Effects of Ambient Humidity on the Optimum Annealing Time of Mixed-Halide Perovskite Solar Cells

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Abstract

Mixed halide Perovskite solar cells are commonly produced by depositing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ from a common solvent followed by thermal annealing, which in an up-scaled manufacturing process is likely to take place under ambient conditions. However, it has been reported that, similar to the effects of thermal annealing, ambient humidity also affects the crystallisation behaviour and subsequent growth of the Perovskite films. This implies that both of these factors must be accounted for in solar cell production. In this work, we report for the first time the correlation between the annealing time, relative humidity and device performance for inverted, mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ Perovskite solar cells with active area $\approx 1 \text{ cm}^2$. We find a trade-off between ambient humidity and the required annealing time to produce efficient solar cells, with low humidities needing longer annealing times and vice-versa. At around 20% RH, device performance depends relatively weakly on annealing time, but at higher (30 - 40% RH) or lower (0 - 15 % RH) humidities it is very sensitive. Processing in humid environments is shown to lead to the growth of both larger Perovskite grains and larger voids; similar to the effect of thermal annealing, which also leads to grain growth. Therefore, samples which are annealed for too long under high humidity show loss of performance due to low open circuit voltage caused by an increased number of shunt paths. Based on these results it is clear that humidity and annealing time are closely interrelated and both are important factors affecting the performance of Perovskite solar cells. The findings of this work opens a route for reduced annealing times to be employed by control of humidity; critical in roll-to-roll manufacture where low manufacturing time is preferred for cost reductions.

Introduction

Perovskite solar cells (PSCs) based on organic-inorganic metal halide materials, primarily $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI), are a promising renewable energy technology [1]–[4], with reported efficiencies exceeding 20% on small area cells of around 0.1 cm^2 [5], [6], 15% on square-centimetre MAPI devices [7] and over 22% using novel compositions at lab scale after only a few years' research effort (see chart at nrel.gov). However, there exist a number of problems to be overcome before transfer to volume production, including the use of Pb [8], [9] and challenges in scale-up from small- to large-area devices [7]. One further major issue which could hinder large-scale deployment is the sensitive nature of PSCs to atmospheric conditions under which they are processed. It is well known that PSCs degrade on storage in humid atmospheres [10]–[12]; however, the humidity under which the cells are produced also plays a role in determining structure and thus performance [13]–[21].

Previous studies have shown that atmospheric moisture plays an important role in the crystallisation of the MAPI absorber layer when used in planar devices in both normal [13], [21] and inverted [14], [15] architectures, with more humid environments tending to lead to faster conversion of the precursors and more rapid crystal growth. In addition to any morphological effects, moisture exposure during production has been reported to affect the photo-physical properties of the Perovskite material [13]. However, limited attention has been paid to any effect that this acceleration in the Perovskite formation process may have on the annealing time required to achieve the optimum performance at different humidities, which could be a critical factor in the design of future production processes. Therefore we have investigated the relationship between humidity and required annealing time for Perovskite solar cells.

Simple observation of the film colour while annealing reveals that the humidity does certainly play a role in determining how quickly the films turn from yellow to dark brown, indicating conversion to the final Perovskite phase, with films annealed at 100°C and 0% RH taking 28 minutes, while films at 40% RH take as low as 15 minutes for the colour change to occur. This observation, which is consistent with previous reports [13], implies that the two factors are indeed interrelated, and furthermore that it may be possible to use control of humidity to reduce the necessary annealing time in future mass production scenarios. Generally, a reduced annealing time is preferred for roll-to-roll manufacturing systems for cost reduction and to reduce the physical size of the required production line.

Therefore, in order to elucidate the nature of this interrelationship, the performance of Perovskite solar cells in a planar inverted architecture was studied as a function of both ambient humidity and annealing time. The humidity during annealing was controlled using a large-volume dry box, which was chosen to avoid subjecting the devices to unduly increased air pressure or high gas flow rates, both of which might affect the reaction via influencing the local vapour pressure and flux of potential reactants above the films.

