Enhanced Efficiency and Stability of an Aqueous Lead-Nitrate-Based **Organometallic Perovskite Solar Cell**

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Supporting Information

ABSTRACT: We investigate the stability of an active organometallic perovskite layer prepared from a two-step solution procedure, including spin coating of aqueous lead nitrate $(Pb(NO_3)_2)$ as a Pb^{2+} source and sequential dipping into a methylammonium iodide (CH₃NH₃I) solution. The conversion of CH₃NH₃PbI₃ from a uniform Pb(NO₃)₂ layer generates PbI₂free and large-grain perovskite crystallites owing to an intermediate ionexchange reaction step, resulting in improved humidity resistance and, thereby, improved long-term stability with 93% of the initial power conversion efficiency (PCE) after a period of 20 days. The conventional fast-converted PbI₂-dimethylformamide solution system leaves small amounts of intrinsic PbI₂ residue on the resulting perovskite and MAPbI₃ crystallites with uncontrollable sizes. This accelerates the generation of PbI₂ and the decomposition of the perovskite layer, resulting in poor stability with less than 60% of the initial PCE after a period of 20 days.

KEYWORDS: perovskite, lead nitrate, stability, aqueous, solar cell

1. INTRODUCTION

Solar cells based on the organometallic perovskite family with an ABX₃ form (A = CH₃NH₃⁺; B = Pb²⁺; and X = Cl⁻, l⁻, and/ or Br⁻) have attracted considerable attention in recent years, owing to their high absorption ability and long-range electronhole diffusion lengths of at least 100 nm.¹⁻¹⁰ Since the publication of groundbreaking work by Miyasaka et al. in 2009,⁸ numerous efforts at improving active perovskite layers have been attempted using new chemical compositions and fabrication processes that are strongly related to the power conversion efficiency (PCE) of devices. In addition to PCE, stability is a key characteristic in this field but is currently little investigated. Perovskites are highly unstable against moisture; therefore, protection against moisture is of importance to improve their long-term stability. In general, a hole-transporting layer covers the active perovskite layer. 2,2',7,7'-Tetrakis(N,Ndi-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeO-TAD), the most conventional hole-transporting material (HTM), exhibits low hole mobility ($\sim 10^{-5}$ cm² V⁻¹ s⁻¹) in its pristine form and thus requires dopants such as tertbutylpyridine(*t*BP) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) to increase its hole mobility (~10⁻³ cm² V⁻¹ s^{-1}). Li-TFSI can absorb moisture, and this is considered one possible cause of perovskite degradation. The stability of the perovskite layer can be improved by either protecting against moisture with HTL or increasing the intrinsic stability of perovskites. We recently reported a method to improve



moisture resistance using donor-acceptor (D-A) conducting polymers, which are more hydrophobic than the conventional spiro-MeOTAD and exhibit better moisture resistance, resulting in improved long-term stability. We also developed a polymer with a high hole mobility of up to $\sim 3 \times 10^{-3}$ cm² V^{-1} s⁻¹ in the absence of *t*BP and Li-TFSI, maintaining an initial efficiency of over 1400 h at 75% humidity.¹¹ Few studies to improve the intrinsic stability of perovskites have been carried out.12-15

Herein, we investigate the degradation process of perovskites prepared by a sequential two-step fabrication method, focusing on CH₃NH₃PbI₃ (MAPbI₃) as a light absorber. During the sequential two-step fabrication method, a predeposited PbI₂ film is quickly converted to MAPbI3 by dipping it in an CH₃NH₃I (MAI) solution. It is therefore possible that unreacted PbI₂ could remain on the resulting MAPbI₃ film. This could play an important role in the stability of photovoltaic devices. Recently, Miyasaka et al. reported a two-step solution-processed PbI2-free MAPbI3 perovskite solar cell with a PCE value of 12.6%. They used an eco-friendly aqueous lead nitrate $(Pb(NO_3)_2)$ solution as a Pb^{2+} source in place of a conventional PbI₂-dimethylformamide (DMF) solution.¹⁶ Here, we compare the degradation processes of

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Figure 1. Structural schemes and optical views of (a) mp-TiO₂, (b) $Pb(NO_3)_2$ and PbI_2 , and (c) MAPbI₃ layers sequentially stacked on an FTOcoated glass substrate.



