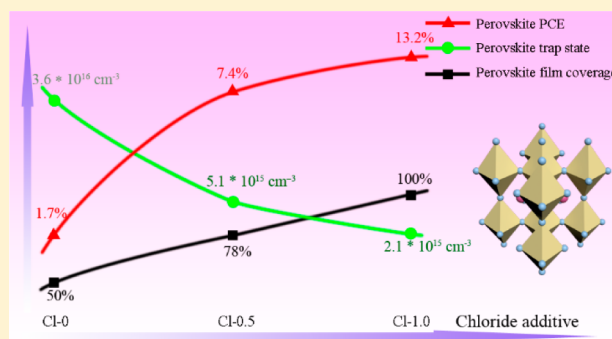


Evolution of Diffusion Length and Trap State Induced by Chloride in Perovskite Solar Cell

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ABSTRACT: Chloride (from PbCl_2 or $\text{CH}_3\text{NH}_3\text{Cl}$) has been reported to improve the morphology of perovskite thin film and power conversion efficiency (PCE) of corresponding perovskite solar cells (PSCs). However, the mechanism why chloride functions well in perovskite is unclear. In this work, we investigate the effects of chloric additive (from $\text{CH}_3\text{NH}_3\text{Cl}$) on the morphology, diffusion length, and trap state of perovskite thin film, as well as the PCE of PSC. We find that the chloric additive can significantly increase the hole and electron diffusion length and also reduce the bulk trap-state density in perovskite thin film, which is considered to be the main reason for improving the performance of PSC. These results contribute to better understanding of the function of chloride in perovskite and suggest room to further improve the PCE of PSC via decreasing the trap state in perovskite film.



1. INTRODUCTION

Hybrid organometallic lead halide-based perovskite materials have attracted huge attention due to their excellent optoelectronic properties. The hybrid organometallic lead halide, especially methylammonium lead triiodide (MAPbI_3), is reported to possess long carrier diffusion length, biomolecule transport properties, and high mobility, making it most popular candidate for photovoltaic devices.^{1–7} Recent report shows the diffusion length of MAPbI_3 single crystals up to 175 μm under 1 sun illumination.⁸ Besides, the internal quantum efficiency (IQE) approaching 100% in 3 mm (mm) and exceptionally low trap-state densities on the order of 10^9 to 10^{10} per cubic centimeter are reported in the thick single crystal perovskite.⁸

The defects in perovskite absorbers play a critical role on determining the carrier diffusion length and the device performance, especially on the open circuit voltage (V_{oc}) of a solar cell.^{9,10} Defects usually act as nonradiative recombination centers, which are responsible for the short carrier lifetime, the short diffusion length, and low V_{oc} . To improve the performance of halide perovskite-based thin-film solar cells, it is crucial to investigate the formation mechanisms of the defects in perovskite.

So far, the reported diffusion length of perovskite thin film is much smaller than that of the single crystal.^{11–13} The former one is greatly affected by the fabrication process. One of the longest reported diffusion lengths of perovskite thin film is approximately 1 μm ,¹¹ fabricated by precursor containing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ (MAI). Yet no obvious chloride is measured in the final films,^{11,14,15} while the electron–hole diffusion lengths of the films are around 100 nm (nm) made from precursor of

PbI_2 and MAI. The difference in the diffusion lengths for the above two cases should be ascribed to the control of morphology by the presence of chloride.^{16–18} However, the underlying mechanism, i.e., the relationship of morphology, defects, and diffusion length are still unclear.

In this study, we reported the transformation of diffusion length and trap state induced by chloride for efficient perovskite solar cell. Our study revealed the relationship between perovskite film morphology, diffusion length, and trap state through step-up of the chloric additive, which is the underlying reason for determining the perovskite device performance. Through this method, we revealed that chloric additive could largely increase the hole and electron diffusion length and also reduce the bulk trap-state density in perovskite film, which is considered the main reason for improving the perovskite solar cell performance.

