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2019

Solanki, A., Lim, S. S., Mhaisalkar, S., & Sum, T. C. (2019). Role of water in suppressing recombination pathways in CH₃NH₃PbI₃ perovskite solar cells. *ACS Applied Materials and Interfaces*, 11(28), 25474-25482. doi:10.1021/acsami.9b00793

<https://hdl.handle.net/10356/138050>

<https://doi.org/10.1021/acsami.9b00793>

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Role of Water in Suppressing Recombination Pathways in CH₃NH₃PbI₃ Perovskite Solar Cells

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Keywords: CH₃NH₃PbI₃, photovoltaics, additives, photophysics, water.

Abstract: Moisture degradation of halide perovskites is the Achilles heel of perovskite solar cells. A surprising revelation in 2014 about the beneficial effects of controlled humidity in enhancing device efficiencies overthrew established paradigms on perovskite solar cell fabrication. Despite the extensive studies on water additives in perovskite solar cell processing that followed, detailed understanding of the role of water from the photophysical perspective remains lacking, specifically the interplay between the induced morphological effects and the intrinsic recombination pathways. Through ultrafast optical spectroscopy, we show that both the monomolecular and bimolecular recombination rate constants decrease by approximately 1 order with the addition of an optimal 1% H₂O by volume in CH₃NH₃PbI₃ as compared to the reference (without H₂O additive). Correspondingly, the trap density reduces from $4.8 \times 10^{17} \text{ cm}^{-3}$ (reference) to $3.2 \times 10^{17} \text{ cm}^{-3}$ with 1% H₂O. We obtained an efficiency of 12.3% for the champion inverted CH₃NH₃PbI₃ perovskite solar cell (1% H₂O additive) as compared to 10% efficiency for the reference cell. Increasing the H₂O content further is deleterious for the device. Trace amount of H₂O affords the benefits of surface trap passivation and suppression of trap-mediated recombination; while higher concentrations result in preferential dissolution of MAI during fabrication that increases the trap density (MA vacancies). Importantly, our study reveals the effects of trace H₂O additives on the photophysical properties of CH₃NH₃PbI₃ films.

Introduction

Halide perovskite solar cells possesses impressive power conversion efficiencies (PCE) that have captivated the attention of many researchers. Within a short developmental span, the PCEs of perovskite solar cells have exceeded 23%.¹ Early spectroscopic studies revealed that the perovskites, specifically CH₃NH₃PbI₃, possesses many qualities of an ideal photoactive material, such as low bandgap², high absorption coefficient², long carrier diffusion lengths³ and high carrier mobility⁴ and surprisingly high defect tolerance⁵⁻⁶. These amazing PCEs propelled perovskite solar cells to be a leading contender to the

ubiquitous silicon. Growth control of perovskites has long been established as a crucial factor for high-efficiency photovoltaics as well as for other optical devices⁷⁻⁹. The highly adaptable solution-processable perovskites allows for many variations in the active layer formation to improve device performance¹⁰. The different parameters which affect the growth of the perovskite films and device performance are: perovskite composition, solution concentration, stoichiometry, rate of crystallization, temperature of solution and deposited substrate, annealing times, etc. As such, solvent engineering techniques¹¹⁻¹³ to exert greater control over the crystallization and the effects of non-stoichiometry¹⁴ are extremely important. Nevertheless, the biggest weakness of halide perovskites is their inherent vulnerability to air and in particular moisture that will degrade the compound to form PbI_2 and hydrated compounds¹⁵⁻¹⁶, thus eventually destroying the device.

An early report in 2014 by Yang Yang's group on realizing high efficiency perovskite cells with interface engineering under controlled humidity conditions shocked the perovskite community.¹⁷ Since then, extensive studies have validated the benefits of trace amount of water as additives in the perovskite precursors. It has been shown that moisture induces grain boundary creep and recrystallization to merge adjacent grains together and form high-quality films.¹⁸⁻²⁰ Devices produced at ambient conditions under controlled humidity (up to 50%) were also able to achieve high efficiencies²¹⁻²³. However, cells fabricated in relative humidity exceeding 50% began to show significant decomposition²⁴. It was also reported that water additives do not significantly impact film formation and device performance²⁵. Despite these developments, detailed understanding of the exact role of trace water additives on the charge dynamics and device efficiencies remain lacking and the interactions between the induced morphological effects and changes in the intrinsic recombination pathways.