Figure 2. (a, b) UV-vis absorption spectra and (c) variations in the absorbance at 720 nm of MAI-treated $Pb(NO_3)_2$ and PbI_2 films on TiO₂ layers as a function of t_{DIP} .

the perovskites, *N*-MAPbI₃ and *I*-MAPbI₃, as prepared from aqueous $Pb(NO_3)_2$ and the conventional DMF-based PbI₂, to determine the remaining $Pb(NO_3)_2$ and PbI₂, respectively. The decomposition rate of *I*-MAPbI₃, judged from the generation of PbI₂, was rapid at the initial stage (within 5 days); however, the $Pb(NO_3)_2$ residues in the *N*-MAPbI₃ slowed this accelerated decomposition as the $Pb(NO_3)_2$ residue acted as a water scavenger. These results provide important progress toward understanding the role of PbI₂-free solution processing in the realization of low-cost, eco-friendly, and highly efficient perovskite solar cells.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Sample Preparation. MAI was synthesized by stirring a mixture solution containing 27.86 mL of methylamine (40 wt % solution dissolved in methanol (Junsei Chemical Co.)) and 30 mL of an aqueous hydroiodic acid (57 wt %, Aldrich) in a round-bottomed flask at 0 $^{\circ}$ C for 2 h. The solvents were removed by rotary evaporation, and the precipitant was sequentially washed with diethyl ether, recrystallized, and dried at 60 $^{\circ}$ C in a vacuum oven overnight.

To fabricate a perovskite-based solar cell, first, a fluorine-doped tin oxide (FTO)-coated glass substrate was etched with zinc powder (Aldrich) and 2 M hydrochloric acid (HCl, Aldrich). The substrate was subsequently washed with a detergent, deionized water, acetone, and IPA (Aldrich). The cleaned FTO-coated glass substrate was UV- O₃-treated for 15 min, and a titanium dioxide (TiO₂) compact layer was coated on the substrate, as reported elsewhere.^{11,17–21} The TiO₂ layer was sintered at 500 °C for 30 min to induce a mesoporous (mp) structure with percolated nanoparticles.

A Pb(NO₃)₂ layer was spun-cast onto an mp-TiO₂ scaffold/FTO glass substrate from a solution of 460 mg Pb(NO₃)₂ (Aldrich) in 1 mL of H₂O at a speed of 4000 rpm for 30 s and was then thermally treated at 100 °C for 30 min. In addition, a PbI₂ (Aldrich) layer was spun-cast on the mp-TiO₂ scaffold/FTO glass substrate, as previously reported elsewhere.² Each Pb(NO₃)₂ and PbI₂ film was dipped into a solution of 10 mg of MAI in 1 mL of IPA for 10 and 1 min, respectively, and then rinsed with an excess of IPA. The responding perovskite, *N*-, and *I*-MAPbI₃ films were further annealed at 100 °C for 10 min. An HTM was spun-cast onto the perovskite layers from a mixed solution containing 83.32 mg of spiro-MeOTAD in 869.4 μ L of chlorobenzene (CB), 50 μ L of Li-TFSI in acetonitrile (0.18 M), and 80.6 μ L of tBP (1 mL in 9 mL of CB).²² Finally, solar cells were fabricated by depositing silver (Ag) electrodes (area of 0.09 cm², thickness of 100 nm) at a pressure of less than 10⁻⁶ Torr.

2.2. Characterization. Current–voltage (I-V) curves of all solar cells without encapsulation were measured using a Keithley 2400 source meter with an AM1.5G solar photon flux generated by a solar simulator (1 kW Xe lamp with an optical filter, Oriel 69920), to characterize the open-circuit voltage (V_{oc}) , short-circuit current (J_{sc}) , fill factor (FF), and PCE. UV–vis absorption (Optizen POP spectrophotometer) was conducted on the *N*- and *I*-MAPbI₃ films.