2. EXPERIMENTAL METHODS

2.1. Materials. Anhydrous *N,N*-dimethylformamide (DMF, 99.8%), hydroiodic acid (HI, 57 wt % in H_2O), hydrochloric acid (HCl, 37% in H_2O), methylamine (CH_3NH_2 , 33 wt % in EtOH), and PbI_2 (99.999%) were purchased from Sigma-Aldrich. [6,6]-Phenyl- C_{61} -butyric acid methyl ester (PCBM) was purchased from Solarmer Material. Poly(9,9-bis[30-(*N,N*-dimethyl)-*N*-ethylammonium-propyl-2,7-fluorene]-*alt*-2,7-

Received: July 11, 2016

Revised: August 31, 2016

Published: August 31, 2016

(9,9-dioctylfluorene)]dibromide-electrolyte (PFN-Br) was obtained from 1-Material.

For synthesizing $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and $\text{CH}_3\text{NH}_3\text{Cl}$ (MACl), the methylamine (33 wt % in EtOH; 20 mL) was diluted with absolute EtOH (100 mL) in a 250 mL round-bottom bottle in an ice bath. Then, 10 mL of HI (57 wt % in H_2O) or 15 mL of HCl (37% in H_2O) was added dropwise to the bottle, and the solution had been stirred for 2 h. A white precipitate was obtained after putting the solution at 40 °C for 6 h in a vacuum chamber. The white precipitate was recrystallized with diethyl ether and ethanol mix solvent and finally dried in an oven at 60 °C for 12 h.

The perovskite precursor solutions with different MACl ratio were prepared by dissolving 1 mmol PbI_2 , 1 mmol MAI, and x mmol MACl in 1 mL DMF solution and stirring at room temperature for 12 h. If $x = 0$, it is defined as PV: Cl-0; if $x = 0.5$, it is defined as PV: Cl-0.5; if $x = 1.0$, it is defined as PV: Cl-1.0.

2.2. Device Fabrication. Perovskite solar cells were fabricated on precleaned half-coated ITO glass substrates. PEDOT:PSS (Clevios PVP Al 4083) was spin-coated at 2000 rpm on a precleaned ITO substrate, forming a PEDOT:PSS layer with thickness of 40 nm. The perovskite precursor solutions were spin-coated on the top of PEDOT:PSS layer at 4000 rpm, forming a 300 nm thick film. The substrates were then thermally annealed at 60 °C for 1 h and then 100 °C for 20 min in glovebox. The PCBM layer was spin-coated at 1000 rpm from a chlorobenzene solution (20 mg/mL). The PFN-Br layer was forming on the PCBM layer from 0.2% MeOH solution. A 100 nm Ag electrode was finally thermally evaporated on top of the device under a vacuum pressure of 3×10^{-4} Pa, with a device area of 0.06 cm^2 .

2.3. Material and Device Characterization. (a) Time-resolved photoluminescence: The time-resolved fluorescence spectra were measured with a high-resolution streak camera system (Hamamatsu Steak Scope C4334). The excitation pulses were provided by a mode-locked Ti:sapphire femto-second laser system (Mira900, Coherent) and frequency doubled to 405 nm. The repetition rate of the output pulses from the laser system was reduced to 4.75 MHz by the Coherence Model 9200 Pulse Picker. All the samples were measured at room temperature with the excitation fluence in the range from 1 to 2.6 $\mu\text{J cm}^{-2}$ per pulse.

(b) Optical characterization: The time-integrated photoluminescence spectra of the samples were collected with a miniature spectrometer (USB2000 + UV-vis, Ocean Optics). For the excitation power-dependent measurement, the samples are excited at 405 nm (150 fs, 4.75 MHz) by the second harmonic of the mode-locked Ti:sapphire laser. The excitation fluence on the sample was in the range from 10 nJ cm^{-2} to 2 $\mu\text{J cm}^{-2}$ per pulse. For the amplified spontaneous emission (ASE) gain measurement, the samples were excited at 532 nm (6 ps, 100 Hz) pulses with the excitation fluence range from 30 $\mu\text{J cm}^{-2}$ to 600 $\mu\text{J cm}^{-2}$ per pulse.

