

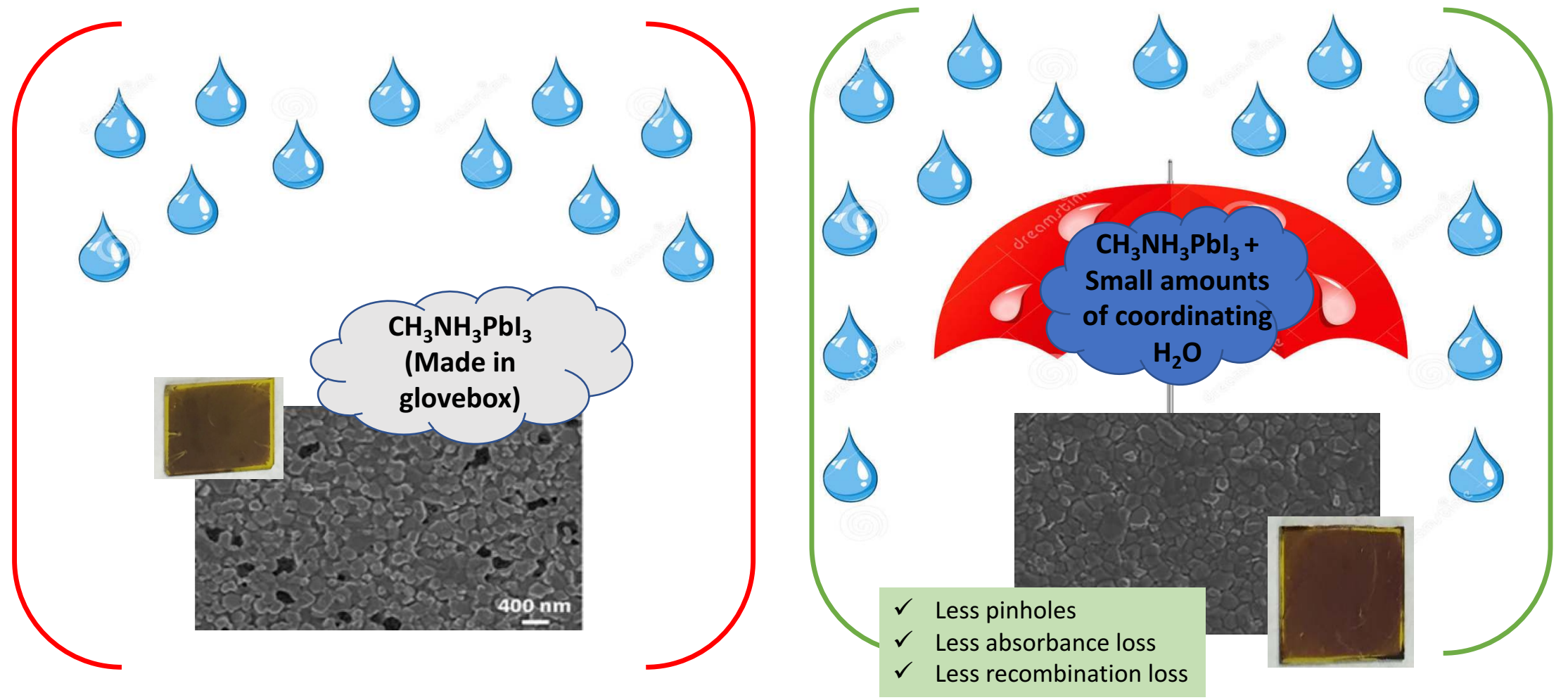
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## Homeopathic Perovskite Solar Cells: Effect of Humidity During Fabrication on the Performance and Stability of the Device

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## Homeopathic perovskite solar cells: Effect of humidity during fabrication on the performance and stability of the device

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**ABSTRACT.** Methylammonium Lead Iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) is the archetypical active component of perovskite solar cells, which stand out due to their impressive photovoltaic performance. A major drawback of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is its rapid degradation in humid environments. In this work, we fabricate  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films and devices by solvent engineering in  $\text{N}_2$  and in ambient conditions with different humidities. Their aging and degradation is monitored by optical absorption and impedance spectroscopy measurements under monochromatic illumination with two different wavelengths. Aged devices show a substantial difference between the recombination rate under red and blue light illumination, attributed to enhancement of local recombination routes upon aging. Interestingly, we observe that devices prepared at higher humidity resist better the aging. We explain this by the presence of coordinating water in the films, as detected by XPS measurements. Hence, small amounts of water in the perovskite structure proves to have a beneficial effect against degradation in humid environments.