In this study, we seek to mitigate the influence of sample-to-sample morphological variation by using the anti-solvent treatment on $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on glass with varying deionized water (H_2O) additive

concentrations (0 vol%, 1 vol%, 2 vol%, and 5 vol%, henceforth shortened to %) prepared by the one-step solution method. At the optimized H₂O concentration of 1%, these perovskite film and devices were found to possess the lowest trap-mediated recombination and trap states, which we attribute to surface or grain boundary traps. Perovskite solar cells using the same range of additive concentrations were also prepared and the devices with the optimized H₂O concentration of 1% possess the highest efficiency of 12.3% (i.e., champion cell $J_{sc} = 20.9 \text{ mA cm}^{-2}$, $V_{oc} = 0.83 \text{ V}$, and $FF = 0.71$), which is a significant improvement over the 0% H₂O reference devices (10% efficiency). The device efficiency decreases with increasing additive concentrations of 2% and 5%. Our study reveals the intrinsic benefits afforded by the trace H₂O additive to the photophysical properties of CH₃NH₃PbI₃ films and subsequently for device operation.

Results

CH₃NH₃PbI₃ is the ubiquitous perovskite system in perovskite solar cell research. Here, perovskite films prepared with stoichiometric ratios of MAI and PbI₂ (see supporting information for experimental details) were used to investigate the role of H₂O on structural changes and photophysical properties correlated with the device properties of inverted perovskite solar cells. X-ray diffraction measurements were first performed to confirm the phase purity and reveal any structural change on addition of H₂O perovskite film. Similar x-ray patterns were observed in pure and H₂O added perovskite films, with peaks at $\sim 14.1^\circ$ and $\sim 28.4^\circ$ originating from the (110) and (220) planes of a 3D perovskite phase (**Figure S1**). However, an in-depth analysis of (110) XRD peaks shows a decrease in full-width half maxima (FWHM) for the 1% H₂O added samples, but subsequent increase with increasing H₂O addition. The initial drop in FWHM indicates an extension of the lattice constant probably due to increased crystallinity while a larger FWHM reflects the reversal. However, existence of the strong (110) and (220) XRD peaks confirm that films in our study are still crystallized and continuous up to the addition of 5% H₂O.

Here, we used an anti-solvent treatment with single step spin-coating processing in the film preparation (see experimental section in the supporting information). Although H_2O is known to cause moisture-induced degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$, it is still an open question how the trace H_2O additives in the perovskite affects its intrinsic properties. Our first step would be to image sample morphology. **Figure 1 a and b** shows the cross-section SEM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films prepared using solutions with 0 and 1 vol% H_2O respectively, and the top-view images are shown in **Figure S2**. The films were observed to be highly uniform with no visible pinholes, characteristic of solvent-engineered films. There is also no significant change in the samples' morphology after their subsequent anti-solvent treatment. Figure 1c and d shows the corresponding morphology images of $2\ \mu\text{m} \times 2\ \mu\text{m}$ scanned area these perovskite films by atomic force microscopy which also confirm the invariant morphology in these films (Figure S3). The grain size across these perovskite films varies between 100 - 300 nm. The root mean square (RMS) roughness is measured to be 4.9 nm, 4.4 nm, 4.5 nm, and 4.7 nm for 0, 1, 2 and 5 vol % H_2O added perovskite films, respectively. The small variation of RMS roughness shows that the addition of water in the precursor solution does not induce any significant non-uniformity on the top surface of the perovskite films. In contrast, many of the previous water additive works in the literature do not use anti-solvent treatment.^{19, 26} Here, we would like to highlight that the anti-solvent treatment is to isolate any resultant change in carrier recombination due to the inclusion of H_2O additives. This is to minimize the impact of morphological-induced effects, which could be a strong factor in influencing device performance.²⁷

SEM cross-section image of films Glass/ITO/PEDOT:PSS (**Figure 1a and 1b**) shows the voids and grain boundaries in control perovskite active layer which can give rise to poorer surface coverage and reduced photo-absorption. These defects also act as recombination centers and cause poor J_{sc} . The addition of 1% H_2O increases the adhesion of perovskite solution on PEDOT:PSS surface, which helps reduce such voids between perovskite grains in the film and increase the surface coverage as shown by the compact

morphology in **Figure 1b**. Furthermore, x-ray diffraction (XRD) spectra (**Figure S1**) of all perovskite films show the characteristic peaks of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$. The variation of full-width half maxima (FWHM) of (110) XRD peak decreases with 1% H_2O (**Figure 1c**) indicating larger perovskite grains beneath the surface though surface morphology remains relatively invariant from the SEM scan of the top surface (**Figure S2**). With increasing H_2O concentration, the effect is reversed and the FWHM of the (110) peak starts increasing. These characterization results prove that the perovskite films in our study still crystallizes and form continuous films up to 5% H_2O . **Figure 1d** shows an increase of the absorption mainly from below 500 nm wavelengths with H_2O additive peaking at 1% in perovskite film. The onsets of the absorption edges of all the spectra nearly overlap at around 780 nm (or 1.58 eV). The bandgap of hybrid perovskite materials is mainly determined by the inorganic lead halide formulation by the dominant transition from I 5p to Pb 6p orbital. The close overlap of the absorption edges between the control and H_2O added films is attributed to the steady band gap in these films.