(c) Data analysis for optical measurement: The time-resolved photoluminescence curves at the PL peak were fitted using mono- or biexponential functions for samples without the quencher layer. For samples with the electron quencher or the hole quencher layer, a charge carrier extraction model based on the one-dimensional diffusion equation was employed to estimate the charge carrier diffusion lengths from their PL decay curves. The densities of the surface traps and bulk traps

of each film were estimated by analyzing the dependence of the temporal-integrated PL intensity (TIPL) on the pump fluence.

3. RESULTS AND DISCUSSION

3.1. Effects of Chloric Additive on Film Morphology.

To investigate how the presence of chloride leads to the uniquely varied morphology, crystallinity, diffusion length, and trap-density, we performed the perovskite film with different ratio of MACl additive to MAI. First, the morphologies present great modification under chloric additive, as shown in Figure 1.

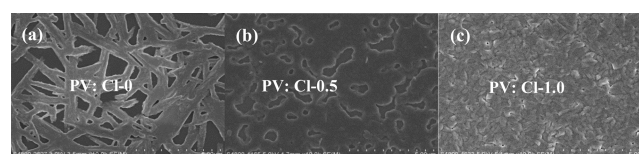


Figure 1. SEM images of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ film morphology with different ratio of chloric additive. (a) Without chloric additive (PV: Cl-0), (b) 0.5 chloric additive (PV: Cl-0.5), (c) 1.0 chloric additive (PV: Cl-1.0). The scale bar is 5 μm .

Figure 1a shows a SEM image of perovskite fabricated from chloric free precursor (PV: Cl-0), spinal structure with coverage about 50%. The gradual increase of chloric additive prompts the formation of small closely packed crystallites. Shown in Figure 1b,c, as we incorporate increasing amounts of chloric additive, the coverage of the perovskite gradually increased to approximately 78% (0.5 chloric additive, PV: Cl-0.5) and almost 100% (1.0 chloric additive, PV: Cl-1.0). This result is consisted with previous reports.^{19,20} The chloric additive could prolong the crystallization perovskite time and alter the grain-growth direction. As is evident from the SEM image, the film from the chloric free precursor (MAI + PbI_2) formed a spinal structure, while the film from chloric precursor (MAI + PbI_2 + $x\text{MACl}$) tended to crystallize at plane direction. The crystallization time of chloric perovskite film is 1 h under 60 °C thermal annealing, compared with instant crystallization of chloric free perovskite film. The crystal's surface might be restructured upon the formation of the intermediate phase, forming a thermodynamically favored structure through chloric atomic diffusion to minimize surface energy.

3.2. Effects of Chloric Additive on Diffusion Length.

Carrier recombination lifetimes measured by transient photoluminescence are commonly taken as hallmark of semiconductor film quality, with longer decay lifetimes used as indicators of better performing materials.^{21–23} We probed the fundamental impact of different chloric additive ratio on the perovskite film by the time-resolved photoluminescence (PL) measurement at room temperature. The selective perovskite films were excited by femtosecond (fs) laser pulses in vacuum, and the PL transients were measured with a streak camera (Hamamatsu Steak Scope C4334). Figure 2a shows the PL decays of the perovskite films collected at the PL peak (~ 780 nm) under the excitation of 405 nm laser pulses (4.75 MHz, 150 fs). The pump fluences on sample PV: Cl-0.5 and sample PV: Cl-1.0 were $\Phi \approx 1 \mu\text{J cm}^{-2}$. Sample PV: Cl-0 was excited under pump fluence of 2.6 $\mu\text{J cm}^{-2}$ due to the relative weaker PL emission intensity. Perovskite films grown from non-stoichiometric mixed halide (Cl/I) precursor solutions followed similar single-exponential-decay trends and exhibited lifetimes about 100 ns. On the contrary, the PL lifetimes of films grown from chloride-free precursors were generally much shorter. One

