Investigation of chlorine-mediated microstructural evolution of CH$_3$NH$_3$PbI$_3$(Cl) grains for high optoelectronic responses

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A B S T R A C T

An organic-inorganic hybrid perovskite is considered as a next generation solar energy harvester due to the high power conversion efficiency. The starting precursor solution for the organolead halide perovskite is of significant interests because the ionic components in the precursor can critically affect the nanostructures and thereby the optoelectronic properties. In this work, the basic and well-known precursor solution for CH$_3$NH$_3$PbI$_3$(Cl) comprised of CH$_3$NH$_3$I and PbCl$_2$, is specifically analyzed to unravel the phenomena in the Cl-mediated solutions. The shift in equilibrium between lead-halide complex and the solvent results into the CH$_3$NH$_3$PbI$_3$(Cl) grain evolution with Cl incorporation, which is confirmed through x-ray fluorescence and diffraction. The effects of Cl on the optoelectronic properties are further verified by conductive atomic force microscopy, and the existing Cl leads to the 30-times-increased and inhomogeneously distributed photocurrent for CH$_3$NH$_3$PbI$_3$(Cl) grains compared with CH$_3$NH$_3$PbI$_3$. Moreover, photocurrent noise from the mixed-halide perovskite is reduced than that from the triiodide perovskite phase. Combining the microstructural evolution with the optoelectronic properties of mixed-halide perovskite, it is concluded that additional Cl reduces the defects of recombination centers resulting high photocurrent.

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1. Introduction

An organic-inorganic hybrid perovskite is considered as a next generation solar energy harvester, and the perovskite solar cell has reached ~20% high power conversion efficiency recently [1]. Its high absorption coefficient, low exciton binding energy, long charge carrier diffusion length, and low trap density enable the methylammonium lead iodide perovskite (MAPbI$_3$: triiodide perovskite) to be an excellent material as a light harvester. The basic principles lying in the superior solar cell performance are the high charge generation in the light harvesting material, and facile separation followed by the collection of generated charges into each electrode without the significant loss through the recombination [2]. Since MAPbI$_3$ phase intrinsically meets these demands for high cell performance, many strategies have been attempted to improve the power conversion efficiency, mainly focusing on the fine tuning of crystallinity, morphology, and the composition [3–5]. Several earlier studies reported on the improvement of the overall perovskite quality by reducing the intrinsic traps and minimizing any recombination paths in the cell through complete coverage [6–9]. To resolve these, various synthesis methods such as vapor deposition, vapor-assisted solution process, and liquid solution process have been introduced [10–13]. Also, the compositional variation is investigated by replacing the constituents of MAPbI$_3$ with alternative cations/anions like Sn$^{2+}$, HC(NH$_2$)$_2$$^{+}$, Br$^-$, or Cl$^-$ to alter the optical properties [14–17].

Especially, the role of chlorine in the physicochemical evolution of the MAPbI$_3$ phase is one of the most appealing topics. Morphological effects including preferential orientation, crystallinity improvement, and large grain evolution are commonly observed. However, the compositional effects such as doping in the bulk, passivation at the grain boundary, bonding at the interface of the TiO$_2$ electrode, etc. have been reported with various possibilities [18–25]. Considering that reactions among the starting compounds and the phase transformations of the constituents from the liquid solution to the solid perovskite film give an indication of the functions of ionic species in the precursor solution, and finally the
composition and nanostructures in the solid films, precursor characterization is thus of top priority in deeply understanding the crystallization of the perovskite phase [26–30]. Unveiling the details of the reactions and fundamental phase transformations from the elementary step, i.e., basic recipe of MAI and PbCl₂ mixing (hereafter referred as mixed-halide solution, and resulting perovskite as mixed-halide perovskite or MAPbI₃(Cl)) will provide a key to understand the role of chlorine.

Besides the microstructural effects, the optoelectronic role of chlorine and its relation with the nanostructural chemistry are the essence parameters comprising the high solar cell performance. Conductive-probe AFM (cAFM) can measure the current from each grain by directly contacting with the conductive probe, and it is proven to be a powerful tool for characterizing the electronic properties of the light harvesting materials such as CIGS, CZTS, CdTe, MAPbI₃, etc. [31–38]. Simultaneous mapping of the microcrystalline topography with the optoelectronic response from each grain will reveal the electronic role of chlorine directly by comparing the different compositional perovskites.