## INTRODUCTION

Progress in third generation photovoltaics has experienced a remarkable boost in recent years due to the discovery of the exceptional optoelectronic and photovoltaic properties of halide perovskites. This new kind of photovoltaic materials made it possible to reach certified efficiencies above 22% in just a time span of a few years.<sup>1</sup> Halide perovskites are a family of ionic solids where  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is the most archetypical example, providing a high performance due to a near-optimal light-harvesting direct band gap (close to 1.5 eV) and very low non-radiative recombination rates leading to high open-circuit voltages.<sup>2-5</sup>

Despite these favourable features, it was soon realized that perovskite solar cells (PSC) suffer from serious stability issues. These materials tend to easily degrade in the presence of light, heat, oxygen and/or moisture.<sup>6,7</sup> In this work we focus on moisture-induced aging. The mechanism by which water molecules induce the destruction of the perovskite material is not completely clarified yet but there are indications<sup>8</sup> that it takes place via the formation of an intermediate hydrate



The effect of moisture in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is easily detected by absorbance measurements<sup>9</sup> and even with the naked eye when the brownish perovskite film becomes yellow due to the formation of  $\text{PbI}_2$ .

The critical point of the mechanism for sample degradation is that very few molecules of water are sufficient to trigger the process. As a Lewis base,  $\text{H}_2\text{O}$  can coordinate with the ammonium groups. The hydrates which are formed<sup>8,10</sup> can appear locally and modify the electronic properties of the material, even when no defect can be visually detected.

Very recently<sup>11</sup> we have shown that this donor property of the water molecules with the ammonium groups can be taken advantageously to devise a preparation procedure at ambient conditions with relative humidity (R.H.) up to 60 %. By controlling the proportion of the dimethyl sulfoxide (DMSO) additive with respect to the  $\text{Pb}^{2+}$  as a function of the R.H. of the ambient atmosphere it is possible to fabricate highly homogenous films at ambient conditions and solar cells devices with efficiencies approaching 19%. Using precursors formulations in which the two competing donors DMSO and ambient  $\text{H}_2\text{O}$  are not adequately balanced leads to the formation of chemical defects (plumbates, hydrates) that can act as recombination centers.

Although most previous studies on moisture-induced degradation focused on materials properties and monitored the degradation process via optical and X-ray measurements,<sup>8,9,12</sup> it is known that ambient water produces changes in the electrical properties of the films but few analysis in this line have been reported in the literature. We previously studied the change in the optoelectronic

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3 small-perturbation response of perovskite devices upon aging,<sup>13</sup> showing a change of the  
4 recombination mechanism and slower transport in degraded devices by small perturbation  
5 optoelectronics measurements. This effect is attributed to a global acceleration of recombination  
6 and/or the appearance of additional surface recombination processes.<sup>14,15</sup>  
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9 In this work, we investigate the mechanisms and kinetics of moisture-induced aging and  
10 degradation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells fabricated at ambient conditions where  
11 humidity is perfectly controlled. We found that the fabricated films and devices are quite robust  
12 in the medium term stressed under high R.H. conditions. Furthermore, it is observed that devices  
13 prepared in a more humid environment tend to keep their electric original properties better than  
14 those prepared at lower moisture conditions.  
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## 17 18 **EXPERIMENTAL METHODS**

### 19 20 **Fabrication of perovskite solar cells**

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22 Perovskite solar cells were fabricated on FTO-coated glass (Pilkington–TEC15) patterned by  
23 laser etching. The substrates were cleaned using Hellmanex® solution and rinsed with deionized  
24 water and ethanol. Followed this they were sonicated in 2-propanol and dried by using  
25 compressed air. The  $\text{TiO}_2$  blocking layer was deposited onto the substrates by spray pyrolysis at  
26 450 °C, using a titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma  
27 Aldrich) diluted in ethanol (1:3.5, v/v), with oxygen as carrier gas. The  $\text{TiO}_2$  compact layer was  
28 then kept at 450 °C for 30 min for the formation of anatase phase. Once the samples achieve  
29 room temperature, a  $\text{TiO}_2$  mesoporous layer was deposited by spin coating at 2000 rpm during 10  
30 s using a  $\text{TiO}_2$  paste (Dyesol, 30NRD) diluted in ethanol (1:5, weight ratio). After drying at 100  
31 °C for 10 min, the  $\text{TiO}_2$  mesoporous layer was heated at 500 °C for 30 min and later cooled to  
32 room temperature. Subsequently, a pure methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) solution  
33 were prepared to be deposited by spin coating.  
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39 The perovskite precursor solution is obtained from reacting DMF solutions (50 wt %) containing  
40 MAI and  $\text{PbI}_2$  (1:1 mol %) and MAI,  $\text{PbI}_2$  and DMSO (1:1:1 mol %) and for the different  
41 humidity values of 50%, 40%, 30% and 0% (this latter in glovebox), the molar ratio of DMSO  
42 was changed from 0.75; 1; 1; 1.5, respectively. The perovskite precursor solution (50  $\mu\text{L}$ ) was  
43 spin-coated in a one-step setup at 4000 rpm for 50 s. During this step, DMF is selectively washed  
44 with non-polar diethyl ether just before the white solid begins to crystallize in the substrate.  
45 Afterward the substrate was annealed at 100 °C for 3 min (see Ref.<sup>11</sup> for details)  
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49 For the sake of comparison, reference perovskite films fabricated with a standard recipe<sup>13</sup> inside a  
50 glovebox (0% R.H) were also included in the study: Pure methylammonium lead iodide (1.2 M)  
51 was spin coated in a two steps setup at 1000 and 6000 rpm for 10 and 20s respectively. During  
52 the second step, 110 $\mu\text{L}$  of chlorobenzene was dropped on the spinning substrate 15 seconds  
53 before the end of the spinning program. The samples were then annealed (100°C) for 1h in an  
54 argon filled glove box.  
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3 Spiro-OMeTAD was deposited as hole transporting material (HTM) by dissolving 72.3 mg in 1  
4 mL of chlorobenzene as well as 17.5  $\mu\text{L}$  of a lithium bis (trifluoromethylsulphonyl)imide  
5 (LiTFSI) stock solution (520 mg of LiTFSI in 1mL of acetonitrile), and 28.8  $\mu\text{L}$  of 4-tert-  
6 butylpyridine (TBP). The HTM was spin coated at 4000 rpm for 30 s. Finally, 60 nm of gold was  
7 deposited as a metallic contact by thermal evaporation under a vacuum level between  $1 \cdot 10^{-6}$  and  
8  $1 \cdot 10^{-5}$  torr. All the deposition processes were carried out outside the glovebox under different  
9 humidity conditions. Only for humidity conditions of 0% relative humidity (RH) the devices  
10 were prepared inside an argon glove box under controlled moisture and oxygen conditions ( $\text{H}_2\text{O}$   
11 level: <1 ppm and  $\text{O}_2$  level: <10 ppm).  
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16 Aging was studied by subjecting perovskites solar devices prepared under different moisture  
17 conditions (RH: 0%, 30% 40% and 50%) to ambient air in darkness during 15 days under  
18 environmental moisture conditions with a relative humidity in the range of 30% - 60%. In  
19 addition, perovskite films deposited on the  $\text{TiO}_2$  substrate were subjected to an accelerating  
20 degradation treatment by exposing the film to very humid air (>85%) for a relatively long period  
21 of time.  
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### 24 25 26 **Characterization of films and devices**