Figure 1. Cross section SEM images of perovskite films with (a) 0 vol %, (b) 1 vol % H₂O additive concentration coated on PEDOT:PSS/ITO/glass substrate. (c) and (d) are the corresponding morphology images across 2 μm $\times$ 2 μm scanned area by atomic force microscopy, where the root-mean-square roughness is measured to be 4.9 nm, and 4.4 nm for the 0 vol %, and 1 vol % H₂O added perovskite films, respectively. (e) Absorption spectra of the various perovskite films, with obvious increase of the absorption in the shorter wavelengths (< 500 nm). (f) Graphical representation of the variation of full-width half maxima of (110) XRD peak with various H₂O concentration.

Having established the basic physical properties of our H₂O additive samples, we next turn to probe the charge dynamics and recombination mechanisms in these samples using ultrafast optical spectroscopy. The samples were excited by an optical pulse train with a wavelength of 600 nm and we measured both the time-integrated and time-resolved photoluminescence (PL) spectroscopy. We estimated the trap

density of the thin films coated on a glass substrate by measuring the power-dependent photoluminescence (PL) in the low-fluence regime using an excitation wavelength of 600 nm (Figure S4). The excited carrier density is plotted against the integrated PL spectra of each sample as displayed in **Figure 2a**, and fitted with a theoretical model described in our previous publications (see SI for the details).²⁸⁻²⁹ As the concentration of H₂O additive is increased from 0% to 1%, the trap density decreases from $4.8 \times 10^{17} \text{ cm}^{-3}$ to $3.2 \times 10^{17} \text{ cm}^{-3}$, suggesting that small amounts of H₂O could be acting as a passivating agent as well as inducing recrystallization of the grain boundaries that suppresses the defects (more evidence later).¹⁷⁻¹⁸ These results are consistent with the observation of the compact perovskite grains with reduced grain boundaries from the SEM cross-section image. Furthermore, any excess CH₃NH₃I could be aided by the trace H₂O to react with remnant PbI₂ to form CH₃NH₃PbI₃ grains that may further serve to passivate the grain boundaries. However, increasing the water concentration to 5% H₂O counteracted the beneficial properties of the additives, resulting in the trap densities gradually returning to the pre-additive state.

As shown in **Figure 2b**, the differences in trap density has a pronounced impact on the carrier lifetime of the samples, revealed from low-fluence ($0.5 \mu\text{J cm}^{-2}$) TRPL kinetic traces. We observe that the kinetics of each sample is consistent with the trap density estimation, with the 0% H₂O sample having the highest trap density and shortest TRPL lifetime, and the 1% H₂O sample with the lowest trap density and consequently longest TRPL lifetime. Similarly, the TRPL lifetime of the 5% H₂O sample approaches that of the 0 % H₂O sample with its increasing trap density. It is noteworthy that 1% and 2% H₂O samples have delayed onsets of non-radiative recombination. This is consistent with our observation of lower trap states in both 1% and 2% H₂O samples, and thus fewer non-radiative recombination pathways. **Figure 2c** shows the fitted amplitudes of the TRPL lifetime components for the different samples. The amplitude of the long and short lifetime components are denoted by A_1 and A_2 , respectively. The slower transition (A_1) seen in biexponential traces is attributed to radiative bulk lifetime, whereas the faster transition (A_2)

is due to non-radiative recombination, as detailed by deQuilettes *et al*³⁰. From the graphs, we see that only the 1% and 2% H₂O samples have no A₂ term even at 2.5 $\mu\text{J cm}^{-2}$, one order higher than the preceding data point. This suggests that higher order carrier recombination is suppressed for these samples. In our study, the trace amounts of H₂O used would form hydrated compounds that subsequently evaporate completely during the annealing phase. As such, there would not be any H₂O left in the annealed perovskite film that might affect charge recombination and transport.

To gain a further understanding of H₂O's role in the recombination mechanisms, we collected the power-dependent TRPL kinetics of neat perovskite thin films, with a fluence range of 0.5 to 50 $\mu\text{J cm}^{-2}$ corresponding to excitation carrier densities 3.86×10^{16} to $3.86 \times 10^{18} \text{ cm}^{-3}$. These kinetics are also fitted with either a single or biexponential decay function (Figure S5). **Figure 2c** reveals the striking differences between the different recombination rates of the different samples. While all samples exhibit fast initial decay components with increasing pump fluences, from the timescales of the plots, it is clear that both 0 % and 5 % H₂O samples recombine much faster than the others.