Figure 3. 1D XRD profiles of (a) bare, Pb(NO₃)₂, and PbI₂, (b) N-MAPbI₃ and *I*-MAPbI₃ films on mp-TiO₂/FTO-coated glass substrates (the inset presents the scheme of an MAPbI₃ lattice with a tetragonal geometry: a = 8.855 Å and c = 12.66 Å).

X-ray diffraction (XRD; Rigaku D/Max-2200/PC) was also conducted to characterize the crystal phases and their transitions in films exposed to dry air with a relative humidity (RH) of 20%. Film morphologies were characterized by scanning electron microscopy (SEM; Hitachi, S 4800) and atomic force microscopy (AFM, Bruker, Multimode 8).

3. RESULTS AND DISCUSSION

Figure 1 illustrates the structural geometries of MAPbI₃ films fabricated on a mp-TiO₂ layer with discernible features,^{23,24} as well as optical views of each sample, including sequentially deposited TiO₂, Pb(NO₃)₂ or PbI₂, and the resulting MAPbI₃ layers. As shown in Figure 1b, the PbI₂ and Pb(NO₃)₂ layers spun-cast on the transparent TiO₂ surfaces appear yellow and colorless, respectively. Perovskite crystallites were developed by reacting various Pb sources predeposited with MAI dissolved in IPA. The conversion kinetics of Pb(NO₃)₂ to *N*-MAPbI₃ were expected to be significantly slower than those of the conventional direct method from PbI₂ to *I*-MAPbI₃, because Pb(NO₃)₂ contained an intermediate ion-exchange reaction, as follows¹⁶

$$Pb(NO_3)_2 + 2CH_3NH_3I \rightarrow PbI_2 + 2CH_3NH_3(NO_3)$$
(1)

$$PbI_2 + CH_3NH_3I \rightarrow CH_3NH_3PbI_3$$
(2)

As expected, the PbI₂ layer was rapidly converted to I-MAPbI₃ within 1 min after being dipped in the MAI solution, whereas the Pb(NO₃)₂-based system, *N*-MAPbI₃, developed more slowly. After completing these reactions, both the *N*- and *I*-MAPbI₃ samples appear dark brown in color (Figures 1c and S1).

We monitored the dynamics of the formation of the perovskite using optical absorption. The lead sources, Pb- $(NO_3)_2$ and PbI₂ films, were dipped into 1 wt % MAI-IPA solution for various dipping times (t_{DIP}) . Figure 2 presents the UV-vis absorption spectra of the t_{DIP} -solution-treated samples and the variations in light absorbance at $\lambda = 720$ nm with an increase in t_{DIP} , indicating an increase in the MAPbI₃ domains in the films. The complete conversion of Pb(NO₃)₂ to *N*-MAPbI₃ took approximately 600 s (10 min), significantly longer than the PbI₂-based *I*-MAPbI₃ system (within 60 s). The results agree with the perovskite work recently reported by Miyasaka.¹⁶

The crystalline structures of the perovskite films were investigated using XRD analysis. Figure 3 presents typical

one-dimensional (1D) XRD profiles of Pb(NO₃)₂, PbI₂, *N*-MAPbI₃, and *I*-MAPbI₃ films on mp-TiO₂ scaffold/FTO-coated glass substrates. As background scattering, the XRD profile of an mp-TiO₂ scaffold/FTO/glass substrate showed intense peaks for the FTO crystal phase (**#** marked peaks in Figure 3a).²¹ On the mp-TiO₂ scaffold, a Pb(NO₃)₂ film spun-cast from aqueous solution formed a crystalline phase, as determined by intense X-ray reflections at $2\theta = 19.74$, 22.78, and 32.36° (***** marked peaks in Figure 3a). In contrast, the PbI₂ film as another lead source showed intense X-ray reflection at $2\theta = 12.65^{\circ}$ (**♦** marked peak in Figure 3a); specifically, the peak integral at $\theta = 12.65^{\circ}$ for the (001) crystal plane of PbI₂ (with a hexagonal 2H polytype unit cell)²¹ was used as the criterion for the vol % of PbI₂ in the *I*-MAPbI₃ perovskite films.