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28 Current density-voltage (J-V) curves were measured under a solar simulator (ABET-Sun2000)  
29 with an AM 1.5G filter. The light intensity was calibrated at  $100 \text{ mWcm}^{-2}$  using a reference  
30 mono-crystalline silicon solar cell with temperature output (ORIEL, 91150). A metal mask was  
31 used to define an active area of  $0.16 \text{ cm}^2$ . The current-voltage curves were obtained using a scan  
32 rate of 100 mV/s and sweep delay of 20s.  
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36 The illumination for the Impedance Spectroscopy (IS) measurements was provided by a red ( $\lambda =$   
37 635 nm) and blue ( $\lambda = 465 \text{ nm}$ ) LEDs over a wide range of DC light intensities. This allows for  
38 probing the devices with two distinct optical penetrations.<sup>14</sup> A response analyzer module  
39 ((PGSTAT302N/FRA2, Autolab) was utilized to register the impedance spectra. In these  
40 experiments a 20 mV perturbation in the  $10^6$ - $10^2$  Hz range was applied. To avoid voltage drop  
41 due to series resistance, the measurements were performed at the open circuit potential, the Fermi  
42 level (related to the open-circuit voltage) being fixed by the DC (bias) illumination intensity. To  
43 compensate for the different response under blue and red light due to the different optical  
44 absorption all parameters are monitored and plotted as a function of the open-circuit potential  
45 generated by each type of bias light. UV-Visible absorption spectra were recorded by using a  
46 Cary 100 UV-Vis spectrophotometer (Agilent) in the range of 400-850 nm.  
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51 X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical composition and the  
52 presence of water in the samples. The XPS spectra were recorded using a Kratos Axis UltraDLD  
53 spectrometer, with monochromatized Al  $K\alpha$  radiation (1486.6 eV), 20 eV pass energy and an  
54 accuracy of 0.1 eV. Electrostatic charging effects could be stabilized with the help of a specific  
55 device developed by Kratos.  
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## RESULTS AND DISCUSSION

