Understanding the Mechanism of PbCl₂ Additive for MAPbl₃-Based Perovskite Solar Cells

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PbCl₂ additive engineering is an effective method to decrease the charge accumulation in devices. Herein, the influence of PbCl₂ additive on the charge transport properties of inverted planar MAPbl₃ perovskite devices is investigated by capacitance–voltage (C–V) spectroscopy. The C–V curves show that the ΔVpeak of the MAPbl₃–Clₓ-based device is decreased compared to the undoped device, indicating that the introduction of chloride ions effectively mitigates charge accumulation at the interface. Simultaneously, it is proposed that the introduction of chloride ions into the perovskite lattice can decrease the trap density, which promotes charge carrier separation/transport at the electrode interfaces/absorber interface, as evidenced by photoluminescence measurements. The findings of this study clarify that trap states and charge accumulation in the MAPbl₃ perovskite solar cell have a considerable influence on carrier separation/transport, enhancing the device performance to ultimately achieve power conversion efficiency (PCE) from 12.3% to 15.5%. Accordingly, this work paves the way for further improving the efficiency of perovskite solar cells.

1. Introduction

Organic–inorganic perovskite photovoltaics have attracted extensive attention due to their outstanding features such as low cost, excellent ambipolar charge transport capability,[1–4] and low exciton binding energy.[5,6] To date, perovskite solar cells have achieved power conversion efficiencies (PCEs) of over 25.5%[7–10]; this achievement is due to improvements to the preparation process and in the intrinsic characteristics of the materials.[11] Many studies have demonstrated that regulation of the photosensitive layers can effectively improve the photovoltaic efficiency of perovskite solar cells.[12–15] However, the physical mechanism underpinning photovoltaic devices still requires further exploration and optimization to enhance photovoltaic performance. Charge accumulation at the absorber and electrode interfaces impedes the movement of charge carriers during the transportation of electron–hole pairs, leading to a significant loss in the PCE. Impedance analyzers have been used extensively to investigate the interfacial combination/transportation of perovskite solar cells.[16,17] In addition, previous reports have demonstrated that the introduction of chloride ions into perovskites can decrease the trap state density and provide a favorable polarizable system in methylammonium (MA)-based devices.[18,19] Therefore, minimizing localized polarization in perovskite photovoltaic devices and its impacts on device performance would be a significant step in enhancing the PCEs of perovskite solar cells.

In the present study, impedance spectroscopy was used to demonstrate that charge carrier accumulation can modify the potential barrier at the electrode interface during perovskite photovoltaic device operation. The introduction of 0.15 M PbCl₂ additive affected accumulation of charge carriers, affecting the polarization characteristics and internal trap state density of the device and ultimately enhancing the device performance. Adjusting the interplay between the composition of the perovskite absorber layer and the trade-off between charge carrier accumulation/recombination and trap states characteristics...
provided an effective method to enhance the photovoltaic performance of the device.

In addition, transient photocurrent measurements were used to compare the charge extraction ability and transmission variation of the devices with and without PbCl₂ additive, and the mechanism by which PbCl₂ affected the internal physical processes of the devices was determined. The results showed that the charge accumulation and trap state of the perovskite solar cell were greatly influenced by the separation of excited states and charge carriers, which enhanced the PCE of the MAPbI₃-based solar cell device.

2. Results and Discussion

The devices were fabricated with a typical p–i–n device structure: ITO/PEDOT:PSS/perovskite:PCBM/PEI/Ag according to the detailed fabrication procedure described in the Experimental Section. The energy-level alignment is shown in Figure 1a and the corresponding work functions of each functional layer are cited in a previous report. The J–V curves with and without PbCl₂ additive in the active layer of the perovskite solar cells under AM 1.5G are shown in Figure 1b and the corresponding photovoltaic parameters are summarized in Table 1. The addition of 0.15 M PbCl₂ into the perovskite absorber layer improved the performance of the device compared to without PbCl₂ additive; the PCE increased from 12.3% to 15.5% without and with 0.15 M PbCl₂ additive, respectively. In addition, the short-circuit current (J_sc) was notably improved from 16.16 to 19.57 mA cm⁻², whereas the fill-factor (FF) was slightly improved from 0.74 to 0.75. From external quantum efficiency (EQE) results, the integrated J_sc values were 16.13 and 19.32 mA cm⁻² for the control and PbCl₂-additive devices, respectively; this finding was consistent with the J–V measurement values, as shown in Figure 1c. To verify the repeatability of the device, the device efficiency distribution over 30 devices without and with PbCl₂ additive is shown as a statistical histogram in Figure 1d. None of the devices were protected with an extra capping layer.

