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Inhomogeneous Degradation in Metal Halide Perovskites

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Abstract: Although the rapid development of organic-inorganic metal halide perovskites solar cells has led to certified power conversion efficiencies of above 20%, their poor stability remains a major challenge preventing their practical commercialization. In this paper, we investigate the intrinsic origin of the poor stability in perovskite solar cells by using confocal fluorescence microscope. We find that the degradation of perovskite films start from grain boundaries and gradually extend to the center of the grains. Firmly based on our findings, we further demonstrate that the device stability can be significantly enhanced by increasing the grain size of perovskite crystals. Our results have important implications to further enhance the stability of optoelectronic devices based on metal halide perovskites.

The power conversion efficiencies of perovskite solar cells have rocketed from ~ 3% to over 20% within only a few years.¹⁻⁴ With such a high efficiency, the community has now paid increasing attention to the device stability, which is currently a limiting factor for the commercialization of this emerging technology.

The stability in perovskites can be simply categorized into two classes, i.e. moisture stability and thermal stability. Although these two stability issues are usually entangled in practical applications, we can disentangle them in materials and device design, as they have different origins. The poor thermal stability of methylammonium (MA)-based perovskites is ascribed to the easily volatile MA molecules.⁵ And hence the MA is replaced by formamidinium (FA) or inorganic Cs, or a mixture of FA and Cs.⁶⁻⁸ Indeed, the device stability improves significantly in the FA- and/or Cs- based perovskites.

In contrast, the moisture stability is more difficult to tackle, as it is rooted in the ionic nature of the perovskites.⁹ Previous investigations mainly focused on the electron- and hole- transport layers, aiming to make these two layers more moisture-resistant and protect the perovskite layer between them.¹⁰⁻¹² Some recent work also tried to modify the perovskite layer, by adding large-sized organic cations into the perovskites to protect the perovskite from the moisture.¹³⁻¹⁷ Although the stability is enhanced in these devices with large-sized organic cations incorporated, the device efficiency is often sacrificed. In order to develop even more efficient approach to enhance the moisture stability of metal halide perovskites, a microscopic picture and a mechanic understanding of degradation process are needed, but currently missing.

In this paper, we employ confocal fluorescence microscope to investigate the degradation process of the bench-mark MA-based perovskite in details. We find that the degradation of metal halide perovskites is inhomogeneous, starting from the grain boundaries and gradually extending towards the center of the grains. This result indicates that an effective approach to enhance the stability of perovskite solar cells is to increase the grain size of perovskite crystals. We also demonstrate the feasibility of

this approach by changing the perovskite grain size over a large range.

MAPbI_{3-x}Cl_x films are deposited on the ITO/PEDOT:PSS substrate by a hot-casting technique,¹⁸ where we use a mixed halide precursor solution composed of CH₃NH₃Cl and PbI₂ (1:1) in N,N-dimethylformamide. The X-ray diffraction spectrum of the MAPbI_{3-x}Cl_x film are in good agreement with the previously published result,¹⁸ indicating perfect formation of the perovskite film by this technique (Supplementary Figure S1).

Confocal fluorescence microscope¹⁹⁻²² is employed to obtain the morphology and fluorescence properties related to the microstructure of perovskite films. Figure 1(a) shows the microscopy and corresponding PL images of a perovskite film, which shows typical micrometer-sized grains, similar to those reported by Nie *et al.*¹⁸

Comparing the microscopy image and fluorescence map, we observe a significant variation in local PL intensity between the grains and grain boundaries. Although these different regions demonstrate the same fluorescence emission at 758 nm, the centers of grains show a higher luminescence intensity compared to the grain boundaries under the same photoexcitation condition, as shown in Figure 1(b). Scan electron microscopy (SEM) measurements suggest that the film is continuous and dense (Supplementary Figure S2).