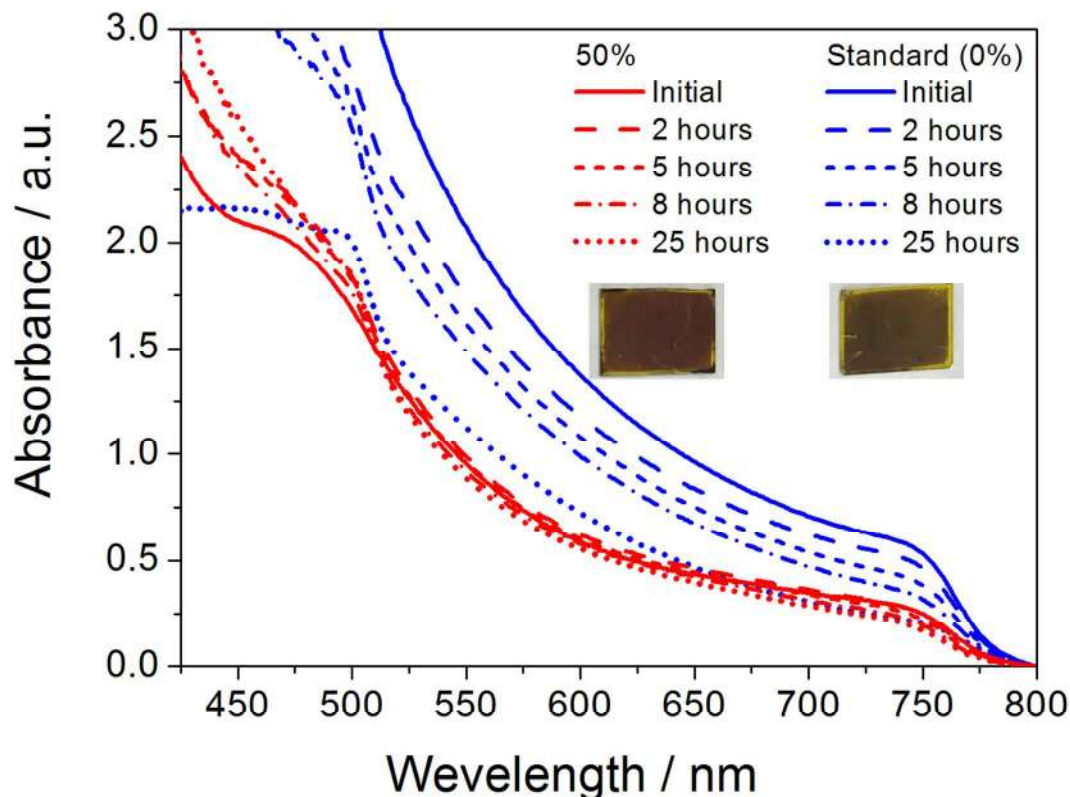
The photovoltaic parameters of fresh and aged devices are compared in Figure S1 and Table 1. Devices are aged by subjecting devices to ambient air at R.H.=30-60% humidity in darkness during 15 days, similar to the ISOS-D1-shelftest protocol where the humidity is controlled.<sup>16</sup> Fresh devices show an almost constant average energy conversion efficiency of around 14% (see Table 1). After aging, this efficiency is reduced by 1% for the devices fabricated in dry conditions. In contrast, the devices made under the highest humidity (50%) get their efficiencies even increased, with recorded values well exceeding 15%. It is observed that the efficiency loss is mainly due to a deterioration of the fill factor of the devices. The efficiency boost is, though, linked to an enhancement of the short-circuit photocurrent. This effect can be related to the increase of the optical absorbance of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  upon accelerated degradation as shown and discussed in the Supporting Information (section S2). The open-circuit potential remains basically unaltered after aging although a slight decrease can be detected.

**Table 1.** Photovoltaic parameters under AM1.5 1 sun illumination of fresh (top) and aged (bottom)  $\text{MAPbI}_3$  solar cells fabricated under humid conditions. Error bars extracted from the statistics extracted from the measurements of 3-5 devices are added to the data.

R.H (%)	$J_{sc}$ ( $\text{A}\cdot\text{cm}^{-2}$ )	$V_{oc}$ (V)	FF (%)	EFF (%)
FRESH				
0	$19.70 \pm 0.88$	$1.05 \pm 0.01$	$69.0 \pm 0.6$	$14.4 \pm 0.7$
30	$21.20 \pm 0.52$	$1.01 \pm 0.02$	$65.3 \pm 1.9$	$14.0 \pm 0.6$
40	$20.63 \pm 1.41$	$1.04 \pm 0.01$	$66.2 \pm 6.5$	$14.2 \pm 0.8$
50	$20.53 \pm 0.35$	$1.04 \pm 0.01$	$66.6 \pm 1.6$	$14.2 \pm 0.3$
AGED				
0	$20.62 \pm 0.18$	$1.04 \pm 0.08$	$61.0 \pm 4.7$	$13.1 \pm 1.3$
30	$22.13 \pm 0.89$	$0.96 \pm 0.02$	$62.0 \pm 3.3$	$13.4 \pm 0.5$
40	$23.36 \pm 0.81$	$0.95 \pm 0.03$	$63.0 \pm 4.0$	$14.1 \pm 1.0$
50	$24.53 \pm 0.52$	$1.01 \pm 0.06$	$62.2 \pm 3.3$	$15.4 \pm 0.5$

In Figure 1 a comparison between the absorbance degradation kinetics of samples prepared under dry and high humidity conditions is depicted when stressed with humid air.<sup>13</sup> The absorption spectrum of a perovskite film prepared under very high humidity conditions (R.H. 50%) remains basically unaltered after being vented in very humid air (>85% R.H.) up to 8 hours. Additional exposure to ambient conditions for 18 additional hours ( $\approx 50\%RH$ ) even led to a slight increase of the absorbance at short wavelengths. This increase in absorbance has been correlated

previously with a decrease of under-coordinated plumbate ions.<sup>17</sup> In contrast, the films prepared in the glovebox showed a dramatic decrease of the absorbance, especially after 25 hours. This result confirms the exceptional stability of the films formed under humid conditions towards moisture-induced degradation.