Methods

Patterned Indium Tin Oxide (ITO)/glass substrates (Lumtec) were cleaned in methanol by 10 minutes' ultrasonication, followed by an O₂ plasma treatment for 10 minutes at 100 W and 15 SCCM. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, P VP Al 4083, Hereaus) was deposited by spin coating for 40 seconds at 5000 RPM, using a static dispense, and dried at 150°C for 15 minutes. The PEDOT-coated substrates were transferred to a N₂ glovebox (<0.1 ppm O₂ and H₂O)

and placed on a hotplate at 100°C. Keeping the Perovskite precursor solution at 70°C, the substrates were removed from the hotplate and quickly put on to the spin coater followed by a dynamic dispense of the Perovskite precursor solution (methyammonium iodide (MAI):PbCl₂ from Dyesol/Sigma Aldrich respectively, at a 3:1 molar ratio in anhydrous DMF, using 158.9 mg MAI and 92.6 mg PbCl₂ in 1.06ml DMF to give ≈20wt%) at 2000 RPM for 30 seconds. The films were allowed to dry in the glovebox for ≈2 minutes and then removed from the glovebox and placed into the humid environment. Relative humidity was controlled from 15 ± 2 to 40 ± 2 %RH at an ambient temperature of 23 ± 2°C by means of controlled evaporation of deionised water inside a dry box, and devices were annealed on a hot plate at 100 ± 1 °C for 15 to 45 minutes. When 0 %RH was desired, the films were annealed inside the nitrogen glovebox. After annealing, the films were immediately returned to the glovebox, and stored under nitrogen in the dark prior to any characterisation. The films were characterised by SEM and EDX using a JEOL JSM-7100F microscope and UV-VIS-NIR spectroscopy using a Varian Cary 5000 spectrophotometer. XPS analyses were performed on a ThermoFisher K-Alpha+ spectrometer, using a monochromated Al Kα X-ray source (hν = 1486.6 eV) and an X-ray spot of ~400 μm radius. Elemental compositions were calculated from core level spectra, acquired with a Pass Energy of 50 eV, following the removal of a non-linear (Shirley) background.

For device formation, a layer of Phenyl-C₇₀-butyric acid methyl ester (PC₇₀BM, Dyesol) was spin coated from a 50 mg/ml solution in dichlorobenzene at 1000 RPM for 30 seconds using a static dispense. Finally, 5 nm of bathocuproine and 65-100 nm of Ag were thermally evaporated. The devices were stored in the glovebox until testing in ambient air using a solar simulator (ABET 10500, class AAB), under AM 1.5 G illumination and calibrated to 1 sun using a calibrated Si reference cell. Cells were tested by both forward and reverse voltage sweeps; reverse sweeps (from 1.2 V forward bias to -0.2 V reverse bias, in 0.01 V steps and at a scan rate of -0.05 V/s) were used to extract parameters for further analysis.

Results and Discussion

Morphological and chemical characterisation was carried out on MAPI active layers deposited on glass/ITO/PEDOT:PSS substrates and annealed for various times at different humidities by SEM and EDX. Representative SEM micrographs are shown in Figure 1 for a range of humidities and annealing times. From these images, two distinct types of crystalline features were observed, termed rod-like and plate-like morphologies. The rod-like morphology can be observed most clearly at long anneal

times and high humidities, and is characterised by a network of disoriented high aspect ratio structures with significant film roughness and porosity. The plate-like forms are more prevalent at short times and lower humidities, and are characterised by flatter, plate-like structures which show lower overall porosity than the rod-like phase. However, there always exists a portion of the rod-like phase at all times and humidities.

The increase in porosity with increasing anneal time and humidity would be expected to lower overall device performance via increased formation of shunts leading to lowered V_{OC} . This is consistent with morphological effects of humidity previously reported [13], however here the trade-off between humidity and annealing time becomes clear. It appears that exposure to humidity speeds the conversion of the precursors to the final Perovskite phase, leading to larger grains for a given annealing time. The thermal effects of annealing, inducing grain growth and densification through free energy minimisation, essentially parallel this last effect of humidity, at least for short anneal times.. Therefore, cells produced under higher humidity conditions (e.g. 40% RH) need to be annealed for shorter times in order to avoid over-annealing and increasing the size of voids. Additionally, for longer annealing times under humid conditions there is a danger of degrading the film via reaction with atmospheric moisture.

Figure 1 – SEM micrographs of Perovskite films, annealed (in columns from left to right) at 20%, 30% and 40% RH respectively, for 20 (a-c), 30 (d-f) and 45 minutes (g-i). All scale bars are 1 µm.