Figure 2: Characterization results from ultrafast optical spectroscopy detailing the recombination dynamics in the perovskite samples. a) Calculation of trap density by plotting measured integrated photoluminescence (PL) intensity against photoexcited carrier density. b) Time-resolved PL (TRPL) kinetic traces of the samples in the low fluence regime, showing the superiority of 1% H_2O additive. c) Amplitude of lifetime components obtained from fitting of power-dependent TRPL kinetics. d) Recombination rates obtained by fitting the recombination rate equation (Equation 1), with an estimated error of 10%.

Table 1 shows the recombination rates that were decoupled by global fitting the power-dependent decay kinetics of each sample (**Figure S6**) with the recombination rate equation:

$$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n \quad \text{Equation 1}$$

Where n is the charge-carrier density, k_1 , k_2 , and k_3 are the monomolecular, bimolecular and Auger recombination rate constants, respectively. Monomolecular recombination rate consists of either a bound electron-hole pair (exciton), a free single conduction-band electron or valence-band hole. Since the exciton binding energy of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ is low at room temperature, monomolecular recombination

is trap-assisted³¹. On the other hand, bimolecular recombination comprises of two particles, namely a free hole and electron, which leads to radiative decay. Auger recombination is an event that involves multiple particles, and thus strongly dependent on excitation fluence. An electron and hole recombine to release energy and/or momentum that is absorbed by another electron and hole, known as an Auger particle. The curves can be well-fitted considering only monomolecular and bimolecular rate constants and the fitted rate constants are summarized in **Table 1**.

Table 1: Recombination rate constants and diffusion lengths calculated from TRPL measurements on CH₃NH₃PbI₃ films containing H₂O additives.

vol % H ₂ O	Recombination rate constants		Diffusion Length (nm)	
	Monomolecular k_1 ($\times 10^8$ s ⁻¹)	Bimolecular k_2 ($\times 10^{-9}$ cm ³ s ⁻¹)	Electron	Hole
0	4.7 ± 0.3	2.6 ± 0.2	70 ± 20	310 ± 40
1	0.502 ± 0.006	0.234 ± 0.006	230 ± 20	440 ± 50
2	1.10 ± 0.02	0.26 ± 0.01	180 ± 20	290 ± 30
5	3.08 ± 0.07	2.23 ± 0.06	60 ± 20	100 ± 20

The monomolecular rate obtained for the 0% sample is 4.7×10^8 s⁻¹, which is consistent with previously reported values³¹⁻³². Since the monomolecular recombination in CH₃NH₃PbI₃ is dominated by trapping, as previously mentioned, passivating these trap states would decrease the monomolecular rate constant. When the H₂O concentration is increased by the optimal concentration of 1%, the monomolecular rate decreases by one order of magnitude to 0.5×10^8 s⁻¹. Large crystal grains were reported to slow recombination³³, but the invariance of our XRD and SEM images across different samples suggests that the morphology alone need not be a main factor in the lifetime or photovoltaic improvements in our samples. Analysis of the XRD data reveals that the 1% sample has slightly larger domains and coupled with the invariant morphology, this indicates that the trace H₂O additive has played a role at the grain

boundaries. We find correlations with slightly larger domain size, reduced trap densities and lower trap-mediated recombination, in agreement with the literature³⁴. This same behavior was reported by deQuilettes at the grain boundaries, where darker PL and shorter lifetimes were observed at grain boundaries.³⁰ Therefore, this reduction is also very likely due to the trap passivation afforded by trace H₂O. However, as the additive content is increased to 5%, the monomolecular rates increase to $3.1 \times 10^8 \text{ s}^{-1}$, which is approaching that of the 0% H₂O sample. The preferential dissolution of CH₃NH₃I in H₂O relative to PbI₂ in higher H₂O concentrations could potentially have resulted in CH₃NH₃ vacancies and surface traps along the grain boundaries. This results in an increase in the trap density, and thus the trap-dominated monomolecular recombination rate. The bimolecular recombination rate constants also follow the same trend as the monomolecular rate constant, which decreases in the 1% H₂O sample, but increases subsequently when higher concentrations of H₂O were added. The extraordinarily low recombination rates of the 1 % H₂O sample are reflected in the higher PCE.

We next extend the photophysical study to determine the charge carrier diffusion lengths within these samples. This can help us provide some guidance on the device architecture and subsequent performance. By using a similar approach as discussed in SI, the carrier diffusion lengths were extracted using TRPL measurements on neat CH₃NH₃PbI₃ films, films with PC₆₁BM electron extraction layer, and films with PEDOT:PSS hole extraction layer. PEDOT:PSS was used in this scenario to emulate charge extraction in the inverted architecture. Such low bimolecular recombination rates yield long carrier diffusion lengths, making CH₃NH₃PbI₃ suitable for solar cells utilizing the planar heterojunction geometry. The low monomolecular and bimolecular recombination rates are evidently reflected in the longer carrier diffusion lengths as shown in **Figure 3a**. The greatly reduced bimolecular recombination rate in the 1 % H₂O sample exhibits carrier diffusion lengths that is a factor of four longer as compared to the 5 % H₂O sample.