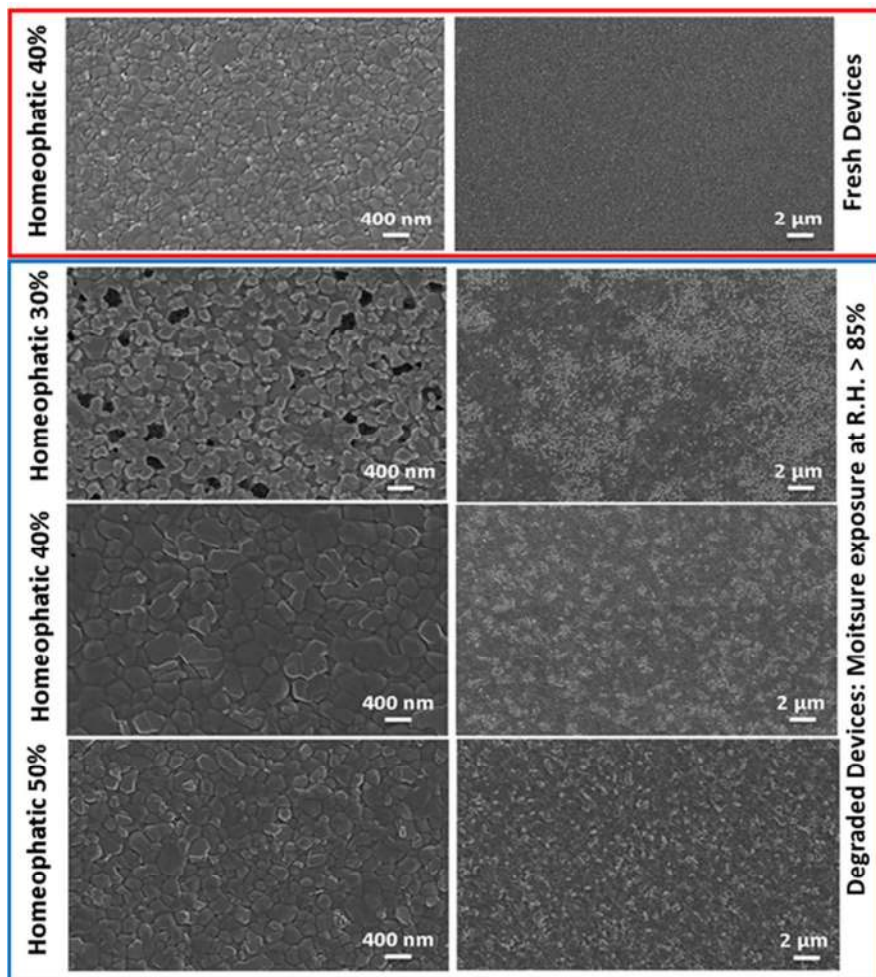


**Figure 1.** Optical absorption data of bare MAPbI<sub>3</sub> films deposited on TiO<sub>2</sub> substrates by solvent-engineering under 50% R.H. (homeopathic) and by reference (standard) recipe at dry conditions.<sup>13</sup> Between 0 and 8 hours the films were subject to a flow of humid air (> 85% RH). Between 8 and 25 hours the films were left exposed to the ambient atmosphere at an approximate 50% R.H. Photographs of the two films after the degradation treatment are also added to the picture. Note that the two recipes do not produce the same film thickness, hence the different initial absorption.

The stability of the perovskite films after moisture exposure can also be studied by SEM images of fresh and degraded films fabricated at three different humidity conditions: 30%, 40% and 50% (Figure 2). The used recipe produces homogeneous films with no pinholes and an approximately constant crystal size of around 200 nm. Degradation upon exposure to humid air (>85% R.H.) show up in the form of inhomogeneities and pinholes. An increase of the grain size is also observed.<sup>18</sup> These features appear to be less important for films fabricated at higher humidity (50% RH) than those made at lower values of humidity (30% R.H.). On the other hand, as mentioned, ambient water promotes increased crystalline domains from about 100 nm for the reference device to up to 500-600 nm. This observation can be explained by the action of ambient



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3 water, which acts an additive that can promote Ostwald ripening effect and increasing the domain  
4 size as recently reported with Guanidinium Thiocyanate.<sup>19</sup>  
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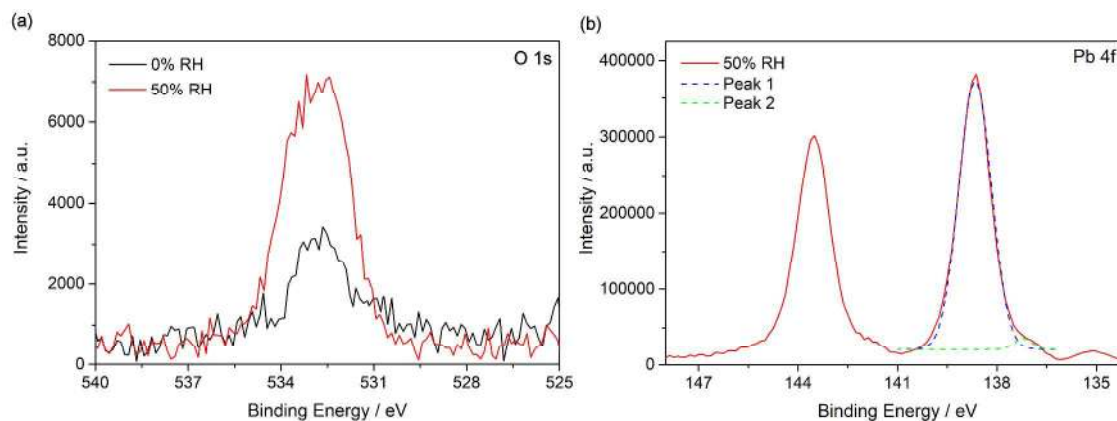