It is known that the morphology of the perovskite active layer is crucial to the device performance. To investigate the effect of the modulated perovskite active layer, AFM and XRD measurements were performed on the perovskite films with and without PbCl₂ additive, as shown in Figure 2. All perovskite samples showed distinct diffraction peaks at 14.1°, 28.3°, and 43.1°, which correlated with the (110), (220), and (330) perovskite crystal planes, respectively. The peak intensity was stronger with additive. It was also observed that the perovskite grain size was slightly larger after a small amount of PbCl₂ was introduced. Based on previous findings, larger crystals are beneficial for decreasing the number and size of grain boundaries, reducing defects, and promoting efficient charge transfer across devices, thereby improving device efficiency. It has been reported that chlorine additives can facilitate efficient charge transfer through

Table 1. Photovoltaic parameters of without and with 0.15 M PbCl₂ additive-based perovskite solar cells over 30 devices.

| PbCl₂  | J_sc [mA cm⁻²] | Voc [V] | FF [%] | PCE [%] |
|--------|----------------|---------|--------|---------|
| 0      | Average 16.08 ± 0.58 0.99 ± 0.02 73 ± 1.4 11.7 ± 0.4 |
|        | Best 16.16 1.02 74 12.3 |
| 0.15 M | Average 18.30 ± 0.84 1.06 ± 0.02 0.74 ± 1.1 14.5 ± 0.6 |
|        | Best 19.57 1.06 75 15.5 |

Figure 1. a) Energy alignment diagram of p–i–n structure device. b) J–V characteristics. c) EQE spectra of devices. d) Statistics histogram of device efficiency distributions over 30 devices without and with PbCl₂ additive. All devices were without encapsulated.
perovskite crystals, thereby improving the film quality. The chemical reactions can be described as follows:

\[ \text{PbI}_2 + \text{MAI} \rightarrow \text{MAPbI}_3 \]  

\[ \text{PbCl}_2 + 3\text{MAI} \rightarrow \text{MAPbI}_3 + 2\text{MACl} \]

According to previous literature reports, following introduction into the precursor solution in the form of \( \text{PbCl}_2 \), chloride eventually volatilizes in the form of \( \text{MACl} \). This chemical process introduces \( \text{PbI}_2 \) into the obtained film, which passivates the grain boundary and facilitates charge transfer. To further explore the effect of the improved perovskite surface morphology on its charge transfer properties, photoinduced dielectric response spectra were measured using an impedance analyzer. The interfacial charge carrier accumulations in the perovskite solar cell devices with and without \( \text{PbCl}_2 \) additive were determined using impedance spectroscopy. It should be noted that charge carrier accumulation at the interface provides a barrier potential for charge transport, and this ultimately influences the \( V_{OC} \) and \( J_{SC} \). All measurements were performed under irradiation intensities that varied from dark to 1 sun, as shown in Figure 3a,b, respectively. Based on the \( C–V \) curves, it was determined that the capacitance under dark conditions were 4.15 and 4.49 nF for the devices with and without \( \text{PbCl}_2 \) additive, respectively. Specifically, a perovskite solar cell device can be treated as a parallel plate capacitor while applying vertical bias. As a result, the increased capacitance at the interface provides a barrier potential for charge transport, and this ultimately influences the \( V_{OC} \) and \( J_{SC} \). The capacitance increased rapidly with an increasing applied voltage between 0 V and \( V_{peak} \) (corresponding to the maximum capacitance). The \( V_{peak} \) of the perovskite device with \( \text{PbCl}_2 \) additive decreased from 87 to 45 mV due to photogenerated charge carriers accumulation at the interface with increasing irradiation intensity. The reduced \( \Delta V_{peak} \) was determined by the charge barrier at the interface, which was a favorable transmission to increase the device performance.