Herein, the microstructural evolution of MAPbI₃(Cl) grain was scrutinized, specifically focusing on the identification of the ionic components in the mixed-halide precursor solution and the equilibrium shift therein. The as-deposited mixed-halide perovskite film was annealed at different temperatures to monitor the chlorine effect, and the simple temperature control gave an evidence of chlorine remaining in the mixed-halide perovskite from x-ray diffraction and fluorescence analyses. Finally, the role of chlorine on the optoelectronic properties and the noise characteristics, which is for the first time to our knowledge, was examined. Consequently, the existing chlorine led to the 30-times-increased photocurrent and decrease of recombination centers in MAPbI₃(Cl) compared with MAPbI₃.

2. Experimental procedures

2.1. CH₃NH₃I synthesis

CH₃NH₃I (MAI) was synthesized from mixing the CH₃NH₂ solution and the HI solution by 1:1 molar ratio in a round-bottom flask at 0 °C for 2 h under stirring. The solvent was evaporated, and the precipitate was washed with diethyl ether for 3 times and then further washed with the 1:1 vol ratio mixture of anhydrous ethanol and diethyl ether. The precipitate was dried at 60 °C for 24 h in a vacuum oven.

2.2. PbI₂ pre-coating and perovskite deposition

For mixed-halide perovskite precursor solution, MAI (2.64 M) and PbCl₂ (0.88 M) were dissolved in n,n-dimethylformamide (DMF) and the solution was stirred at 100 °C for 10 min. The selection of the temperature and the time for the heating were critical for the perovskite film formation since the high temperature heating induced the color change of the solution from yellow to dark brown by the formation of triiodide ion which blocked the perovskite crystallization from charge imbalance of triiodide ion as shown in Fig. S1 (including the details of experimental conditions). Dissolved oxygen reacted with I⁻ ion and H⁺ resulting I₃⁻ ion and H₂O formation, and therefore the preheating conditions for the solution were carefully chosen [39]. For triiodide precursor solution, MAI and PbI₂ with identical concentrations to the mixed-halide solution were dissolved in DMF and the solution was stirred at the same condition. Prior to the conventional one-step perovskite deposition, the PbI₂ pre-coating was performed by spin-coating the 1.0 M of PbI₂ solution (DMF) on the porous TiO₂ electrode (TiO₂ on FTO). The PbI₂ solution was preheated at 100 °C and vigorously stirred to disperse the PbI₂ particles in the solution uniformly, and the TiO₂ substrate was preheated likewise to prevent the supersaturation of the solution drop. The pre-coated PbI₂ layer was then dried to remove the remaining solvent at 70 °C for 30 min. Perovskite precursor solution (either triiodide or mixed-halide) was spin-coated at 2000 rpm for 60 s on the PbI₂ pre-coated layer or the TiO₂ substrate, and the films were annealed at 100 °C for 50 min. To check the x-ray peak shift, mixed-halide perovskite was annealed differently where annealing temperature was controlled from 90 °C to 160 °C with 10 °C interval at constant annealing time. Further analyses were examined from the perovskite made using pre-coating method except for the perovskite with specially mentioned. All the perovskite deposition was pressed in air, and the films were kept under dark and vacuum conditions before the analyses.

2.3. Characterization

2.3.1. Precursor analyses

The extinction of the solution was recorded through a UV-vis spectrophotometer (Cary 5000: Agilent Technologies). For mixed-halide solution, the concentration of PbCl₂ was varied from 305 μM to 20 mM while constantly maintaining the 3:1 molar ratio between MAI and PbCl₂. The solutions were pretreated identically to the film deposition condition before the measurement. Triiodide precursor solution was made by dissolving 100:1 molar ratio between MAI and PbI₂ with the concentration of 260 μM (PbI₂), and the chosen of 1:0.1 molar ratio was to clearly distinguish both the PbI₃⁻ and PbI₂⁻ complexes [26]. The PbI₂ solution (in DMF) was measured as a reference for comparison.