EDX and XPS analyses were used to investigate the possibility of chemical change in the films after annealing as a function of time and humidity. These analyses can be seen as complementary, because while EDX gives bulk information (which is the most relevant to the present study), the elemental quantification can be imprecise, and furthermore detection of Cl in these samples can be complicated by the close overlap of Cl and Pb peaks, leading to detection limits of approximately 1 at% [22]. XPS, by contrast, achieves more precise elemental quantification but only probes the top $\approx 10\text{nm}$ of the sample, and so the results may be affected by surface contamination or segregation of mobile species.

The ratio of the atomic % of I/Pb as measured by EDX is shown in Figure 2A, while the same parameter as measured by XPS is shown in Figure 2C. Both analysis methods show that the I/Pb ratio is close to 3 at all humidities and annealing times, although with a slight drop off as annealing time is

increased. A reduction of this ratio from the ideal value of 3 could indicate the onset of chemical decomposition of the films, since the expected decomposition product PbI_2 would have an I/Pb ratio of 2. Degradation due to the loss of Iodine by the evolution of methylamine and HI as gases occurs for Perovskites under longer-term storage in air, which is a well-known property of halide Perovskites [11]–[13], [23]–[26]. Samples annealed for 90 minutes and analysed by EDX showed a more marked reduction in the I/Pb ratio, which would be consistent with such a mechanism. The samples analysed by XPS showed slightly higher I/Pb ratios than the EDX samples, which may point to minor surface segregation of Iodine. However the I/Pb ratio in the most extreme cases is still within $\sim 10\%$ of the ideal value. Therefore, while chemical degradation may indeed occur during extended annealing, at short anneal times this is not sufficient to explain the device performance results.

Figure 2B shows the atomic percentage of chlorine detected in the films by EDX as a function of time and humidity, and Figure 2D shows the same parameter measured by XPS. As analysed by both methods, the Cl content in all cases is low ($< 2.5 \text{ at}\%$), and decreases strongly with annealing time. This would be consistent with the hypothesis that the samples annealed for 20 minutes are ‘under-annealed’, i.e. not quite fully converted to the final Perovskite; a process which proceeds by the removal of chlorine in the form of methylammonium chloride gas [13], [22]. Furthermore, previous XRD studies of halide Perovskites produced from a PbCl_2 precursor [22] detected a chloride-rich precursor phase, for which the associated peak was found to disappear after approximately 20 minutes annealing at 100°C in a glovebox. It seems likely from the present results that longer than 20 minutes annealing is required to fully remove chlorine regardless of the humidity.

From the chemical characterisation of the MAPI films we can conclude that, while there are notable differences in Cl content as a function of annealing time, the prevailing humidity does not lead to a significant departure from stoichiometry at any of the annealing times studied. The MAPI films were further characterised optically by UV-Vis-NIR spectroscopy using a Varian Cary 5000 spectrometer (Figure S2). The absorption spectra of the films showed no distinct trends with annealing time or humidity, which supports the conclusion that the major effect of changing these parameters on the MAPI films is morphological.

Figure 2 – Results of (a), (b) EDX and (c), (d) XPS analysis of the Perovskite films. The EDX analysis was used to obtain information about the bulk composition of the samples, while the XPS data provides more precise compositional information but relates only to the samples' surfaces. The I/Pb ratio would be 3 and the Cl content 0 in the ideal case.

In order to investigate the performance of PSCs as a function of time and humidity, solar cells containing PC₇₀BM electron transport layers and Ag electrodes with an active area $\approx 1 \text{ cm}^2$ were made using MAPI films annealed at different humidities for different times as described previously. The average values extracted from JV characterisation of a group of 39 such devices under 1 sun illumination are shown in Figure 3 and Figure S1, which are based on data in Table S1. It is noted that for the purpose of this study, we have deliberately avoided efficiency enhancing techniques such as solvent engineering or multi-stage annealing in order to investigate the effects of moisture and annealing time as such techniques may have obscured underlying trends.