These findings suggested that the incremental changes in the capacitance with increasing voltage changed to rapidly decreased capacitance when the applied voltage was greater than \( V_{peak} \). In this voltage range, charge carriers were injected from the electrode toward the active area, resulting in insufficient charge and charge recombination; thus, \( Q_{eff} \) and capacitance were decreased. By comparison, the capacitance decreased as a function of voltage \( (\Delta C/V) \) under dark conditions, and AM 1.5G, as shown in Figure 3c,d. Under dark conditions, the rates of capacitance change of the devices without and with \( \text{PbCl}_2 \) additive were 7.9 and 38.7 nF V\(^{-1}\), respectively. These results indicated that the \( \text{PbCl}_2 \) additive vastly increased the electric polarization of perovskite film, thus reducing the binding energy of electron–hole pair recombination. Considering that the rate of capacitance increased as a function of voltage, it was found that the rates of capacitance change in the devices without and with \( \text{PbCl}_2 \) additive were 12.7 and 35.1 nF V\(^{-1}\), respectively, which indicated that there was significant charge buildup at the electrode interface. The rate of incremental variation of photogenerated charge carriers reflects the charge transport efficiency across solar cell devices, which indicates that localized electron polarization is enhanced via additive engineering.

In conclusion, the \( C–V \) results appeared to be consistent with the AFM measurements. The effect of the \( \text{PbCl}_2 \) additive on the charge carrier properties of the device was determined by steady-state and transient PL
spectroscopy (Figure 4). The perovskite films were excited by a 532 nm laser beam with constant photoexcitation intensity for steady-state PL measurements. The steady-state PL intensity of the perovskite film increased when PbCl₂ additive was present, as shown in Figure 4a, indicating that the introduction of chloride ions promoted radiative recombination and suppressed non-radiative recombination. Essentially, there were fewer defects in the perovskite film when PbCl₂ was added, which led to suppression of nonradiative recombination.

Meanwhile, a lower trap state density is conducive to more efficient charge transfer and subsequent separation. The carrier lifetime was used to evaluate the concentration of trap states in the perovskite film from the transient PL spectra, with the lifetime being proportional to the diffusion length.\(^{35}\) By performing appropriate fitting on the transient PL spectra (Figure 4b), the corresponding lifetime values were obtained using the single exponential decay function \(y = y_0 + Ae^{-(x-x_0)/\tau}\). The lifetime \((\tau_2)\) of the perovskite film with PbCl₂ was 75 ns and the lifetime \((\tau_1)\) of the perovskite film without adjustment was 32 ns. The longer carrier lifetime for perovskite containing PbCl₂ indicated that the perovskite layer had fewer trap states, which is beneficial for effective charge transport.\(^{22,36}\)

The charge trapping and charge extraction time of the perovskite photovoltaic devices were quantitatively assessed by transient photocurrent measurements, with the results verifying the charge transfer and trap state properties of the devices (Figure 5). To carefully compare their performance, the transient photocurrent of the MAPbI₃ and MAPbI₃₋ₓClₓ-based devices were measured under different photoexcitation intensities of 6.8, 7.9, 13.3, and 21.2 mW cm\(^{-2}\). The perovskite layer absorbs photons from pulsed light excitation to generate photogenerated charge carriers. The photogenerated charge carriers initially filled

\[ y = y_0 + Ae^{-(x-x_0)/\tau} \]
the existing trap states, with the remaining charge carriers being converted into readable photocurrent. A higher trap state density indicates low device efficiency performance. In the present study, it was found that the rising and falling edges of the photocurrent curve of the devices were strikingly different when the pristine and PbCl₂-doped samples were compared, indicating that the perovskite solar cells had non-negligible trap states. The saturation speed of the MAPbI₃/C₀ₓClₓ perovskite photovoltaic device was faster than that of the MAPbI₃ perovskite photovoltaic device, as shown in Figure 5a,b. This indicated that PbCl₂ additive reduced the internal trap state density of the device. Specifically, the saturation speed of the device was faster under the higher photoexcitation intensity. This can be understood as being due to a faster trap filling process driven by sufficient photogenerated charge carriers.

The quantity of trapped charge extraction (Figure 5c) under different light intensities was obtained by integrating the falling edge of the transient photocurrent curve. The trapped state charge in the MAPbI₃₋ₓClₓ-based device was lower than that in the MAPbI₃-based device, suggesting that the PbCl₂ additive would decrease the trap state density in the device. The single exponential decay function was used to fit the falling edge of the transient photocurrent curve to estimate the charge extraction time (Figure 5d) of the trapped charge in the photovoltaic device. Based on the fittings, it was found that the MAPbI₃₋ₓClₓ-based photovoltaic device required a shorter extraction time than its MAPbI₃ counterpart.

Therefore, it is proposed that the addition of PbCl₂ to the MAPbI₃-based perovskite played a crucial role in decreasing the trapped charge density of the solar cell device. The demonstrated change in the extraction time provides a promising new avenue for the improvement of the charge transport performance of MAPbI₃₋ₓClₓ-based photovoltaic device via additive engineering.