The 1D XRD profiles of MAPbI₃ crystallites on mp-TiO₂ scaffolds show intense reflections at $2\theta = 14.2$, 28.46, and 31.88° for the (110), (220), and (312) crystal planes, respectively, of a tetragonal perovskite with lattice parameters: a = 8.855 Å and c = 12.66 Å (inset in Figure 3b).^{2,8} Note the obvious differences in X-ray reflections between the as-prepared *N*- and *I*-MAPbI₃ films, originating from Pb²⁺ sources, that is, the aqueous Pb(NO₃)₂ and PbI₂-DMF solutions. As shown in Figure 3b, the as-prepared *I*-MAPbI₃ film clearly shows X-ray reflection at $2\theta = 12.65^{\circ}$ (\blacklozenge marked peak), indicating a PbI₂ residue, whereas the as-prepared *N*-MAPbI₃ shows incomplete conversion of Pb(NO₃)₂ to MAPbI₃, as determined by the reflection at $2\theta = 19.74^{\circ}$ (* marked peak).⁶

To monitor the dynamics of perovskite formation from $Pb(NO_3)_2$ as a lead source, XRD was also conducted on various t_{DIP} -treated Pb(NO₃)₂ films (Figure S2 in the Supporting Information). At $t_{\text{DIP}} = 1$ min, the initial X-ray reflections of $Pb(NO_3)_2$ crystallites disappeared completely, whereas new reflections were indicated as primarily PbI₂ and tiny perovskite phases. As t_{DIP} increased, it was found that the vol % of perovskite in the MAI-treated films increased, whereas that of PbI₂ decreased. At $t_{\text{DIP}} = 15 \text{ min}$, X-ray reflections related to the PbI_2 crystallites disappeared completely. Note that above $t_{DIP} =$ 15 min, the dissolution of perovskite was obvious even to the naked eye, whereas the X-ray reflections of N-perovskite increased monotonically with an increase in t_{DIP} . The result is mainly related to the dissolution-recrystallization mechanism, which can form larger perovskite crystals at the later conversion stage.²⁵



Figure 4. 1D XRD profiles of (a) N-MAPbI₃ and (b) I-MAPbI₃ perovskites measured after storing the films under 20% RH air as a function of time. (c) Variations in the portion of PbI₂ in the perovskite films exposed to air.



Figure 5. AFM topographies of (a) mp-TiO₂, (b) Pb(NO₃)₂, (c) PbI₂, (d) N-MAPbI₃, (e) I-MAPbI₃, and (f) HTM layers sequentially stacked on the previously deposited layers.

It is generally accepted that most organometallic perovskites decompose into HI, CH₃NH₂, and PbI₂ in the presence of moisture (H_2O) or oxygen (O_2) as catalysts.^{26,27} If perovskite (MAPbI₃) is exposed to moisture and oxygen, it reverts its crystal structure to an intermediate hydrate, which accelerates degradation.²⁸⁻³⁰ Christians et al. report that H₂O-exposed MAPbI₃ forms an intermediate hydrate, (CH₃NH₃)₄PbI₆. 2H₂O, before reverting to PbI₂.³⁰ To verify the environmental stability of N- and I-MAPbI₃ formed by two different methods, the as-prepared samples were stored without encapsulation in a 20% RH air condition and were monitored using X-ray analysis (Figure 4). Interestingly, the 1D XRD profiles of N-MAPbI₃ stored in 20% RH air supported the slow decomposition of perovskite, as determined by the presence of PbI₂ at $2\theta = 12.7^{\circ}$ (Figure 4a), in comparison to the *I*-MAPbI₃ system exposed to the same conditions (Figure 4b). Note that the vol % (ϕ_{PbL}) values of PbI₂ in the air-exposed samples were calculated from the integration of typical X-ray reflections of PbI₂ and MAPbI₃ at 2θ = 12.65 and 14.2°, respectively: $\phi_{\rm PbI_2}$ = $I_{\rm PbI_2}/(I_{\rm PbI_2}$ + I_{MAPbI_3}), where I_{PbI_2} and I_{MAPbI_3} are the integral intensities of Xray reflections at $2\theta = 12.65$ and 14.2° , respectively.