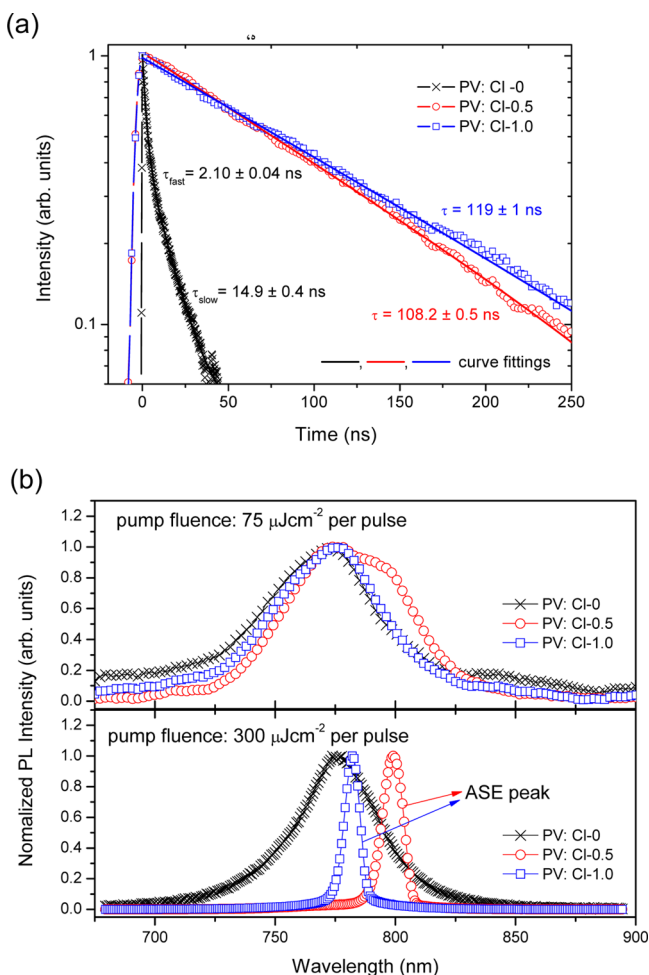


Figure 2. Time-resolved PL decay curves (a) and the temporal-integrated PL spectra (b) for perovskite films grown from chloride-free precursors (PV: Cl-0, black crosses), with 0.5 chloric additive (PV: Cl-0.5, red circles) and 1.0 chloric additive (PV: Cl-1.0, blue squares) under excitation of 405 nm laser. The solid lines in (a) are the single-exponential (red and blue) or double-exponential (black) fits of the PL decay transients. The PL spectra of the three films in (b) were measured in vacuum under excitation of 532 nm (100 Hz, 6 ps) laser. The upper panel in (b) shows the PL spectra under low excitation intensity where the emission is due to spontaneous emission, while the lower panel is under high pump fluence, which the high quality samples show ASE effect with spectral narrowing.

should notice the fast component present in the initial PL dynamics with the $1/e$ decay times of 2.1 ns was due to Auger recombination, while the longer-time decay corresponded to the trap or defect effects.²⁴ This observation indicates cleaner material system with low levels of disorder or impurity for films fabricated from chloric precursor, which was also confirmed by the lower amplified spontaneous emission (ASE) threshold and consequently the narrower full width at half-maximum (fwhm) of the PL peaks in the films (Figure 2b) under the same excitation conditions. For example, the ASE threshold of $(193 \pm 12) \mu\text{J cm}^{-2}$ and a gain of $(229 \pm 7) \text{ cm}^{-1}$ pumped at $260 \mu\text{J cm}^{-2}$ were obtained for the PV: Cl-1.0 film, while these values are $(360 \pm 20) \mu\text{J cm}^{-2}$ and $(161 \pm 3) \text{ cm}^{-1}$ (pumped at $492 \mu\text{J cm}^{-2}$), respectively, for PV: Cl-0.