The device performance data show two distinct trends, with devices produced at lower humidities (0%, 15% and 20% RH) requiring longer times to reach the peak Power Conversion Efficiency (PCE). At higher humidities (30% and 40% RH), the time must be kept short to avoid rapid loss of device performance. 20% RH and 30 minutes annealing was found to be the optimum when considering average PCE, with a small standard deviation; however, it should be noted that the champion device was actually annealed at 20% RH for 20 minutes. The cause of the high standard deviation in the 20% RH/20 minutes population is likely to relate to the fact that at 20% RH, full conversion to the Perovskite takes almost precisely 20 minutes, as estimated by observing the colour change in the films. Therefore any uncontrolled fluctuations in humidity and/or temperature may lead to devices which contain unconverted regions of precursors, which would be likely to significantly impede charge transport. When annealing for 20 minutes, working devices could be produced at 20%, 30% and 40% RH, while at lower humidities conversion was clearly incomplete and devices were very poor. However at longer times, the lower humidity devices began to show improved performance, while those produced at 30 and 40% RH rapidly degrade. At 20% RH the device performance did not degrade significantly over the range of annealing times studied (which can be seen more clearly in Figure S1). This also corresponds with no CI being detected in any of the films, implying complete conversion of any precursor phases.

Figure 3 – Photovoltaic parameters of Perovskite SCs as a function of relative humidity, sorted by annealing time at 100°C. Humidities were controlled to within $\pm 2\%$ RH while the uncertainty on the time parameter was less than ± 1 minute. Points show average values and error bars show standard deviation of a group of devices produced across multiple batches.

From the device performance data it is clear that as humidity increases, the optimum annealing time becomes shorter. As shown in the SEM micrographs in Figure 1, the effect of having simultaneous high humidity and long annealing time is to increase the porosity in the Perovskite films. This is reflected in the open circuit voltage (V_{OC}) measurements shown in Figure 3B, in which devices annealed for 20 minutes showed the highest V_{OC} at 30% RH, while those annealed for longer times showed the highest V_{OC} at 20% RH. This is likely due to reduced shunting in the less porous films produced under these conditions. The devices annealed for 20 minutes at 30% and 40% RH, despite their high V_{OC} , showed a slight drop in PCE compared with 20% RH, driven by a loss of short circuit current density (J_{SC}) and Fill Factor (FF). This could point to the continuing presence of Cl-rich

precursor phases in these devices as implied by the EDX results in Figure 2B, which is expected to lead to reduced light absorption and charge transport due to this material's non-optimal band gap and recombination pathways.

The inter-dependence between annealing time, humidity and performance is consistent with the mechanisms suggested by You et al. and Eperon et al. [13], [14] in which exposure to moist air speeds both the conversion of the precursors to the final Perovskite compound and leads to faster grain growth. The proposed mechanism for Perovskite formation from the precursors is [13], [22], [27], [28];

This reaction is rate-limited by the reaction of the large excess of methylammonium in the precursor to form methylammonium hydrochloride gas. Since methylammonium is hygroscopic, it has been proposed [13] that reaction 1 is accelerated in the presence of moisture. This is consistent with the observed faster conversion to Perovskite under high humidity conditions, but also leads to morphological modifications in the films as a function of humidity, both because the reaction ensues more quickly (and thus the films are essentially annealed for a longer time after conversion), and possibly due to adsorbed moisture partially solvating the precursor species, leading to faster mass transport as suggested previously [13]. The chemical degradation, the onset of which has been observed in the 90 minute EDX results in Figure 2A, is driven by the reaction;

which is known to occur more quickly in humid environments [11]–[13], [23]–[26]. Therefore we propose that the devices showing poor performance in this study can be classified into two categories; over-annealed and under-annealed, where the first category have not had a sufficient level of humidity for a long enough time; while the second have had too long an annealing time for the prevailing humidity. Both over- and under-annealed devices are characterised by a significant loss of V_{OC} , J_{SC} and Fill Factor, indicating incomplete formation of the Perovskite from the precursors in the first case, and increased porosity and possibly chemical degradation in the second case.

This trade-off can be most clearly seen by plotting the response surface generated when treating the average PCE of the cells as the output resulting from a function of two inputs; anneal time and humidity, which is shown in Figure 4. This plot shows the regions within the time-humidity input space in which working devices could be produced (coloured areas), as well as the peak value combinations. This plot allows the optimum parameter space to be clearly seen, which could be a useful guide in future industrial scale up of this technology.

Figure 4 – Response surface contour plot of PCE of Perovskite devices as a function of humidity and annealing time. Note the ‘ridgeline’ of maximum performance between 20% and 30% RH, along with two distinct areas (shown in black) in which working devices could not be produced.