By adopting the approach used by Wehrenfennig *et al.* to model the diffusion lengths as a function of experimentally determined charge carrier density, n , the diffusion lengths can be modelled and compared at solar cell operating conditions ($n = 1 \times 10^{15} \text{cm}^{-3}$). The total decay rate of each sample can be calculated from the recombination rate constants according to the expression,

$$\begin{aligned} k_{total}(n) &= -\frac{1}{n} \frac{dn_0}{dt} = \phi^2 k_3 \left(\frac{n_0}{\phi}\right)^2 + \phi^2 k_2 \left(\frac{n_0}{\phi}\right) + k_1 \\ &= \phi^2 k_3 n^2 + \phi^2 k_2 n + k_1 \end{aligned} \quad \text{Equation 2}$$

where $n = \frac{n_0}{\phi}$, and ϕ is the branching ratio of photogenerated charge carriers to the absorbed photon density, and it is assumed that $\phi = 1$ for simplicity. From the diffusion coefficient and total recombination rate, the diffusion lengths can be modeled as a function of n ,

$$L = \sqrt{\frac{D}{k_{total}(n)}} \quad \text{Equation 3}$$

The computed results of the electron and hole diffusion lengths using the model are shown in **Figure 3b** and **c**, respectively. From the graphs, the diffusion lengths sufficiently exceeds perovskite layer thickness (about 275 nm) at low charge carrier densities that correspond to solar cell operating conditions. In the low carrier concentration regime, the Auger k_3 term (solid line in **Figure 3b** and **3c**) plays an insignificant role because of its multi-particle nature that requires high carrier concentrations to have an effect. When we model the diffusion lengths and assuming $k_3 = 10^{-28} \text{cm}^6 \text{s}^{-1}$ (dashed line in **Figure 3b** and **3c**), a value typical of perovskite solar cells, the diffusion lengths get understandably much shorter at higher carrier densities. Nonetheless, these trends in H_2O additive diffusion lengths is similarly observed in device performances, where the 1 % H_2O device exhibits slightly higher performance in power conversion efficiency (PCE) and other parameters, notably the fill factor and J_{SC} .

Figure 3. (a) Electron (square) and hole (cross) diffusion length of the various samples with the respective quencher measured at a fluence of $0.5 \mu\text{J cm}^{-2}$ and calculated with a 1D diffusion model (Figure S7 shows the fitting of TRPL data for different perovskite films). PC_{61}BM is used as the electron quencher in a bilayer architecture to estimate the electron diffusion length, and PEDOT:PSS is used as the hole quencher. Modeling the diffusion lengths as a function of carrier density using Equation 2(b) with a PCBM electron quencher, and (c) PEDOT:PSS hole quencher. Solid lines denote the results assuming $k_3 = 0$, since this term is not required when fitting the power-dependent transients. Dashed lines denote the results assuming $k_3 = 10^{-28} \text{ cm}^6 \text{ s}^{-1}$, a value typical of perovskite solar cells.

Gong *et al.* incorporated a small fraction of H_2O into $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite solution to enhance the grain size in thin film to improve the PCE in solar cell devices¹⁹. On the other hand, Liu *et al.* improved the device stability under illumination using aqueous perovskite solution containing mixed host solvent using same perovskite composition³⁵. As reported, two-step spin coating or without any anti-solvent treatment was used to prepare H_2O incorporated perovskite films where significant morphological variation leads to the lower defect density and thus higher PCE in these devices.^{18, 26} Here, we isolated the morphological variation by anti-solvent treatment of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films to investigate the effects of H_2O on the recombination dynamics and device performance.

The solar cell devices using the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer with various H_2O volume concentration were fabricated with the inverted planar heterojunction geometry ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ / PC_{61}BM /Ag (see the supporting information for the device preparation method). The schematic of the device architecture is displayed in **Figure 4a**. The J - V curves for each corresponding additive concentration are shown in **Figure 4b** and extracted photovoltaic parameters are summarized in **Table 2**. The 0 % H_2O control device has an average PCE of $9.9 \pm 0.5 \%$, which increases to $10.3 \pm 0.4 \%$ upon adding 0.5%

H₂O and rises further to 11.4 ± 0.9 % when 1 % H₂O is added, with the champion cell exhibiting a PCE of 12.3 % with its $J-V$ curve shown in **Figure 4c**. Moreover, the common $J-V$ hysteresis problem is also found to be negligible in solar cells prepared with perovskite films added 1 % H₂O in CH₃NH₃PbI₃ precursor solution (**Figure 4c**). Despite the H₂O additive, it does not induce hysteresis. A PCE histogram for the control (0 % H₂O) and 1 % H₂O added devices is present in **Figure 4d**. Surprisingly, the incorporation of 1 % H₂O does not induce any significant degradation of the device performance and PCE is comparable to the control device as measured for 200h (Figure S8). During the stability tests, devices (without any encapsulation) were stored under dark condition inside the glovebox.