2.3.2. Microstructural and optoelectronic analyses

The crystal structure was examined by x-ray diffraction (XRD) (D8 Advance: Bruker). Wavelength-dispersive x-ray fluorescence (WDXRF) (XRF-1800: Shimadzu) using Rh Kα as x-ray source (20.216 keV) was adopted to analyze the elements in the perovskite film, and the analyzing single crystals were LiF (200) and Ge (111). The surface was analyzed by x-ray photoelectron spectroscopy (XPS) (AXIS-His: Kratos) using Al Kα x-ray (1486.7 eV). The field-emission scanning electron microscope (FESEM) (Merlin Compact: Zeiss) was used to observe the film morphology.

An atomic force microscope (AFM) instrument (XE-70: Park System) was utilized to measure the topography and photocurrent maps on the perovskite film. A conductive Pt probe (25Pt300B: Park System) installed on the AFM was in direct contact with the surface of the perovskite sample. The contact force between the AFM probe and the surface was maintained to ~1.5 μN during the measurements by using an AFM force feedback circuit. To induce the photocurrents, a white light of ~10 mW cm⁻² (LS-F100HS: Seokwang Optical) was illuminated on the sample with a dc bias of 1.2 V between the tip and the TiO₂/FTO substrate using a function generator (DS345: Stanford Research Systems). The photocurrent signal was amplified by a low-noise preamplifier (SR570: Stanford Research Systems), and the signals were collected during the AFM scanning of the perovskite film to obtain the photocurrent map simultaneously with the topography map. The scan rate was ~0.20 Hz, and all measurements were conducted in an ambient condition with a closed box to block stray lights. Noise vs. frequency spectra were measured by positioning the tip at the perovskite domain with the identical bias. The power spectral density (PSD) spectra of the amplified current signals were measured using a fast Fourier transform (FFT) network analyzer (SR770: Stanford Research Systems). The current-normalized noise PSD spectra were obtained by normalizing the PSD spectra with respect to the power of the photocurrents.
3. Results and discussion

To understand the perovskite crystallization, the precursors were scrutinized to identify the effects of solution constituents on the microstructure evolution. When PbI₂ and MAI are dissolved in DMF, plumbate PbI₃−₂⁻ complexes are formed through van der Waals interactions between the I-terminated PbI₂ crystals and ionized I⁻ ions from MAI [26,27]. The absorption onset of the mixed-halide solution was similar to that of triiodide solution (Fig. 1(a)). In triiodide solution, PbI₂⁻ and PbI₃⁻ are featured distinctively as much higher concentration of MAI are dissolved than PbI₂ (100:1 molar ratio of MAI:PbI₂). Basic recipe of 3:1 molar ratio of MAI and PbCl₂ to observe the shift in equilibrium of the mixed-halide solution was controlled at the constant 3:1 ion-exchange as expected. However, the complicated plateau region should be further investigated.

In order to examine the absorption behavior, the concentration of the mixed-halide solution was controlled at the constant 3:1 molar ratio of MAI and PbCl₂ to observe the shift in equilibrium between the products from the MAI and PbCl₂ mixing and the solvent (Fig. 1(b)). As the PbCl₂ concentration was varied in mixed-halide solution, peak intensities from PbI₂ (370 nm) and PbI₄⁻⁻ (425 nm) followed a quadratic (bimolecular reaction) dependence on the PbCl₂ concentration (Figs. 1(c) and (d)). Based on these results, yellowish mixed-halide solution originates from the PbI₄⁻⁻ complex from PbCl₂ and MAI, as in Eq. (1). PbI₄⁻⁻ reacts with DMF differently as a concentration, and the reaction of PbI₄⁻⁻ complex in DMF indicates that the complex decomposes at low concentration as in the reaction (Eq. (2)). The complex in DMF increases quadratically in the early stage, and absorbs completely below 430 nm as the concentration of precursor solution increases (Eq. (3)) resulting in the absorption plateau. The occurrence of yellow color in the mixed-halide solution and the possible reactions between PbI₄⁻⁻ complex and polar DMF solvent depending on the concentrations are summarized as follows:

\[\text{PbCl}_2 + x \text{MAI} \rightarrow \left[\text{PbI}_x^{(x-2)^-} \cdots \text{Cl}^-\right] + x \text{MA}^+ + \text{Cl}^- \quad (1)\]

\[\text{PbI}_x^{(x-2)^-} \cdots \text{Cl}^- \rightarrow \text{Pb}^{2+} + x \text{I}^- + \text{Cl}^- \text{(in DMF)} \quad (2)\]

\[\left[\text{PbI}_x^{(x-2)^-} \cdots \text{Cl}^-\right] \rightarrow -(\text{Pb}-\text{I}-\text{Pb}-\text{I} \cdots \cdots \cdots \text{Cl}^{-}-\text{Pb}-\text{I})^- \quad \text{(framework)} \quad (3)\]