In addition, we also perform PL lifetime measurements (Supplementary Figure S3(a)), aiming to further demonstrate that the grain boundaries are intrinsically different from the bulk of the grains. It can be observed that PL lifetimes vary across different grains and grain boundaries. The spatial variations in PL lifetime in the perovskite films indicate variations in local non-radiative decay rates. As depicted in Supplementary Figure S3(b), the grain boundary unveils a shorter fluorescence lifetime than that in the grain domain, indicating stronger non-radiative recombination loss in grain boundary regions. Our observation is consistent with previous report from the Ginger group, who believe that the dark boundaries result from more defects and trap states.¹⁹

We proceed to investigate how the degradation develops across the perovskite films, which are exposed to the 633 nm laser during the PL mapping measurement (intensity 0.45 μW , spot size 450 nm) in ambient air (16 $^{\circ}\text{C}$, 60% relative humidity). We find that the emission of perovskite films decreases with increasing time. At the same time, we also notice that the emission from the grain boundaries decrease more quickly than that from the bulk grains, with the dark grain boundaries evolving into large dark gaps. We can clearly see the development of this process in Figure 2(a) (Multimedia view), where the bottom right grain in Figure 2(a) is gradually etched to a small particle and the top left grain is split into two parts with increasing time. This is likely due to the structural inhomogeneity of perovskite crystal, which leads to water intercalation across the edge of perovskite.²³ We quantitatively illustrate the different degradation rates in Figure 2(c), which shows the normalized PL intensity as a function of degradation time for selected grain and grain boundary under illumination. It obviously shows that the grain boundary undergoes a much faster degradation rate than the grain. After 240 min continuous test, the grain boundary exhibits a 50% drop in the PL intensity, while the bulk grain only shows an 11% decrease. In addition, Supplementary Figure S4 shows that the full width at half maximum (FWHM) of emission from the bulk grains is almost constant while that from the grain boundaries keeps increasing with increasing time, suggesting the grain boundaries becomes more and more disorder under the illumination. These results indicate that the defect-rich boundaries are more vulnerable to moisture, and the degradation further increase the trap densities in the boundaries. Supplementary Figure S5 also shows that after degradation, there is PbI_2 peak at 12.7° and the peak from MAPbCl_3 at 15.6° became dominant. The degradation rate of perovskite films under illumination is dependent on the intensity of the light irradiation.²⁴ Supplementary Figure S6 shows that the perovskite film stored in air without illumination has a much slower degradation rate.

It was reported that environmental factors play a crucial role in the PL performance of perovskite films.^{24,25} Galisteo-López *et al.* found that moisture can cause strong photodarkening of MAPbI_3 film, while oxygen will induce photoactivation of the PL

emission.²⁴ Fang *et al.* reported oxygen and water molecules cause PL enhancement of MAPbBr₃ single crystals.²⁵ In order to reveal the role of water in the degradation process, we perform the confocal fluorescence microscopy measurements under controlled moisture-free atmosphere conditions. The moisture-free atmosphere is a mixture of 79% N₂ and 21% O₂ to simulate the air, and the setup is schematically shown in Supplementary Figure S7. In contrast to the situation with moisture (Figure 2(a)(c)), the sample in the moisture-free atmosphere (Figure 2(b) (Multimedia view) and Figure 2(d)) shows almost no degradation after 6000 min measurement, suggesting the perovskite degradation in our case is mainly due to the existence of moisture. Actually the PL intensity even shows enhancement during the first 1000 min and remains steady after that. Illumination-induced PL enhancement has recently been investigated in details by several groups.^{24,26,27} who attributed the PL enhancement to the reduction of trap densities by illuminating perovskite films. Interestingly, Fang *et al.* found the combination of moisture and illumination also can enhance the PL intensity of FAPbI₃ films, where moisture has a weaker effect than that of MAPbI₃.²⁷ In our case, the moisture plays a more negative effect than the positive effect of light (Figure 2(c)), so the light-induced PL enhancement can only be observed in dry atmosphere. The difference in the emission change between the grain boundaries and bulk grains can also be observed with long term illumination (Figure 2(d)). The PL degradation in grain boundaries are faster than that in bulk grains even in the moisture-free environment, indicating that this degradation process, presumably due to the thermal or photo instability, is also inhomogeneous.