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39 **Figure 2.** SEM images of fresh perovskite films fabricated at R.H.=40% (top) and after degradation  
40 (bottom). Results for degraded films with very humid air (> 85% R.H.) but prepared at different ambient  
41 humidity values are shown.  
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45 The robustness of the films fabricated under ambient conditions suggests that these films retain  
46 some water molecules in the crystalline structure, thus preventing further invasion by moisture.  
47 To test this hypothesis XPS measurements were performed for samples exposed at different  
48 relative humidity, that is 0%, 30%, 40% and 50%. Figure S3 in the Supporting Information shows  
49 the survey spectra for the samples. The peaks are assigned to the elements which composed the  
50 perovskite phase, that is C, N, Pb and I. In turn, no evidence of Ti is observed, which confirms  
51 that only the perovskite layer is analysed. However, a weak O 1s signal, produced by small  
52 amounts of water in the perovskite structure, can be detected. Figures S4 and 3a show the O 1s  
53 signal obtained for the samples. The binding energy (BE) for O 1s signal for the four samples is  
54 about 531.5 eV. As reported previously, the presence of coordinating (hydrating) water appears  
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3 in the range between 531.0 - 531.6 eV.<sup>20</sup> This signal at BE of 531.5 eV cannot be assigned to O<sup>2-</sup>  
4 in the lattice of oxide species as this type of signal is typically observed at BE lower than 530 eV.  
5 For instance, in the case of lead oxides, they appear between 528.4 and 529.4 eV.<sup>21</sup> Other typical  
6 assignment for O 1s signal is to adsorbed species, such as water, hydroxyl groups or carboxylates  
7 species, but these contributions normally show up at BE higher than 532 eV.<sup>22-24</sup> On the other  
8 hand, Figure 3b shows the Pb 4f signal for the sample exposed to 50% RH, which is considered  
9 as representative for all the samples analysed. The peaks for Pb 4f<sub>7/2</sub> and 4f<sub>5/2</sub> appear at 138.4 eV,  
10 and 143.3 eV, respectively. The 4.9 eV separation between this spin-orbit components is typical  
11 for Pb(II).<sup>20</sup> Figure 3b also includes a deconvolution of the Pb 4f<sub>7/2</sub> signal. Two contributions can  
12 be extracted. The main contribution (peak 1) at a BE of 138.4 eV is assigned usually<sup>20</sup> to PbI<sub>2</sub>.  
13 This is the contribution from the Pb-I bonds of the perovskite. The small contribution (peak 2)  
14 appears at about 137.4 eV. The signals around this value of BE for Pb 4f<sub>7/2</sub> are usually ascribed to  
15 species in which Pb-O interactions are present.  
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21 Therefore, for XPS measurements, the presence of coordinating water can be deduced from the  
22 energy position of the O 1s signal and it is confirmed with the analysis of the Pb 4f signal.  
23 Although a signal is observed in the 0% sample (probably due to residual water during sample  
24 manipulation before measurement), it is significantly smaller than the signal obtained for the 50%  
25 film. Nevertheless, due to the low intensity of the signal, the evolution of the water content with  
26 respect to the relative humidity (Figure S4) cannot be safely monitored from these measurements.  
27 In any case, the presence of coordinating water molecules around the Pb cations explain the  
28 molecular stability of the perovskite films towards inclusion of additional water during aging or  
29 degradation experiments.  
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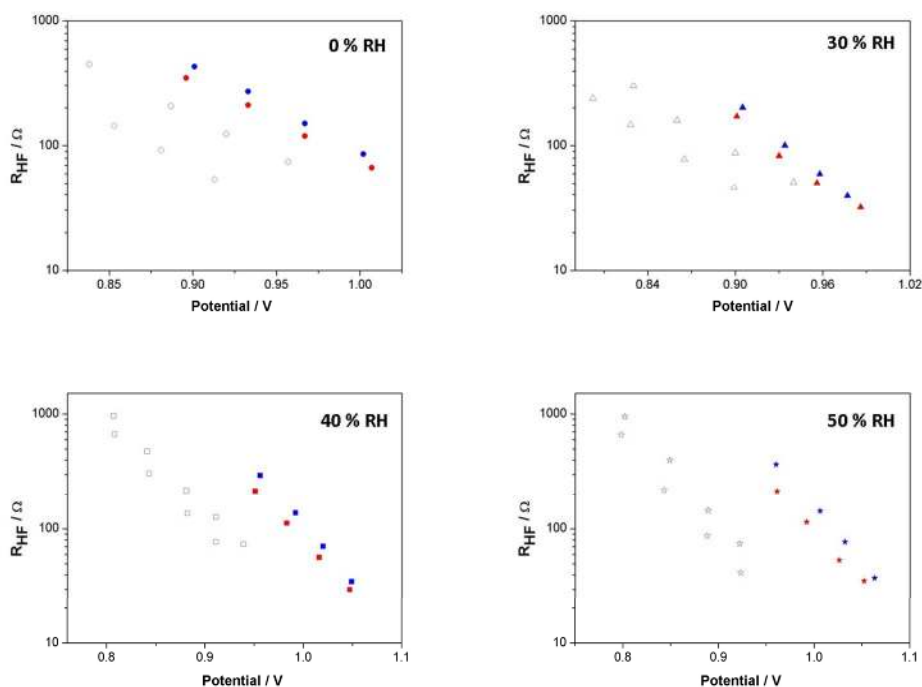