3. Conclusion

The effect of the addition of PbCl₂ on charge transportation in MAPbI₃-based photovoltaic devices was studied using electrical spectroscopic measurements. The introduction of chloride ions improved the morphology of the perovskite films, which led to a reduction in trap state density, thereby enhancing charge transport performance. The grain size and morphology of the perovskite film with PbCl₂ additive was more prominent, which decreased the trap state density. In addition, the probability of nonradiative recombination of perovskite was suppressed, which consequently improved the charge transport performance. The C–V curves under dark and light conditions showed that PbCl₂ regulation enhanced the electric polarization of the perovskite, eventually increasing the charge distribution within the photovoltaic device sufficiently to enhance device efficiency. Furthermore, the transient photocurrent illustrated that upon addition of PbCl₂ into the pristine perovskite the trap state density was decreased, which in turn increased the speed of charge extraction. As a result, additive engineering delivered a PCE increase from 12.3% to 15.5% with a negligible hysteresis effect.

4. Experimental Section

Material Processing and Device Fabrication: The perovskite absorber layers were prepared using an antisolvent method and assembled in a
p–n structure device. The MAPbI₃ precursor solution was formed using a 1:1 ratio of PbI₂ and MAI in mixed DMSO–γ-GBL solvent (7:3, 1.4 M). PbCl₂ (0.15 M) replaced PbI₂ for the MAPbI₃, CI₂ precursor solution. PbI₂ and MAI was evaporated to form the electrode on the fabricated to obtain C