3.3. Effects of Chloric Additive on Trap State. The much shorter photoexcited carrier lifetime in the perovskite thin film PV: Cl-0 and the relative higher ASE threshold

suggest the competing nonradiative pathways rapidly deplete the carrier population. These nonradiative pathways include the bulk or surface trap-assisted recombination, and the multi-particle effects such as bimolecular and Auger charge recombination processes.^{18,25,26} To further investigate the impact of different chloric additive ratio on the perovskite thin film quality, we estimated the trap states density of the films by analyzing the dependence of the temporal-integrated PL intensity (TIPL) on the pump fluence. Under the low fluence excitation region, where Auger recombination is negligible, the dynamics of photogenerated charge carrier density can relax either through band-edge emission or trap-mediated nonradiative pathways.^{27–29} The relationship between the time-integrated photoluminescence intensity I_{PL} and the initial photogenerated charge carrier density $n_c(t=0)$ is (adapted from the Supporting Information of ref 30):

$$n_c(t=0) = \sum_i n_{\text{TP}}^i (1 - e^{(-a_i \tau_0 I_{\text{PL}}/k)}) + I_{\text{PL}}/k \quad (1)$$

where n_{TP}^i is the initial trap states density, a_i is the product of trapping cross section and carrier velocity, τ_0 is the PL decay lifetime, and k is a constant.³⁰ The initial charge carrier density injected by optical pumping at the film surface was estimated by multiplying the laser pulse photon fluence times the film absorption coefficient. It was in the range from 10^{15} to 10^{18} cm^{-3} , for laser pulse fluence varied from 10 nJ cm^{-2} to $2 \mu\text{J cm}^{-2}$ (405 nm, 150 fs, 4.75 MHz). As shown in Figure 3, the

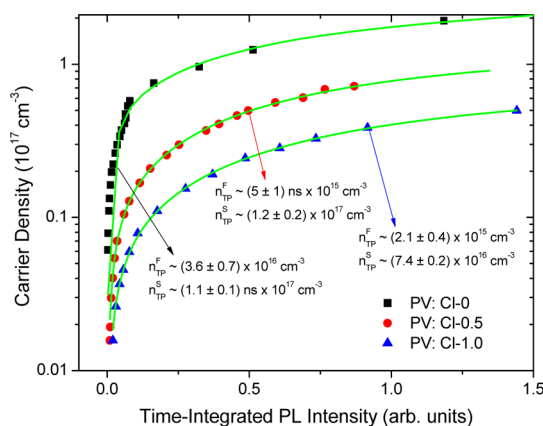


Figure 3. Trap state densities determined for the perovskite films by fitting the PL intensity as a function of photon-generated charge carrier density within the low pump fluence range. n_{TP}^{F} is the density of the fast bulk traps, and n_{TP}^{S} is the density of the slow surface traps. The symbols represent the experimental data for the perovskite thin films and the green curves are the fittings using eq 1. The excitation of the fluence-dependent PL measurement was performed with laser pulses centered at 405 nm, with pulse width of 150 fs, and the repetition rate of 4.75 MHz. The pumping fluence ranged from 10 nJ cm^{-2} to $2 \mu\text{J cm}^{-2}$ per pulse.

experimental data can be well-fitted with eq 1 using two types of traps, the fast bulk traps and the slow surface traps. The bulk trap densities are in the range of $n_{\text{TP}}^{\text{F}} \approx 10^{15} \text{ cm}^{-3}$ for the perovskite films fabricated from precursors with chloric additive, which are an order of magnitude smaller than the one from chloride-free precursors. This is consistent with the time-resolved PL experiment results in Figure 2a that the sample PV: Cl-0 exhibits a much faster trapping time compared to the other two samples. What's more, the reduced trap density in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ compared with $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin

film has also been reported by Hutter et al.³¹ and Stewart et al.³² On the condition of excitation laser pulse fluence $\Phi > 1 \mu\text{J cm}^{-2}$ (corresponding to an optical injected carrier density of $n_c \approx 6.9 \times 10^{16} \text{ cm}^{-3}$), trap states in PV: Cl-0.5 and PV: Cl-1.0 were filled and the relaxation of the charge carriers were dominated by the radiative decay process, giving rise to the strong PL emission and a relative long PL decay lifetime in the films.