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48 **Figure 3.** O 1s and Pb 4f signals obtained from XPS measurements of perovskite thin films deposited on  
49 top of mesoporous TiO<sub>2</sub> layers fabricated at different ambient humidity values.  
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53 Finally, to verify the change in the internal functioning of the perovskite solar cell upon aging,  
54 impedance spectroscopy (IS) measurements at open circuit were carried out. This technique  
55 allows to discriminate between electronic processes occurring at separated frequencies (defining  
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consequently different characteristic time constants). The IS response of perovskite solar cells is typically characterized by the appearance of two signals, visualized as peaks in the frequency plots (either phase vs. frequency or imaginary impedance vs. frequency) or arcs in the Nyquist plot. Although both signals are found to be coupled<sup>25,26</sup> it is generally accepted that the low frequency (LF) signal is related to ion migration affecting charge accumulation at the contacts<sup>27-29</sup>, whereas the high-frequency (HF) signal is affected by the transport in the selective contacts and interfaces.<sup>27,30</sup> However the assignment of each feature observed by impedance to a single process is not correct as high and low frequency features change mutually and both arcs can be related with recombination<sup>26,31-33</sup>. Consequently the analysis of the evolution of these arcs can be inversely related with the recombination rate. In this work, we focus in the HF region, in the  $10^3$ - $10^6$  range. The measurements were carried out with two excitation wavelengths, characterized by a different penetration of the light into the perovskite layer.<sup>29</sup>

The HF resistance has been extracted from the impedance spectra by fitting the data to a simple Voight circuit, composed of two RC elements in series plus a series resistance term.<sup>34</sup> The corresponding high frequency resistance  $R_{HF}$  is plotted in Figure 4 as a function of the open-circuit potential, originated by the different illumination intensities applied, and the two excitation wavelengths employed in the experiment.



**Figure 4.** High frequency resistance versus open-circuit potential for devices prepared under different humidity conditions, as indicated. Red and blue symbols stand for the data extracted under red and blue light illumination, respectively. Solid symbols correspond to fresh devices and open symbols to aged devices.

$R_{HF}$  is found to vary exponentially with the open circuit potential as predicted by the following equation<sup>14,15</sup>

$$R_{HF} = \left( \frac{\partial J_{rec}}{\partial V} \right)^{-1} = R_{00} \exp \left( \frac{-\beta qV}{k_B T} \right) \quad (1)$$

where  $J_{rec}$  is the recombination current,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $R_{00}$  is the resistance at zero potential and  $\beta$  is the transfer or recombination parameter. We have previously found that this parameter is the inverse of the ideality factor  $m = 1/\beta$  and coincides with that extracted from the slope of the open-circuit potential vs. light intensity plot.<sup>14</sup> In Table 2 ideality factors extracted from the solar cells studied in this work are reported.

