface of the MAPbI₃ lattice between positions 2 and 3 for (c) and between positions 1 and 2 for (d).

and (100) surfaces, respectively. The insertion barrier potential of the (100) surface is more than three times lower than that of the (001) surface. The observed exponential and gentle growth in the barrier potentials of the (001) and (100) surfaces, respectively, reflects the accessible area along the water molecule insertion pathway.³⁹ In the case of the (001) surface, the narrow accessible area for water insertion causes strong electrostatic repulsive interaction of the MA and I atoms with the water molecules, leading to an exponential increase in the barrier potential up to approximately 2.72 eV. On the other hand, the wide

accessible area at the (100) surface causes a moderate increase in the barrier potential and enables the water molecules to migrate by a hopping mechanism.⁴⁰ The insertion process on the (100) outer surface layer requires 0.5–0.6 eV to overcome the energy barrier, in agreement with the experimental results. This is because the *c*-axis of the MAPbI₃ tetragonal lattice is longer than the *a*- and *b*-axes, and therefore, the water molecules can easily penetrate the MAPbI₃ tetragonal lattice through the channels on the (100) surface. Once a water molecule penetrates the surface of the MAPbI₃ lattice via the (100) channels, the potential in the crystal becomes flat. We confirmed that there is no potential gradient due to the surface charge of the slabs that could lead to an artifact. The MAPbI₃ crystals are highly oriented in the $\langle 110 \rangle$ direction. As shown in the atomic force microscope (AFM; MultiMode 8, Bruker) image [Fig. 5(a)] and the scanning electron microscopy (SEM; JSM-6060LA, JEOL) image [Fig. 5(b)], the (110) surface of the film is not perfectly flat. The mean roughness was measured to be ~ 30 nm. Moreover, the grain sizes of the MAPbI₃ crystals were estimated to be in the range of 100–200 nm, which is significantly smaller than those previously reported.¹⁵ This suggests that the MAPbI₃ crystals in this study are surrounded by more grain

boundaries. Therefore, the water molecules can easily penetrate the crystals along the grain boundaries and, subsequently, through the (100) plane of the MAPbI₃ surface. Once a water molecule is inserted in the MAPbI₃ tetragonal lattice, electrostatic interaction induces the liquid-like methylammonium units⁴¹ to approach the water molecules. A chemical reaction between the MAPbI₃ crystal and the water molecule then occurs, distorting the framework of the MAPbI₃ tetragonal lattice.

In summary, we have performed *in situ* XRD experiments and first-principles theoretical calculations on an inorganic–organic hybrid perovskite, MAPbI₃, during its reaction with moisture to understand its degradation mechanism. Both the experimental and calculation results indicate that an active water molecule with an energy of more than ~ 0.6 eV penetrates the MAPbI₃ lattice, and subsequently, the chemical reaction of the water molecule inside the MAPbI₃ lattice distorts the lattice framework. In addition, the energy required for an isolated water molecule to penetrate the MAPbI₃ crystal is higher than the activation energy (0.18 eV) for an I[−] ion of the MAPbI₃ crystal to dissolve in condensed water molecules.⁴² This suggests that the reaction between the MAPbI₃ crystal and liquid water starts from a solution of the I[−] ions of the MAPbI₃ crystal in liquid water, whereas the reaction between the MAPbI₃ crystal and water vapor results from the penetration of water molecules into the MAPbI₃ crystal. The insights obtained in this study should prove to be helpful for reinforcing the durability of the light-absorbing layer of solar cells, specifically, with respect to enhancing their moisture resistance, and should lead to further applications of inorganic–organic hybrid perovskite materials.

See the [supplementary material](#) for the experimental details of the *in situ* XRD measurements used to obtain the temperature dependence of the XRD patterns of the MAPbI₃ thin film samples.

AUTHORS' CONTRIBUTIONS

M.H. and M.A.A.A. contributed equally to this work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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FIG. 5. (a) AFM image showing the surface morphology of the MAPbI₃ film and (b) SEM image showing the grain size of the MAPbI₃ crystals.

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