The existence of PbI₂ (320 nm) was not accurately detected due to the near-complete extinction. However, the ion exchange reaction between I⁻ and Cl⁻ results in the formation of neutral or ionized Pb-I complexes. The slight red shift of PbI₂⁻⁻ peak (by ~5 nm, as shown in Fig. S2) may be due to the coordination of Cl⁻ into the Pb-I complex and the complete extinction below 430 nm in the mixed-halide solution (compared to the triiodide solution) were observed possibly from the colloidal formation (e.g., soft Pb-
halogen ion framework), and we hereafter refer them as Pb-halide components (either complex or colloid) [26,27,30]. Various ions and neutral/ionized Pb-halide components penetrate into the porous TiO2 layer forming the perovskite nanocrystals, as an equilibration between Pb-halide components and DMF shifts to the direction in increasing the concentration of Pb-halide components, resulting in the formation of the perovskite phase with chlorine in it during the annealing process. Any remaining Pb-halide components which do not penetrate into the porous TiO2 react with MAI and finally transform into the perovskite capping layer.

The complete capping layer is essential for the application in the photovoltaic device [9]. Increasing the nucleation sites through the pre-deposition of precursor for the perovskite growth would result in the coverage enhancement with negligible voids. Distinct preparation methods of perovskite films control the crystalization kinetics, and thereby the film nanostructures and morphologies [13,40,41]. The I-terminated PbI6 octahedrons in the PbI2 layer form weak van der Waals interactions between iodine and I-terminated PbI6 octahedrons by iodine-iodine bonding. This interaction between PbI2 and Pb-halide components in the precursor is expected to assist the coverage improvement, and therefore, the conventional one-step method of dissolving two compounds in one common solvent was slightly modified by the additional PbI2 coating on the substrate prior to the one-step process. Fig. 2 shows the effect of the PbI2 pre-coating on the coverage, and this method clearly enhanced the coverage irrespective of MAPbI3(Cl) or MAPbI3 film, as expected without any remaining PbI2 impurity (diffraction data in Fig. S3). A noteworthy feature is the film morphology synthesized from the PbI2 pre-coating and the mixed-halide solution. It exhibits distinctive capping-layer comprising large grains (≈10 μm) with smaller ones (≈1 μm) for the mixed-halide perovskite film, as shown in SEM (upper right image in Fig. 2). Since the pre-coated PbI2 evolves easily into the corner-shared perovskite structure by the intercalation reaction, the original framework of layer-structured PbI2 is retained to form MAPbI3 with the additional MAPbI3(Cl) nanocrystals which are grown from the Pb-halide components in the precursor [42].

Simple experimental design of annealing-temperature control of the as-deposited precursor film can be used to check the chlorine incorporation in the mixed-halide perovskite (after the complete annealing) since the non-stoichiometric MAI or MACl component in precursor has different sublimation rate at different temperatures [43]. Different amount of excessive MAI or MACl in the precursor evaporates, thus the as-deposited precursor film will develop into microcrystalline grains with differently chlorine amounts. Therefore, x-ray diffraction was further performed to investigate the influences by the annealing-temperature variations. When PbI2 was not pre-coated, the (110) diffraction peak from MAPbI3(Cl) shifted by different annealing temperature (Figs. 3(a) and (b), and further in Fig. S4), indicating that MAPbI3(Cl) grain was developed with chlorine in it, which was coincidently observed in the precursor analyses from the slight peak shift in absorption (Fig. S2). On the other hand, such diffraction peak shift was negligible for the pre-coating case. By the development of film with blended two-type grains (upper right SEM image in Fig. 2, probably MAPbI3(Cl) and MAPbI3), the peak shift was much reduced. These observations connote that the mixed-halide solution develops MAPbI3(Cl) with chlorine in its lattice, and the Cl contents vary by different annealing