On the basis of the XRD results, it was found that the decomposition of MAPbI₃ to PbI_2 was discernible in these

perovskite films. As shown in Figure 4c, the as-prepared I-MAPbI₃ film already contains a high PbI₂ content, greater than 6.7%. The vol % of PbI₂ increased steeply to 41% in 5 days, then gradually continued to increase to 49% in 20 days. In contrast, the as-spun N-MAPbI₃ layer did not indicate the presence of PbI₂ in the XRD profile after storage in 20% RH air, and the vol % of PbI₂ in the 3 day exposed films was lower than 3% but steadily increased up to ca. 18% for the 20 day exposed sample. To explain the difference between the PbI₂ and $Pb(NO_3)_2$ residues in the perovskites and to understand their roles in interacting with water, we consider the solubility of the PbI_2 and $Pb(NO_3)_2$ residues and the perovskites in water. PbI_2 is only soluble in hot water, whereas $Pb(NO_3)_2$ is highly soluble even in cold water and more easily dissolved in water than perovskites. Therefore, water may react first with the $Pb(NO_3)_2$ residues in the perovskites and then with the PbI_2 residues in the perovskites. This result suggests that the Pb(NO₃)₂ residues in the N-MAPbI₃ retarded the accelerated decomposition, because the $Pb(NO_3)_2$ residue acts as a water scavenger, resulting in enhanced environmental stability in the perovskite crystallites. Interestingly, the peak intensities of $Pb(NO_3)_2$ crystallites in the 20% RH air-exposed N-MAPbI₃ films decreased monotonically with an increase in air-exposure time, resulting from the dissolution of $Pb(NO_3)_2$ via absorbed

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Figure 6. (a) Current density–voltage (J-V) curves of N-MAPbI₃- and *I*-MAPbI₃-based solar cells operated under 1 Sun illumination. (b) Normalized PCE values of the corresponding solar cells before and after storage in a dark chamber with 20% RH for various lengths of time.

 H_2O . Because the decomposition may begin at the outer shell of the MAPbI₃ crystallites directly exposed to H_2O , it can be speculated that the grain size and packing of MAPbI₃ considerably affects the decomposition of the perovskite to PbI₂.

The morphologies of the perovskite layers developed from various Pb sources were investigated using AFM. Figure 5 presents typical AFM topologies of each layer developed on FTO-coated glass substrates. The AFM topography of an mp-TiO₂ layer with a thickness of approximately 250 nm is shown, where 20-30 nm sized nanoparticles were percolated on an FTO-coated glass substrate (the inset in Figure 5a). Unlike the $Pb(NO_3)_2$ layer presenting percolated nanoparticles with a size of 20 \pm 10 nm (Figure 5b), 200–250 nm sized PbI₂ crystallites were observed on the mp-TiO₂ scaffold from the PbI₂-DMF solution (Figure 5c), owing to the solution-induced crystallization because of its limited solubility in DMF.³¹ As shown in Figure 5d,e, the different conversion kinetics of perovskite formation from the $Pb(NO_3)_2$ and PbI_2 layers yielded distinct crystallites. In comparison to the size of the I-MAPbI₃ grains (100-300 nm), the N-MAPbI₃ system exhibits the topmost crystallites with a laterally larger size ranging from 200 nm to 1.5 μ m. The transformation of the MAI-contacted Pb(NO₃)₂ layer into MAPbI₃ crystallites was slowed by passage through the intermediate state related to the ion-exchange reaction (see eq 1). The crystal growth of N-MAPbI₃ from the relatively lesspopular nucleation sites yielded larger crystallites; however, it is known that the confined structure of the mp-TiO₂ scaffold forces the embedded perovskite to adopt a nanostructure.^{3,32} In addition, the AFM topologies (Figure 5d,e) limitedly provide the topmost crystallites, instead of MAPbI₃ domains near and inside the mp-TiO₂ scaffold. As shown in Figure 5f, a spun-cast spiro-OMeTAD layer as an HTM completely covers the perovskite crystallites, and the Ag electrodes were deposited to fabricate perovskite solar cells. The resulting solar cells had a well-known geometry including stacked glass/FTO/TiO₂/mp-TiO2/perovskite/HTM/Ag layers,^{20,34-50} as also determined by cross-sectional SEM (Figure S3).