With these understanding, we aim to develop an effective approach to enhance the moisture stability of perovskites. Since the degradation is dependent on the grain size, we propose that the stability to be enhanced by increasing the grain size (i.e. decreasing the grain boundaries). In order to examine the feasibility of this approach, we fabricate two devices composed of perovskites with different grain sizes, simply by adjusting solution concentration and substrate temperature in the hot-casting technique as Nie *et al.*¹⁸ Typical microscopy images of solar cells are shown in Figure 3(a) and 3(b), and

corresponding current-voltage (J - V) curves (AM 1.5 conditions) are displayed in Supplementary Figure S8. Cell A with a large size of perovskite grains ($\sim 12\ \mu\text{m}$ in diameter) gives a PCE of 8.9%, a short-circuit photocurrent density (J_{sc}) of $17.03\ \text{mA cm}^{-2}$, an open-circuit voltage (V_{oc}) of 0.82 V and a fill factor (FF) of 0.64, while Cell B with a small grain size ($\sim 5\ \mu\text{m}$ in diameter) shows a much worse PCE of 5.0%, with a J_{sc} of $10.88\ \text{mA cm}^{-2}$, a V_{oc} of 0.60 V and a FF of 0.75. We compare the grain-size-dependent stability of perovskite solar cells by exposing them to ambient air (60% relative humidity). Figure 3(c)(d)(e)(f) show the relative change of the photovoltaic metrics recorded every 25 seconds under continuous illumination. It is obvious that the J_{sc} and FF of Cell B (small size) decreases much faster than those of Cell A (large size). The V_{oc} shows slight increase with increasing time. From the confocal fluorescence microscopy measurements in Figure 2(c), we know that the emission intensity of perovskites decrease with increasing exposure time. Therefore, we can rule out the possibility that the V_{oc} enhancement is due to increased radiative recombination. Instead, it might result from the changes in the energetic levels of perovskites or the energetic alignment between the perovskites and the charge transport layers. The time ($t_{1/2}$) of PCE decaying to half the initial value for the perovskite cell A with large grain size is about 135 min, whereas that of the cell B with small grain size is much decreased to ~ 7 min under the same condition of aging.

In order to demonstrate the generality of our approach of enhancing the device stability by increasing the grain size, we fabricate around forty devices with different grain sizes. As shown in Figure 4(a), the PCEs of perovskite solar cells are improved from $\sim 4\%$ to $\sim 9\%$ in pace with the increase of perovskite grain size (decreasing grain boundaries). To clearly reveal the relation of device stability and grain size, the time of cell efficiency decaying to half the initial value is plotted in Figure 4(b). Note that our devices are not encapsulated, and continuously scanned in air with a 60% relative humidity. We can clearly observe a trend that the device stability is significantly improved with increasing grain size, further indicating that our approach is an effective way to enhance the device stability.

In summary, we employ confocal fluorescence microscope to investigate the degradation of perovskite solar cells in details. Consistent with previous reports, we confirm that the degradation is mainly due to the moisture in ambient conditions. We find that the degradation is inhomogeneous, starting from the grain boundaries and gradually extending to the bulk grains. We point out that an effective approach to enhance the device stability is to increase the grain size of perovskite crystals. We further demonstrate the effectiveness of this approach on devices with a large range of grain sizes. Our results provide a straightforward approach to tackle the intrinsic stability problem of metal halide perovskites, and have important implications not only for solar cells but also for other optoelectronic devices based on metal halide perovskites.

Supplementary material

See supplementary material for more information.

Acknowledgements

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Figure captions

(a)

(b)

Figure 1. (a) Microscopy image and corresponding fluorescence intensity maps of a pristine perovskite film prepared by hot-cast technique. (b) Steady state PL spectra of grain and boundary regions in Figure 1(a).

Figure 2. Fluorescence intensity maps of a pristine perovskite film exposed to (a) ambient air of 60% relative humidity (Multimedia view) or (b) a mixture of 79% N₂ and 21% O₂ under continuous light irradiation (Multimedia view). (c) and (d) Evolution of PL intensity along with time under different conditions. PL intensities were recorded from grain or boundary region in Figure 2(a) or 2(b) and further normalized with the corresponding initial values.

Figure 3. Microscopy images (a) and (b) of solar cells with different perovskite grain size. Evolution of (c) short-circuit current density, (d) open-circuit voltage, (e) fill factor and (f) power conversion efficiency of solar cells with corresponding perovskite grain sizes. The photovoltaic metrics were recorded every 25 seconds in ambient air of 60% relative humidity under continuous AM1.5G illumination of 100 mW cm^{-2} .

Figure 4. (a) Power conversion efficiency (η) and (b) lifetime ($t_{1/2}$) of perovskite solar cells as a function of average grain size. $t_{1/2}$ represents the time of cell efficiency decaying to half of the initial value. Average grain sizes of perovskites are estimated from the microscopy images by means of measuring the diameter of perovskite grains.