To compare the free charge mobility for the solution-processed perovskite thin films, a layer of PCBM or P3HT was fabricated on top of the MAPbI_3 perovskite film, which acted as the electron quencher or the hole quencher layer. Under identical excitation conditions, the PL emission was greatly reduced, and the PL lifetimes were much shorter in these bilayer systems (Figure 4). A charge carrier extraction model based on the one-dimensional diffusion equation was employed to estimate the charge carrier diffusion lengths:^{11,30}

$$\frac{\partial n_c(x, t)}{\partial t} = D \frac{\partial^2 n_c(x, t)}{\partial x^2} - kn_c(x, t) \quad (2)$$

where $n(x, t)$ is the number and distribution of the laser pulse generated charge carrier density in the active material film, which follows the boundary condition of $n(L, t) = 0$, L is the perovskite film thickness, D is the diffusion coefficient of the charge carrier, and $k = 1/\tau_e$ is the original PL decay rate in the absence of the quencher layer. The diffusion length L_D of the charge carriers in the perovskite thin film was then determined from $L_D = \sqrt{D\tau_e}$. Figure 4 shows the diffusion model fits on the experimental data of PV: Cl-0 ($L \approx 450 \text{ nm}$), PV: Cl-0.5 ($L \approx 310 \text{ nm}$), and PV: Cl-1.0 ($L \approx 400 \text{ nm}$) with the electron (PCBM) or hole (P3HT) quencher layer, and the fitting parameters D and L_D are indicated in the figure. The diffusion lengths exceed 100 nm in the films grown from chloric additive precursor for both electrons and holes. Besides the hole diffusion coefficients and lengths are 3 times greater than those of the electrons. The inequivalent mobility between holes and electrons suggests that following photoexcitation, electrons are the trapped species while the holes are the predominant diffusion species.

3.4. Effects of Chloric Additive on Perovskite Solar Cell Performance. We fabricated a series of planar heterojunction perovskite solar cells (PSC) to study the trap state transformation effect on the overall solar cell performance. The device architecture is composed of a PEDOT:PSS³³ as the hole-collection layer deposited on ITO/glass, a MAPbI_3 perovskite absorber layer, a PCBM/PFN-Br as electron-selective layer,³⁴ and Ag as electrode. We measured the current density–voltage (I – V) characteristics of such devices under a simulated air mass (AM) 1.5G (100 mW/cm^2 of sunlight), as shown in Figure 5a. For the device without Cl additive, the average device efficiency is as low as 1.7%. While the devices with a small amount of Cl additive (Cl-0.5) has improved efficiency with short-circuit current density (J_{sc}) of 16 mA/cm^2 , an open-circuit voltage V_{oc} of 0.85 V, fill factor (FF) of 0.54, and a power conversion efficiency (PCE) of 7.4%. For more Cl additive to become Cl-1 devices, it delivered J_{sc} of 19.3 mA/cm^2 , V_{oc} of 0.92 V, FF of 0.75, and PCE of 13.23%. The PCE distribution is shown in Figure 5b, which presents good reproducibility of the perovskite devices. Table 1 summarizes the device performance of the three devices with different amounts of chloric additive.