It is known that the crystalline structures of organometallic perovskites determine the optoelectronic properties of the corresponding solar cells.^{9,25,51–56} Figure 6a represents typical current density–voltage (J-V) curves of the MAPbI₃ solar cells measured with the AM1.5G solar photon flux, and the PV parameters are summarized in Table 1. The PCE values of *N*-MAPbI₃ solar cells are 12.6 and 13.7% for a forward and backward measurement, respectively, whereas the *I*-MAPbI₃ system exhibits lower PEC values of 10.1 and 11.6%. The devices using *N*-MAPbI₃ show better PV performance than the

Table 1. Photovoltaic Device Parameters of *N*-MAPbI₃ and *I*-MAPbI₃ Solar Cells Operated under 1 Sun Illumination^{*a*}

device	measuring direction	$\int_{\rm SC} (\rm mA~cm^{-2})$	$V_{\rm OC}$ (V)	FF	PCE (%)
N-MAPbI ₃	forward	21.2	0.90	0.66	12.6
I-MAPbI ₃	backward	21.2	0.90	0.72	13.7
	forward	21.5	0.86	0.55	10.1
	backward	21.5	0.86	0.63	11.6
^{<i>a</i>} Each device	area was 0.09 c	m^2 .			

I-MAPbI₃ system, originating from V_{oc} and FF (Table 1 and Figure S4). It was expected that the formation of the N-MAPbI₃ perovskite layers in a moisture-free environment further enhanced the PCE values. In addition, the forwardbackward operation hysteresis of the N-MAPbI₃ system is relatively smaller than that of the I-MAPbI₃ solar cell. The results are due to the well-dispersed nanocrystal structure of the N-MAPbI₃ perovskite in the mp-TiO₂ scaffold without the initial PbI₂ residue, which significantly affects the optoelectric properties of organometallic perovskite; its conduction band is located at 0.5 eV, a higher level than that of MAPbI₃.^{57–59} The presence of a PbI₂ phase around the MAPbI₃-TiO₂ boundaries acts as a charge injection barrier from the perovskite to ${\rm TiO_{2}}.^{58,60}$ Recently, a dedicated three-step solution method has been applied for the fabrication of PbI2-free MAPbI3 perovskite.⁵⁸ It is worth noting that the PCE value of the *N*-MAPbI₃based solar cells is lower than that of the perovskite solar cells reported recently¹⁶ but higher than that of various PbI₂-free precursor-based perovskite systems.^{2,59} Particularly, it has been shown that the poor reproducibility of PbI2-based perovskite solar cells is a result of the processing-sensitive film formation of PbI₂ crystallites with a low solubility in DMF, leading to irregular film morphologies. In contrast, the N-MAPbI₃ perovskite crystallites converted from the homogeneous $Pb(NO_3)_2$ layer could be effectively reproduced, yielding a narrow deviation in the PCE of the resulting solar cells. Nevertheless, the novel perovskite formation method explained here is relatively eco-friendly and involves an environmentally friendly solvent.

We further monitored the environmental stability of *N*- and *I*-MAPbI₃ solar cells. Figure 6b shows a normalized PCE of these perovskite solar cells with increased air-exposure time. The PCE of the *I*-MAPbI₃ system decreased monotonically in open air, and after 20 days its normalized PCE value was less than 60% that of the fresh device. This phenomenon is attributed to decomposition of perovskite in the presence of light and moisture.⁴ In contrast, the PCE of the *N*-MAPbI₃

system can maintain up to 93% of the PCE value of the fresh device, even after exposure to air for 20 days. The results agree well with the relatively lower PbI_2 content in the air-exposed perovskite films (Figure 4c).