When trace H₂O is added, e.g. 1 vol%, it becomes energetically favorable to infiltrate into the perovskite inorganic lattice. The lower stabilization energy of hydrates compared to the total free energy of the constituents preferentially generates hydrated perovskite compounds (CH₃NH₃PbI₃.*n*H₂O) during the fabrication. To some extent, perovskite films with hydrates can help to restrict moisture-induced degradation, increasing the stability of the devices.¹⁹ The suppression of the defects by optimum amount of H₂O additives is an additional factor to improve device stability. However, at higher H₂O concentration, this may lead to breaking of the hydrogen bonds and causes the perovskite to decompose into CH₃NH₃, PbI₂ and HI molecules, thus deteriorating device performance.³⁶

For this study, all the devices/films are compared and correlated without any ETL such as BCP (bathocuproine) or Bphen (Bathophenanthroline) present and thus, the number of interfaces inside the devices are minimized for the precise determination of the influence of H₂O on the photovoltaic properties. Relatively, low PCE in control device compared to the state-of-art is due to the absence of any ETL in this structure. The inclusion of ETL will indeed improve the PCE of control as well as with H₂O additive but the PCE trend will remain the same. Furthermore, without efficient transport layers, we

found that a current density $\sim 17\text{-}20 \text{ mA}\cdot\text{cm}^{-2}$ and fill factor $\sim 70 \%$ is comparable to the reported literature.³⁷⁻³⁸

Notably, the short circuit current density (J_{SC}) and fill factor (FF) of the 1 % H₂O device is higher compared to 0 % and 0.5% H₂O and thus has a dominant role in controlling the PCE. On the contrary, at increasing H₂O concentrations, J_{SC} decreases and thus PCE drops to $10.1 \pm 0.7 \%$ and subsequently to $8.8 \pm 0.5 \%$ at 2 % and 5 % H₂O, respectively. This decrease in PCE was also previously documented in the literature. **Figure 1c** shows an increase of the photon absorption mainly below 500 nm wavelength with H₂O additive peaking at 1% in perovskite film with subsequent drop consistent with J_{SC} . Thus, the improved performance of devices with 1 % H₂O can be correlated with the better photo-absorption and suppressed recombination losses to yield better charge transport properties compared to control devices.

Figure 4: (a) Schematic of the inverted device architecture used for these devices, (b) current density-voltage curves of the various additive concentration: 0 vol% H₂O control film, 0.5 %, 1 vol%, 2 vol% and, 5 vol% H₂O. (c) The champion cell performance with an additive concentration of 1 vol% H₂O and hysteresis. (d) The statistical PCE data based on 25 devices.

Table 2: Summary of the perovskite solar cells photovoltaic parameters under 1 Sun illumination with different H₂O concentrations.

vol % H ₂ O	PCE (%)	J _{sc} (mA-cm ⁻²)	V _{oc} (V)	FF
0	9.9 ± 0.5	17.8 ± 0.5	0.82 ± 0.01	0.69 ± 0.02
0.5	10.3 ± 0.4	18.5 ± 0.4	0.82 ± 0.01	0.68 ± 0.02
1	11.4 ± 0.9	19.5 ± 0.9	0.81 ± 0.02	0.72 ± 0.02
2	10.1 ± 0.7	18.1 ± 0.7	0.82 ± 0.02	0.68 ± 0.02
5	8.8 ± 0.5	17.7 ± 0.8	0.78 ± 0.02	0.64 ± 0.02

Discussion

Charge trapping centers due to the formation of uncoordinated Pb bonds at $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces and grain boundaries can increase trap-assisted recombination. By introducing a small amount of H_2O during film processing, a fraction of the H_2O molecules can attach to the uncoordinated bonds via hydrogen bonding, while the remaining will be completely evaporated during annealing. The existence of hydrogen-bonded H_2O molecules in the inorganic PbI_6 cage was observed by Müller *et al.* using infrared spectroscopy³⁹.

From our experiments, we found that an optimum concentration of 1 vol% H_2O sufficiently passivates the uncoordinated bonds and is low enough to prevent moisture-induced degradation. The low activation energies of water adsorption (0.27 eV - 0.31 eV)⁴⁰⁻⁴¹ enable H_2O molecules to penetrate readily into the bulk and surface as well to form hydrated perovskite phases via water-intercalation. The formation of these hydrated phases with large bandgap (~ 3.1 eV)¹⁶ helps form a diffusion barrier that to some extent, offers some protection to the perovskite from further H_2O exposure. This leads to a suppression of the trapping sites, thus reducing trap-assisted recombination, lengthening the lifetimes, diffusion lengths and improving the performance.