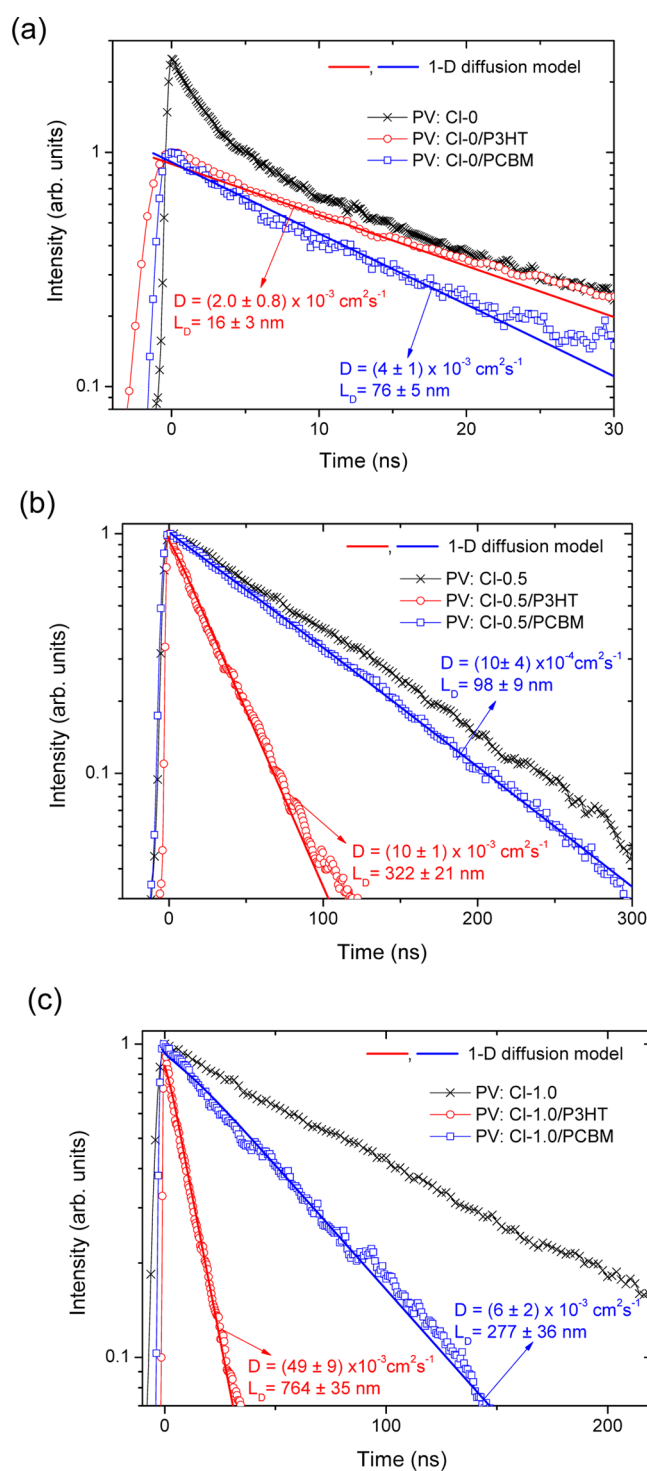


Figure 4. Time-resolved PL measurements for perovskite films grown from precursor without (a) and with (b,c) chloric additive, along with fits to the diffusion model for the perovskite films in the presence of quenchers. The diffusion coefficient D and the diffusion length L_D was determined by fitting the PL transients of samples with a hole (P3HT, red circles) or electron (PCBM, blue squares) quencher layer using the one-dimension diffusion model. The fast decay component present in the initial PL dynamics of PV: Cl-0 was ignored when estimating the original PL lifetime of the sample for the diffusion model fitting.

Figure 5c presents X-ray photoelectron spectroscopy (XPS) for perovskite film prepared from $\text{CH}_3\text{NH}_3\text{I}:\text{PbI}_2:\text{CH}_3\text{NH}_3\text{Cl}$ precursor, thermally annealed at 60 °C for 1 h, and then 100 °C

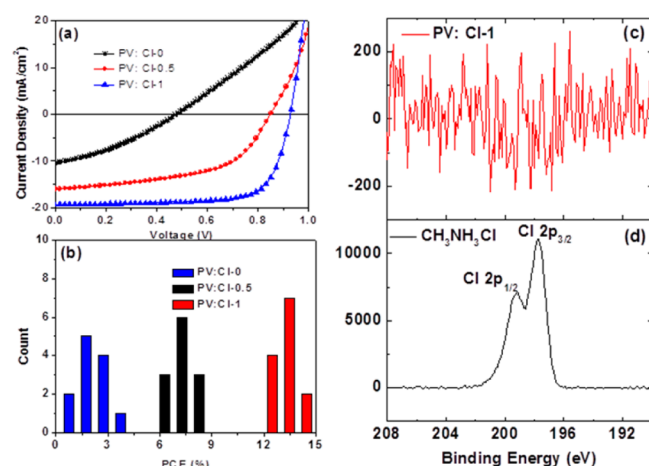


Figure 5. Perovskite solar cell with different ratio of chloride additive. (a) Current density–voltage characteristics and (b) solar cell efficiency distribution from 12 tested devices. XPS spectra (Cl 2p core level) of (c) a perovskite film derived from $\text{CH}_3\text{NH}_3\text{I}:\text{PbI}_2:\text{CH}_3\text{NH}_3\text{Cl}$ precursor, thermally annealed at 60 °C for 1 h and then 100 °C for 20 min in glovebox, and (d) MACl film.