We successfully demonstrate that the PbI₂-replaced fabrication process of MAPbI₃ using an aqueous Pb(NO₃)₂ precursor solution yields excellent environmental stability in the resulting solar cells. We propose that the environmental stability of perovskite crystallites depends on the surface area of the intrinsic forms. The *N*-MAPbI₃ crystallites in our study had larger and better forms when compared to those of *I*-MAPbI₃. As the grain size increases, the optical properties increase due to improved crystal quality.^{61,62} Considering the degradation mechanism by water, the mechanism resembles the enzymatic reactions because water behaves like an enzyme as follows²⁶

$$4CH_{3}NH_{3}PbI_{3} + 4H_{2}O$$

$$\rightarrow 4CH_{3}NH_{3}PbI_{3} \cdot H_{2}O$$

$$\rightarrow 4PbI_{2} + 4CH_{3}NH_{3}I + 4H_{2}O$$
(3)

Accordingly, the degradation kinetics of the system can be explained by the Michaelis–Menten model, where the enzymatic reaction rate in a humid condition, ν , is affected by the surface area as follows²⁶

$$\nu = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{dt}} = \frac{\mathrm{V}_{\mathrm{max}}[\mathrm{S}]}{\mathrm{K}_{\mathrm{M}} + [\mathrm{S}]} \tag{4}$$

where [S] is the concentration of the surface and [P] is the concentration of the product. V_{max} is a constant of the maximum reaction rate, and K_{M} is the Michaelis constant.

In the case of the MAPbI₃ perovskite system exposed to humid air, [S] and [P] represent the concentrations of the MAPbI₃ surface and PbI₂ generated from perovskite, respectively. The degradation rate of MAPbI₃ is converged on the constant value as the perovskite surface area increases. *N*-MAPbI₃ is expected to exhibit a much slower degradation rate than *I*-MAPbI₃ because its grain sizes are much bigger than those of *I*-MAPbI₃, resulting in the improved stability of *N*-MAPbI₃. The relationship between grain size and humidity stability is based on this kinetic reactivity, indicating that *N*-MAPbI₃ perovskite, which used Pb(NO₃)₂ as a basic material, is more stable under ambient conditions than *I*-MAPbI₃ perovskite.

4. CONCLUSIONS

We have developed an eco-friendly approach to the fabrication of hybrid perovskite layers. We determined that the formation of MAPbI₃ from lead nitrate is a slow reaction involving ionexchange steps and that the *N*-MAPbI₃ layers are relatively phase-purer than *I*-MAPbI₃ and are more stable than the latter in an ambient atmosphere. In particular, our method can be applied to form other types of perovskite, such as FAPbI₃, which also exhibits a phase-pure structure and higher stability, highlighting the general applicability of our method. Photovoltaic devices fabricated from *N*-MAPbI₃ show a reasonable PCE of 13.7% even when fabricated in high RH. Efforts to improve the photovoltaic conversion efficiency and stability are underway in our laboratory.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b01864.

XRD patterns of the $Pb(NO_3)_2$ film dipped in 10 mg/mL propanol solution for various time intervals; cross-sectional SEM image of the perovskite solar cell structure (PDF)

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Notes

The authors declare no competing financial interest. The authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

PCE, power conversion efficiency; spiro-MeOTAD, 2,2',7,7'tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene; HTM, hole-transporting material; *tBP*, *tert*-butylpyridine; Li-TFSI, lithium bis(trifluoromethanesulfonyl)imide; *D*-*A*, donor-acceptor; MAPbI₃, CH₃NH₃PbI₃; FTO, fluorinedoped tin oxide; MAI, Pb(NO₃)₂, lead nitrate; IPA, isopropyl alcohol; DMF, dimethylformamide; TiO₂, titanium dioxide; mp, mesoporous; *I*-*V*, current-voltage; *V*_{oc}, open-circuit voltage; *J*_{sc}, short-circuit current; FF, fill factor; XRD, X-ray diffraction; RH, relative humidity; SEM, scanning electron microscopy; AFM, atomic force microscopy; *t*_{DIP}, dipping times; *J*-*V*, density-voltage; *ν*, reaction rate

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