At exceedingly high H_2O content, the high chemical potential of H_2O promotes perovskite decomposition to these light-insensitive hydrates; resulting in weak absorption and PL emission⁴². Hence, charge transport properties and performance are poor. Subsequently, they readily decompose into PbI_2 and organic moieties are released, resulting in complete degradation¹⁶.

Conclusions

In summary, we investigated the carrier dynamics in H_2O additives perovskite films and correlated our photophysical results with photovoltaic device data. We found that trace amounts of H_2O effectively recrystallizes $\text{CH}_3\text{NH}_3\text{PbI}_3$ grain boundaries and passivates the trap states leading to reduced

recombination rates and higher J_{SC} . At the optimal additive concentration of 1 vol% H_2O , the greatly reduced monomolecular and bimolecular recombination rates were correlated with an increase in power conversion efficiencies. As the H_2O additive concentration is increased past the optimal additive concentration, competing factors affect the carrier recombination and photophysical constants. In high H_2O concentrations, the preferential dissolution of CH_3NH_3I compared to PbI_2 can increase the trap density. Thus, a corresponding increase in monomolecular and bimolecular recombination rates was observed in the 2 to 5 vol % H_2O samples. This shows that H_2O additive concentration of strongly influences trap densities and the carrier dynamics in the perovskites, and correspondingly, the photovoltaic performance. Higher concentrations of H_2O would instead counteract the beneficial effects, and lead to degradation of the films and devices. Importantly, a clear understanding of these structure-function relations provides crucial guidance for device fabrication and also the design of newer perovskites.

Experimental

Preparation of $CH_3NH_3PbI_3$ perovskite solution

The 40wt% perovskite solution was prepared using equal molar of CH_3NH_3I (Dyesol, 98%) and PbI_2 (Acros Organics, 99%) were mixed with anhydrous DMF (Sigma Aldrich, 99.9%) and stirred at 70°C for two hours. The base perovskite solution is then divided equally into four separate bottles. To achieve the desired additive concentration (0, 1, 2 and 5 vol% H_2O) in the perovskite solutions, different volume ratios of de-ionized water were then added in the corresponding bottles. All these solutions were further stirred for 30 minutes and filtered with 0.45 μm polytetrafluoroethylene (PTFE) filter before spin coating for device fabrication.

Device fabrication and thin film samples

To fabricate the inverted architecture perovskite solar cell devices, indium-tin-oxide (ITO)-coated glass substrates (Xin Yan Technology Company, 15 Ω /square) were first cleaned in an ultrasonic bath

sequentially by using deionized water followed by a mixture of acetone, ethanol and isopropyl alcohol in equal volumes. A 30 ± 5 nm thick hole transporting layer of PEDOT:PSS (Clevios HTL Solar SCA388P VP Al 4083) was spin-coated onto the plasma-treated substrates. The PEDOT:PSS-coated substrates were then heated on a hotplate at 130°C for 15 min and transferred into a N_2 glove box. The perovskite active layers were individually prepared by spin-coating the corresponding perovskite solutions (with and without H_2O additive) on the PEDOT:PSS-coated substrates at a speed of 5000 RPM for 12 seconds. Solvent engineering of the perovskite active layer was performed using 100 μL of toluene, dripped 3 seconds into the start of the spin-coating and the samples were subsequently annealed at 100°C for 30 minutes. Afterward, PC_{61}BM (Sigma Aldrich), dissolved in chlorobenzene with a concentration of 20 mg mL^{-1} , was spin-coated at 1200 RPM for 45s. Finally, a 100 nm thick silver cathode was deposited on the active layers by thermal evaporation through a shadow mask with an active area of 0.07 cm^2 . For characterization and optical spectroscopy, we used thin film samples that were prepared by spin-coating perovskite solutions for each additive concentration on plasma-treated glass substrates using the same fabrication method as the devices' active layer. Samples used for diffusion length measurements are prepared in a bilayer architecture, with either PC_{61}BM or PEDOT:PSS used as the electron and hole quencher, respectively, and these samples are prepared using the recipes described earlier.

Device characterization

The current density-voltage (J - V) characteristics of the perovskite devices were measured using a Keithley SMU 2400 under 100 mWcm^{-2} simulated AM 1.5G illumination.

Thin film sample characterization

UV-Vis absorption spectra of the thin films were measured using a Shimadzu UV-2510PC spectrophotometer. The XRD spectra of the perovskite films were measured with a Bruker A8 Advance X-Ray diffractometer ($\text{Cu K}\alpha$, $\lambda=1.5406\text{\AA}$). SEM images were obtained using a JEOL JSM6700F field

emission scanning electron microscope. BioScope Resolved atomic force microscopy from Bruker was used to scan the morphology.