Table 1. Performance Summary of Perovskite Solar Cells with Different Ratio of Chloride Additive

devices	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
Cl-0	10.08 ± 4.13	0.47 ± 0.12	0.36 ± 0.08	1.70 ± 1.28
Cl-0.5	16.02 ± 2.21	0.85 ± 0.05	0.54 ± 0.07	7.35 ± 1.14
Cl-1.0	19.33 ± 1.19	0.92 ± 0.02	0.75 ± 0.02	13.2 ± 0.82

for 20 min in glovebox. Upon thermally annealing the film 60 °C for 1 h and then 100 °C for 20 min, the elemental contents of chlorine decreased to below the detection limit of 0.01 atom %. We conclude that chlorine compound is removed upon thermal annealing, which is similar to our previous study.²⁰ The XPS result suggests that the chlorine was completely removed from the film, so it did not act as a dopant to influence the trap state and diffusion length.

Combining the analysis of morphology, diffusion length, trap-state, and device performance, we could obtain a full view of the function of chloric additive in PSCs. By gradually adding chloric additive, the morphology coverage of the perovskite thin film is increased, and PSCs device performance gradually improves (i.e., see Figure 1). The film coverage and device performance was reported to have a corresponding relationship.³⁵ The better the film coverage, the higher the PSC performance. Except for that, we find that the diffusion length, trap-state, and device performance have the same corresponding relationship with the film morphology. When the film changes from lower coverage to good dense film, the total number of surface defects reduce. Meanwhile, since high dense and good crystallized film will form when chloride additive increases, the bulk defects will reduce.²¹ The trap states/defects form nonradiative recombination center that limits the carrier diffusion length and device performance.²⁶ For Cl-0 device, the perovskite film had high bulk trap states of $3.6 \times 10^{16} \text{ cm}^{-3}$ and short hole diffusion length of 15 nm and electron diffusion length of 76 nm, resulting in the very poor device performance. By adding Cl additive with ratio of 0.5, the bulk trap state of perovskite film greatly decreased to $0.51 \times 10^{16} \text{ cm}^{-3}$. The electron diffusion length increased to 98 nm, and the hole diffusion length increased to 322 nm. The V_{oc} of the Cl-0.5

device increased from 0.47 to 0.85 V, due to the reduced trap state and lower carrier recombination. When ratio of Cl additive was increased to 1, the film coverage reached almost 100%, and the trap state density continued to decrease. Long electron and hole diffusion lengths (277 and 764 nm) were obtained. These results suggest that the Cl could increase the coverage of the film and simultaneously reduce the trap state. The Cl was finally removed from the film, so it would not act as dopant to influence the trap state and diffusion length. Accordingly, the device perovskite performance was improved. We could see a trend that the device efficiency is governed by the trap state of the perovskite film. Lower trap-state density leads to high performance perovskite solar cell.

4. CONCLUSIONS

In sum, we have studied the effects of chloride additive (induced of MACl/MAI = 0, 0.5, and 1.0) on the diffusion length and trap state transformation of perovskite solar cells. Our study reveals the relationship between perovskite film morphology, diffusion length, and trap state through increasing the amount of chloric additive. We find that the underlying reason for determining the perovskite device performance is the trap state. We reveal that chloric additive can largely increase the hole and electron diffusion length and also reduce the bulk trap-state density in perovskite film, which is considered the main reason for improving the perovskite solar cell performance. These observations suggest the room for improvement upon already remarkable PSC efficiencies via decreasing the trap state in perovskite film.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study is supported by the General Research Fund grant HKU711813 and HKU17211916, the Collaborative Research Fund grant C7045-14E, Area of Excellence Scheme AoE/P-02/12 from the Research Grants Council of Hong Kong Special Administrative Region, China, grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories, and ECF Project 33/2015 from Environment and Conservation Fund.

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