Conclusion

The trade-off between ambient humidity and the annealing time necessary for optimum PV performance for Perovskite solar cells was investigated for the first time. Perovskite cells were produced under various humidities for various times and characterised. The results reveal a trade-off between anneal time and humidity, whereby humidity exposure initially has the effect of causing faster conversion of the precursors to form the Perovskite and of speeding grain growth within the deposited layer, similar to the desired effects of thermal annealing. In order to produce a dense active layer with the lowest level of voids, leading to optimum performance, devices need a combination of moderate humidity and moderate anneal time. Devices annealed for short times at low humidities show incomplete conversion, and those annealed for longer times at higher humidities show a porous film morphology along with the onset of chemical degradation.

Knowledge of this trade-off is likely to be important in a future industrial scale up of this technology, where a process would be designed to suit a desired humidity level. Additionally, by introducing a known quantity of humidity while annealing the Perovskite layer, this effect could be utilised to lead to a faster method for producing devices, avoiding lengthy anneal times while retaining well-controlled performance, which is commercially desirable in order to increase throughput and reproducibility.

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References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells.," *J. Am. Chem. Soc.*, vol. 131, no. 17, pp. 6050–1, May 2009.
- [2] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, "Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites.," *Science*, vol. 338, no. 6107, pp. 643–7, Nov. 2012.
- [3] A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Gratzel, and H. Han, "A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability," *Science*, vol. 345, no. 6194, pp. 295–298, Jul. 2014.
- [4] M. A. Green, A. Ho-Baillie, and H. J. Snaith, "The emergence of perovskite solar cells," *Nat. Photonics*, vol. 8, no. 7, pp. 506–514, Jun. 2014.
- [5] W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo, and S. Il Seok, "High-performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science*, vol. 348, no. 6240, pp. 1234–7, 2015.
- [6] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, N. Mohammad K., S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, and M. Grätzel, "Cesium-containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency," *Energy Environ. Sci.*, 2016.
- [7] W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraful, M. Gratzel, L. Han, M. Grätzel, and L. Han, "Efficient and stable large-area perovskite solar cells with inorganic

- charge extraction layers,” *Science*, vol. 350, no. 6263, pp. 944–948, Oct. 2015.
- [8] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz, and H. J. Snaith, “Lead-Free Organic-Inorganic Tin Halide Perovskites for Photovoltaic Applications,” *Energy Environ. Sci.*, vol. 7, pp. 3061–3068, 2014.
 - [9] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, and M. G. Kanatzidis, “Lead-free solid-state organic–inorganic halide perovskite solar cells,” *Nat. Photonics*, vol. 8, no. 6, pp. 489–494, 2014.
 - [10] B. Philippe, B.-W. Park, R. Lindblad, J. Oscarsson, S. Ahmadi, E. M. J. Johansson, and H. Rensmo, “Chemical and Electronic Structure Characterization of Lead Halide Perovskites and Stability Behavior under Different Exposures - a Photoelectron Spectroscopy Investigation,” *Chem. Mater.*, vol. 27, no. 5, pp. 1720–1731, 2015.
 - [11] A. D. Sheikh, A. Bera, M. A. Haque, R. B. Rakhi, S. Del Gobbo, H. N. Alshareef, and T. Wu, “Atmospheric effects on the photovoltaic performance of hybrid perovskite solar cells,” *Sol. Energy Mater. Sol. Cells*, vol. 137, pp. 6–14, Jun. 2015.
 - [12] J. H. Yun, I. Lee, T.-S. Kim, M. J. Ko, J. Y. Kim, and H. J. Son, “Synergistic Enhancement and Mechanism Study of Mechanical and Moisture Stability of Perovskite Solar Cell Introducing Polyethyleneimine into CH₃NH₃PbI₃/HTM Interface,” *J. Mater. Chem. A*, 2015.
 - [13] G. E. Eperon, S. N. Habisreutinger, T. Leijtens, B. J. Bruijnaers, J. J. van Franeker, D. W. DeQuilettes, S. Pathak, R. J. Sutton, G. Grancini, D. S. Ginger, R. A. J. Janssen, A. Petrozza, and H. J. Snaith, “The Importance of Moisture in Hybrid Lead Halide Perovskite Thin Film Fabrication,” *ACS Nano*, vol. 9, no. 9, pp. 9380–9393, Aug. 2015.
 - [14] J. You, Y. (Michael) Yang, Z. Hong, T.-B. Song, L. Meng, Y. Liu, C. Jiang, H. Zhou, W.-H. Chang, G. Li, and Y. (Michael) Yang, “Moisture assisted perovskite film growth for high performance solar cells,” *Appl. Phys. Lett.*, vol. 105, p. 183902, 2014.
 - [15] Q. Zhou, Z. Jin, H. Li, and J. Wang, “Enhancing performance and uniformity of CH₃NH₃PbI₃-xCl_x perovskite solar cells by air-heated-oven assisted annealing under various humidities,” *Sci. Rep.*, vol. 6, no. 21257, 2016.
 - [16] D. a Egger, E. Edri, D. Cahen, and G. Hodes, “Perovskite Solar Cells: Do We Know What We Do Not Know?,” *J. Phys. Chem. Lett.*, pp. 4–7, 2015.
 - [17] S. R. Raga, M.-C. Jung, M. V. Lee, M. R. Leyden, Y. Kato, and Y. Qi, “The influence of air annealing on high efficiency planar structure perovskite solar cells,” *Chem. Mater.*, vol. 27, pp. 1597–1603, 2015.
 - [18] S. Pathak, A. Sepe, A. Sadhanala, F. Deschler, A. Haghighirad, N. Sakai, K. C. Goedel, S. D. Stranks, N. Noel, M. Price, S. Hu, N. a Hawkins, R. H. Friend, U. Steiner, and H. J. Snaith, “Atmospheric Influence upon Crystallization and Electronic Disorder and Its Impact on the Photophysical Properties of Organic - Inorganic Perovskite Solar Cells,” *ACS Nano*, vol. 9, no. 3, pp. 2311–2320, 2015.
 - [19] H.-S. Ko, J.-W. Lee, and N.-G. Park, “15.76% efficiency perovskite solar cells prepared under high relative humidity: importance of PbI₂ morphology in two-step deposition of CH₃NH₃PbI₃,” *J. Mater. Chem. A*, vol. 3, pp. 8808–15, 2015.
 - [20] M. Yang, Y. Zhou, Y. Zeng, C.-S. Jiang, N. P. Padture, and K. Zhu, “Square-Centimeter Solution-