**Table 2.** Ideality factors for fresh and degraded cells as extracted from the high frequency resistances in Figure 4

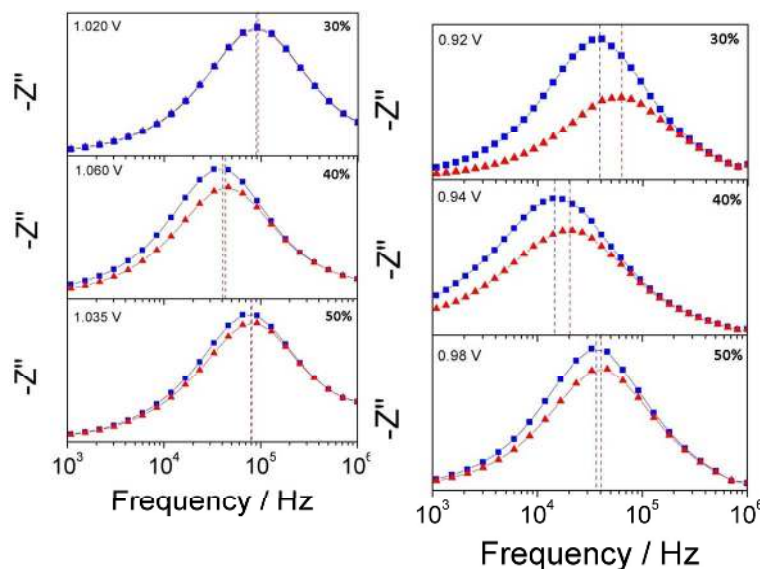
R.H. (%)	Ideality factor			
	Fresh cell		Degraded cell	
	Blue	Red	Blue	Red
0	2.38 ± 0.01	2.44 ± 0.02	2.94 ± 0.08	2.78 ± 0.08
30	1.75 ± 0.01	1.85 ± 0.09	2.44 ± 0.01	2.50 ± 0.06
40	1.69 ± 0.01	1.85 ± 0.01	1.92 ± 0.06	1.96 ± 0.06
50	2.08 ± 0.06	2.08 ± 0.14	1.75 ± 0.05	1.75 ± 0.01

The analysis of the ideality factors reveal that they are approximately the same for both blue and red light illumination, and with values close to 2, which can be attributed to bulk SRH recombination.<sup>14,35–37</sup> However, there is a clear net enhancement in the recombination rate after degradation, as evidenced by the lower values of  $R_{HF}$  in Figure 4. This result is in line with reduction of the open-circuit potential at 1 sun illumination reported in Table 1, and it indicates that the inclusion of ambient water into the perovskite structure introduces recombination centers and additional routes of non-radiative recombination. Furthermore, the degraded devices exhibit a different value of the recombination resistance depending on whether red or blue light is used to generate the open-circuit potential. Red light illumination produces photo-generated carriers further away from the TiO<sub>2</sub>/perovskite interphase in comparison with blue light due to the lower light absorption in the red. Lower values of  $R_{HF}$  are observed under red light illumination in all aged devices. This fact can be interpreted as (1) a magnification of the recombination loss close to the perovskite/hole transport material interface and/or (2) a global acceleration of the bulk recombination rate, leading to shorter diffusion lengths.<sup>14</sup>

An important property also arises from the analysis of the results: those cells which are fabricated at conditions of higher humidity tend to resist better the negative effect of aging. Thus, devices

prepared at 0% and 30% humidity, show a clear splitting of the “red” and “blue” resistances upon degradation. In contrast, cells made at 40% and 50% humidity show less disparity between the two values of  $R_{HF}$ .

Similar conclusions can be extracted from the analysis of the frequency plots (Figure 5). In the studied frequency range, a distinct peak at around  $10^4$ - $10^5$  Hz is detected. Although the inverse of the corresponding frequency signal cannot be considered a real carrier lifetime, its time scale and its behaviour for different architectures and Fermi level positions strongly suggest that it is related with the recombination rate of photogenerated carriers in the device.<sup>31-33</sup> The comparison of the behaviour of this signal for fresh and aged devices reveals that whereas for the former the “lifetime” is basically the same for red and blue light illuminations, the positions of the peaks for the latter are significantly different. Furthermore, the splitting of the red and blue signals tends to be more pronounced for the devices fabricated at lower humidity conditions.



**Figure 5.** Imaginary part of the impedance in the  $10^6$ - $10^3$  Hz frequency range for fresh (left) and aged (right) MAPbI<sub>3</sub> perovskite solar cells. Data obtained under red and blue light illumination are shown. The open-circuit photopotentials generated by the illumination are indicated in the graphs.

The robustness of the prepared devices is also confirmed when the capacitance extracted from impedance is analysed (Figure S5). Results previously reported for devices fabricated by a standard recipe at dry glovebox conditions<sup>13</sup> showed the appearance after aging of an additional capacitive process, evidenced by a distortion of the high frequency arc and the disappearance of the mid-frequency plateau. Interestingly, these features are not observed for the devices fabricated at ambient humid conditions.

## CONCLUSIONS

Ambient water, when considered a Lewis donor additive and when incorporated into the preparation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells, is found to have a positive effect on the stability of the fabricated devices when exposed to humid air. Optical absorption data show an increase of the light harvesting capability of the perovskite films which could be related to the enhancement of the short-circuit photocurrent after moisture exposure. XPS analysis reveal the presence of small amounts of water, in the form of coordinating molecules around the Pb cations. Based on this observation we tentatively attribute the robustness of the perovskite films to the presence of these molecules, which prevent the formation of additional hydrates that trigger the degradation mechanism.

On the other hand, degradation produces an acceleration of recombination, evidenced by a small deterioration of the open-circuit potential and the increase of the recombination rate. Aging also leads to a different impedance response under different optical penetrations of the bias light. This difference is found to be larger for devices prepared at conditions of lower humidity. This work highlights important effects to understand perovskite degradation processes and shows how a “homeopathic” strategy based on a preventive addition of water could be a promising way to struggling against it.

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