Optical spectroscopy

Time-resolved and steady-state photoluminescence of the samples excited with 600 nm pulses were collected using a backscattering geometry at an angle of $\sim 150^\circ$ by a collimating lens pair. A Coherent OPerA Solo optical parametric amplifier pumped with a Coherent LibraTM regenerative amplifier (50 fs, 1KHz, 800 nm) was used for the excitation wavelength. The steady-state photoluminescence was collected using a fibre coupled to an Acton Spectra Pro 2500i spectrometer with a Princeton Instruments PIXIS 400B CCD camera. The time-resolved photoluminescence was collected by an Acton Spectra Pro 2300i monochromator coupled to an Optronis OptoscopeTM streak camera, which has a temporal resolution of ~ 10 ps.

Supporting Information

The XRD data, SEM/AFM images, steady-state/transient pump intensity dependent PL spectra, recombination fitting dynamics for perovskite films with different water concentration and PCE stability data are described in supporting information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

A.S. and T.C.S. conceived the idea for the manuscript. A.S. fabricated the devices and characterized and also prepared samples for optical measurements. S.S.L. conducted optical characterization and simulated the data. T.C.S., S.M., A.S. and S.S.L. analyzed the data and wrote the manuscript.

Acknowledgments

Financial support from Nanyang Technological University start-up grant M4080514 and; the Ministry of Education AcRF Tier 2 grant MOE2016-T2-1-034; from the US Office of Naval Research (ONRGNICOP-N62909-17-1-2155) and from the Singapore National Research Foundation (NRF2018-ITC001-001, and NRF-NRFI-2018-04) is gratefully acknowledged.

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TOC

Supporting Information

Role of Water in Suppressing Recombination Pathways in CH₃NH₃PbI₃ Perovskite Solar Cells

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Results

X-ray Diffraction pattern

Figure S1. X-ray diffraction spectra of the different samples with varying H₂O additive concentrations: (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O.

Scanning electron microscopy images

Figure S2. SEM images of perovskite films prepared from solutions with varying water additive concentration (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O; 1% indicates perovskite solution with 1 vol% H₂O additive.

Figure S3: AFM images (2 $\mu\text{m} \times 2 \mu\text{m}$) of perovskite films prepared from solutions with varying water additive concentration with root-mean-square roughnesses of the various samples: (a) $Rq_{0\%} = 4.9 \text{ nm}$, (b) $Rq_{1\%} = 4.4 \text{ nm}$, (c) $Rq_{2\%} = 4.5 \text{ nm}$ and (d) $Rq_{5\%} = 4.7 \text{ nm}$ for the varying vol% H₂O-added perovskite films.

Figure S4. Power-dependent photoluminescence (PL) measured in the low fluence regime to extract trap densities in the perovskite films with varying H₂O additive concentrations: (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O.

Figure S5. Power dependent time-resolved PL (TRPL) traces fitted with mono- or biexponential decay functions to extract the PL lifetimes and their associated amplitudes in the perovskite films with varying H₂O additive concentrations: (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O.

Figure S6. Power dependent TRPL traces fitted with the recombination rate equation (see main text) to extract the monomolecular and bimolecular recombination rate constants in the perovskite films with varying H₂O additive concentrations: (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O.

Figure S7. Diffusion length measurements of the in the perovskite films with varying H₂O additive concentrations: (a) 0%, (b) 1%, (c) 2% and (d) 5 vol% H₂O with the respective quencher (black: neat film, red: PCBM layer, green: PEDOT layer) measured at a fluence of 0.5 $\mu\text{J cm}^{-2}$. Symbols are the data obtained from PL measurements, solid lines are exponential fits.

Trap density calculation: Initial photogenerated carrier density in different perovskite films were estimated using Plank Equation ($\alpha E = nhc/\lambda$) (Equation S1), where α is the absorption coefficient at 600 ($=\lambda$) nm while E , n , h , c are excitation pump fluence, charge carrier density, plank constant and light velocity, respectively. α is calculated using equation $\alpha = I/L$ (Equation S2) where I is the absolute absorption intensity at 600 nm and L represents the film thickness (~ 275 nm). In order to estimate the defects density, the integrated steady state PL intensity for the different perovskite films was fitted with the model:

$$n_c(0) = \sum n_{TP}(0)(1 - e^{-k_1 I_{PL}}) + k_2 I_{PL} \quad \text{Equation S3}$$

where $n_c(0)$ and n_{TP} represent photogenerated charge carrier density and trap density, respectively while k_1 , k_2 are the constants.

Figure S8: Comparative study of device degradation of 0% and 1% H₂O added solar cell devices.