![Fig. 2. Microcrystalline evolution of perovskite with the PbI2 pre-coating method. (a) CH3NH3PbI3(Cl) (top) and CH3NH3PbI3 (bottom) perovskite without pre-coating of PbI2. (b) The perovskite coverage with the pre-coating of PbI2 layers.](image-url)
temperature due to the different evaporation rate of MAI and MACl. Even though the XPS results in Fig. S5 did not indicate the existence of chlorine (characteristic peaks of $2p_{1/2}$ and $2p_{3/2}$) probably due to the detection limit of few nanometers from the surface, XRF results (Fig. 3(c)) successfully detected the chlorine incorporation in MAPbI$_3$(Cl) [25,44–47].

Conductive AFM (cAFM) analysis was performed to compare the optoelectronic properties of MAPbI$_3$(Cl) and MAPbI$_3$. The cAFM has been widely used to measure the local photocurrents in various light-harvesting polycrystalline films, and the experimental setup is illustrated in Fig. 4. As shown in Figs. 4(a) and (b), the photocurrents from MAPbI$_3$ film were uniform from grain to grain (up to 1.36 nA). However, in MAPbI$_3$(Cl), the photocurrents were inhomogeneously distributed over the film, varying extensively.

![Fig. 3. X-ray diffraction and fluorescence of perovskite. (a) XRD of MAPbI$_3$(Cl) without PbI$_2$ pre-coating (top) and with PbI$_2$ pre-coating (bottom) at different annealing temperatures (from 90 °C to 110 °C). (b) The reference FTO peak at the identical condition. (c) XRF of Pb and Cl from MAPbI$_3$(Cl) and MAPbI$_3$ (synthesized with the PbI$_2$ pre-coating).](image-url)
from grain to grain and with the increased average value (maximum up to 60 nA) than the MAPbI$_3$ phase. The origin of inhomogeneous distribution of photocurrents in MAPbI$_3$(Cl) cannot be attributed to the inhomogeneous distribution of film heights because no distinguishable relationships between photocurrent and film height were observed, as summarized in Fig. 5(a). Moreover, photocurrents were compared at similar grains for the validity: no relationships between the grain sizes and photocurrents were observed, as shown in Fig. 5(b). Different crystallographic orientation can also be ruled out because of its highly preferred texture of (110) orientation (clear from the diffraction in Fig. S3) [48].

The large photocurrents from MAPbI$_3$(Cl) grains can be attributed to its small work function compared to MAPbI$_3$, or the decrease of the defects and consequently the reduced recombination of charge carriers [21,38,49]. To clarify the origin of the recombination decrease, scanning noise microscopy was further utilized to examine the chlorine effect in the perovskite phase [50]. As shown in the noise-spectra comparison between MAPbI$_3$(Cl) and MAPbI$_3$ grains (Fig. 6), current-normalized power spectral density of photocurrent (S/I$^2$) showed the 1/f behavior, and the noise level in MAPbI$_3$(Cl) was lower compared to that of MAPbI$_3$ [51]. One of the noise sources is the defects causing the fluctuations in the charge carrier density or the mobility [52].
the photocurrent was measured at each grain (Fig. 4(c)) reflecting the bulk properties, and in addition, the comparison at the grain boundary is obscure since the grain boundary itself affects the electronic properties [35–37]. For the comparison of electronic properties at the grain interior, several measurements were performed at different points, and the reduced noise levels for the mixed-halide perovskite were commonly observed. Relatively broad distribution of noise level was observed for the mixed-halide perovskite, compared with the approximately identical noise levels for triiodide perovskite. The possible cause for the noise reduction in the mixed-halide perovskite is the diminished defects. Decrease of the recombination sites can lead to high optoelectronic responses [47,56–58]. Moreover, non-uniformly distributed chlorine in MAPbI$_3$(Cl) causes the dispersion of the photocurrents and broad distribution of noise level [25,49]. Theoretical predictions that the Cl doping reduces the electron-hole recombination further support the high optoelectronic responses in MAPbI$_3$(Cl) [59,60].