- Processed Planar CH₃NH₃PbI₃ Perovskite Solar Cells with Efficiency Exceeding 15%," *Adv. Mater.*, vol. 27, no. 41, pp. 6363–6370, 2015.
- [21] H. Gao, C. Bao, F. Li, T. Yu, J. Yang, W. Zhu, X. Zhou, G. Fu, and Z. Zou, "Nucleation and crystal growth of organic-inorganic lead halide perovskites under different relative humidity," *ACS Appl. Mater. Interfaces*, vol. 7, no. 17, pp. 9110–9117, 2015.
 - [22] E. L. Unger, A. R. Bowring, C. J. Tassone, V. L. Pool, A. Gold-Parker, R. Cheacharoen, K. H. Stone, E. T. Hoke, M. F. Toney, and M. D. McGehee, "Chloride in Lead Chloride-Derived Organo-Metal Halides for Perovskite-Absorber Solar Cells," *Chem. Mater.*, vol. 26, no. 24, pp. 7158–7165, 2014.
 - [23] C. Wang, Y. Li, X. Xu, C. Wang, F. Xie, and Y. Gao, "Degradation of Co-Evaporated Perovskite Thin Film in Air," *Chem. Phys. Lett.*, vol. 649, pp. 151–155, 2016.
 - [24] J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. (Michael) Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, and Y. Yang, "Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers," *Nat. Nanotechnol.*, vol. 11, pp. 75–81, 2015.
 - [25] B. Wang and T. Chen, "Exceptionally Stable CH₃NH₃PbI₃ Films in Moderate Humid Environmental Condition," *Adv. Sci.*, no. 1500262, 2015.
 - [26] D. Wang, M. Wright, N. K. Elumalai, and A. Uddin, "Stability of perovskite solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 147, pp. 255–275, 2016.
 - [27] A. Dualeh, N. Ttreault, T. Moehl, P. Gao, M. K. Nazeeruddin, and M. Grtzel, "Effect of annealing temperature on film morphology of organic-inorganic hybrid perovskite solid-state solar cells," *Adv. Funct. Mater.*, vol. 24, pp. 3250–3258, 2014.
 - [28] H. Yu, F. Wang, F. Xie, W. Li, J. Chen, and N. Zhao, "The Role of Chlorine in the Formation Process of 'CH₃NH₃PbI₃-xClx' Perovskite," *Adv. Funct. Mater.*, vol. 24, pp. 7102–7108, 2014.