The monitoring wavelength of the time-resolved PL spectroscopy was 423 nm. The photoluminescence spectra were recorded using an Edinburgh FLS920. A HORIBA Scientific DeltaPro was used to record the PL lifetime of active layers. The measurement wavelength of the time-resolved PL spectroscopy was 770 nm. An Agilent 4294A impedance spectroscopy analyzer was used to obtain C–V spectra from dark to 1 sun at AM 1.5G. The test mode was C–V, replaced from −0.3 to 1.5 V (1 kHz frequency, 50 mV amplitude). X-ray diffraction (XRD) spectra were recorded by a X-ray diffractometer (Bruker D8 Advance).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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[1] J. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, S. I. Seok, Nat. Photonics 2013, 7, 486.
[2] A. K. Tangra, M. Sharma, U. Zainudeen, G. S. Lotej, J. Mater. Sci. Mater. Electron. 2020, 31, 13657.
[3] G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, T. C. Sum, Science 2013, 342, 344.
[4] X. Liu, Z. Liu, J. Li, X. Tan, B. Sun, H. Fang, S. Xi, T. Shi, Z. Tang, G. Liao, J. Mater. Chem. A 2020, 8, 3337.
[5] A. Miyata, A. Mitigou, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, Nat. Phys. 2015, 11, 582.
[6] W. Zhang, M. Saliba, S. D. Stranks, Y. Sun, X. Shi, U. Wiesner, H. J. Snaith, Nano Lett. 2013, 13, 4505.
[7] Y. Chen, S. Tan, N. Li, B. Huang, X. Niu, L. Li, M. Sun, Y. Zhang, X. Zhang, C. Zhu, N. Yang, H. Zai, Y. Wu, S. Ma, Y. Bai, Q. Chen, F. Xiao, K. Sun, H. Zhou, Joule 2020, 4, 1961.
[8] N. J. Jeon, H. Na, E. H. Jung, T.-Y. Yang, Y. G. Lee, G. Kim, H.-W. Shin, S. I. Seok, J. Lee, J. Seo, Nat. Energy 2018, 3, 682.
[9] Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, J. You, Nat. Photonics 2019, 13, 460.
[10] M. Kim, G.-H. Kim, T. K. Lee, I. W. Choi, H. W. Choi, Y. Jo, Y. J. Yoon, J. W. Kim, J. Lee, D. Huh, H. Lee, S. K. Kwak, J. Y. Kim, D. S. Kim, Joule 2019, 3, 2179.
[11] R. Zhang, H. Ling, X. Lu, J. Xia, Sol. Energy 2019, 186, 398.
[12] J. Su, Q. Zheng, Y. Shi, J. Zhao, J. Phys. Chem. Lett. 2020, 11, 9032.
[13] T. Soto-Montero, W. Soltanpoor, M. Morales-Masis, APL Mater. 2020, 8, 110903.
[14] L. Wang, I. King, P. Chen, M. Bates, R. Lunt, APL Mater. 2020, 8, 100904.
[15] C. Dong, Z.-K. Wang, L.-S. Liao, APL Mater. 2020, 8, 100703.
[16] F. Ebadi, N. Taghavinia, R. Mohammadpour, A. Hagfeldt, W. Tress, Nat. Commun. 2019, 10, 1574.
[17] H. Zang, Y. C. Hsiao, B. Hu, Phys. Chem. Chem. Phys. 2014, 16, 4971.
[18] T. Wu, L. Collins, J. Zhang, P. Y. Lin, M. Ahmadi, S. Jese, B. Hu, ACS Nano 2017, 11, 15142.
[19] D. Niesen, H. Zhu, K. Miyata, A. P. Joshi, T. J. Evans, B. J. Kudisch, M. T. Trinh, M. Marks, X. Y. Zhu, J. Am. Chem. Soc. 2016, 138, 15717.
[20] Y. Xie, K. Lu, J. Duan, Y. Jiang, L. Hu, T. Liu, Y. Zhou, B. Hu, ACS Appl. Mater. Interfaces 2018, 10, 14153.
[21] W. Chen, L. Xu, X. Feng, J. Jie, Z. He, Adv. Mater. 2017, 29, 1603923.
[22] F. Jiang, Y. Rong, H. Liu, T. Liu, L. Mao, W. Meng, F. Qin, Y. Jiang, B. Luo, S. Xiong, J. Tong, Y. Liu, Z. Li, H. Han, Y. Zhou, Adv. Funct. Mater. 2016, 26, 8119.
[23] Y. Chen, J. Shi, X. Li, S. Li, L. Xv, X. Sun, Y.-Z. Zheng, X. Tao, J. Mater. Chem. A 2020, 8, 6349.
[24] J. X. Zhong, W. Q. Wu, J. F. Liao, W. Feng, Y. Jiang, L. Wang, D. B. Kuang, Adv. Energy Mater. 2020, 10, 1902256.
[25] W. Qarony, M. I. Hossain, V. Jovanov, A. Salleo, D. Knipp, Y. H. Tsang, ACS Appl. Mater. Interfaces 2020, 12, 15080.
[26] Y. Xie, H. Yu, J. Duan, L. Xu, B. Hu, ACS Appl. Mater. Interfaces 2020, 12, 11190.
[27] S. Shao, M. Abdu-Agye, T. S. Sherkar, H.-H. Fang, S. Adjokatse, G. T. Brink, B. J. Kooi, L. J. A. Koster, M. A. Loi, Adv. Funct. Mater. 2016, 26, 8094.
[28] J. Zhang, J. Qin, M. Wang, Y. Bai, H. Zou, J. K. Keum, R. Tao, H. Xu, H. Yu, S. Haacke, B. Hu, Joule 2019, 3, 3061.
[29] K. Lu, C. Zhao, L. Luan, J. Duan, Y. Xie, M. Shao, B. Hu, J. Mater. Chem. C 2018, 6, 5055.
[30] Q. Chen, H. Zhou, T.-B. Song, S. Luo, Z. Hong, H.-S. Duan, L. Dou, Y. Liu, Y. Yang, Nano Lett. 2014, 14, 4158.
[31] I. Zarazua, G. Han, P. P. Boix, S. Mhaisalkar, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, G. Garcia-Belmonte, J Phys. Chem. Lett. 2016, 7, 5105.

[32] M. Ahmadi, Y.-C. Hsiao, T. Wu, Q. Liu, W. Qin, B. Hu, Adv. Energy Mater. 2017, 7, 1601575.

[33] J. Rivett, L. Z. Tan, M. B. Price, S. A. Bourelle, N. Davis, J. Xiao, Y. Zou, M. Rox, B. Sun, A. M. Rappe, Nat. Commun. 2018, 9, 3531.

[34] Y. Dou, M. Wang, J. Zhang, H. Xu, B. Hu, Adv. Funct. Mater. 2020, 30, 2003476.

[35] W. Ning, F. Wang, B. Wu, J. Lu, Z. Yan, X. Liu, Y. Tao, J. M. Liu, W. Huang, M. Fahlman, L. Hultman, T. C. Sum, F. Gao, Adv Mater. 2018, 30, e1706246.

[36] C. Fei, L. Guo, B. Li, R. Zhang, H. Fu, J. Tian, G. Cao, Nano Energy 2016, 27, 17.