4. Conclusions

In this work, chlorine-mediated CH$_3$NH$_3$PbI$_3$(Cl) grain evolution was explored from the equilibrium shift between lead-halide complex and the solvent in the precursor, and the evidences for the chlorine incorporation in the perovskite phase were further characterized by x-ray fluorescence and diffraction. Experimental observations of the Cl doping in the bulk are expected to lead to the high photocurrents from the reduced electron-hole recombination. Thereby, the optoelectronic properties were compared between CH$_3$NH$_3$PbI$_3$(Cl) and CH$_3$NH$_3$PbI$_3$ grains using conductive AFM, and high photocurrents from the CH$_3$NH$_3$PbI$_3$(Cl) grains were observed with non-uniform distribution from grain to grain, which was a different aspect compared to CH$_3$NH$_3$PbI$_3$. The origin of high optoelectronic response was additionally discussed, and the photocurrent noise which comes from the defects in the material was analyzed as a straightforward way to identify the recombination reduction in the CH$_3$NH$_3$PbI$_3$(Cl) grains. Combining the microstructural characterizations with cAFM and noise analyses, inhomogeneously distributed chlorine in the perovskite was confirmed to diminish the recombination centers resulting high photocurrents. As a future work, photophysical properties with the nanostructures of perovskite will be further characterized.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.04.044.

References


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Fig. 5. Photocurrent distribution and the dependence on the film height or grain size of perovskite. (a) Photocurrent distribution on the height of the perovskite film: MAPbI$_3$(Cl) (red) or MAPbI$_3$ (blue). (b) Photocurrent dependence on the grain size of MAPbI$_3$(Cl) perovskite. Yellow arrows of 1.2 μm (left image from AFM topography), and the corresponding grains with black arrows (photocurrent from cAFM in the right image). Distinctive photocurrents are clear between similar sizes of lateral grains labelling from 1 to 3.

Fig. 6. Current-normalized power spectral density (PSD), compared between MAPbI$_3$(Cl) (red) and MAPbI$_3$ (blue). Both perovskites from different precursors showed the PSD behavior which was inversely proportional to the frequency (green fitting line) with the low level of the noise for Cl-mediated perovskite. (Measurements were performed at different grains and plotted with the standard deviation.).
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Supplemental Materials

Investigation of Chlorine-Mediated Microstructural Evolution of 

$\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ Grains for High Optoelectronic Responses

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Figure S1. Color variation of MAI or MAI + PbCl₂ mixture in DMF at various temperatures and environmental conditions, the films deposited from differently pretreated mixed-halide solutions, and the extinction spectrum of MAI solution. (a) MAI (2.64 M) in DMF, (b) MAI:PbCl₂ in DMF (2.64:0.88 M) at room temperature (RT), 60°C, 90°C, and 120°C (at atmosphere condition for 24 h), and 120°C at N₂ condition for 24 h, respectively, from left to right. (c) Films from mixed-halide solution of RT, 60°C, 90°C, or 120°C preheating under ambient atmosphere, respectively. (d) Extinction spectrum of MAI solution of RT (1/100), 60°C (1/100), 90°C (1/1000), or 120°C (1/1000 dilution before measurement), respectively.
Figure S2. Detailed extinction spectra of MAI + PbI$_2$ and MAI + PbCl$_2$ in DMF. Extinction spectra of MAI + PbI$_2$ mixture (red line) and MAI + PbCl$_2$ mixture (blue line) in DMF. Fitting lines of PbI$_3^-$ (green square), PbI$_4^{2-}$ (orange triangle), Pb-I-Cl complex (purple diamond), and the sum (gray circle) of PbI$_4^{2-}$ (or Pb-I-Cl complex) and PbI$_3^-$. Vertical dashed lines represent the corresponding peak positions.
Figure S3. X-ray diffraction of MAPbI$_3$(Cl) perovskite prepared with or without PbI$_2$ pre-coating method. The inset is the magnification near the PbI$_2$ (001) peak position (JCPDS #07-0235).
Figure S4. X-ray diffraction of MAPbI$_3$(Cl) perovskite at different annealing temperatures. (a) XRD of MAPbI$_3$(Cl) synthesized without PbI$_2$ pre-coating at different annealing temperatures (from 90°C to 160°C for 45 min). (b) The corresponding FTO substrate. (c) Scattering angle of (110) and (220) planes from MAPbI$_3$(Cl) in respect of its annealing temperature.
Figure S5. X-ray photoelectron spectroscopy of MAPbI₃(Cl) and MAPbI₃ perovskite.
(a) MAPbI₃(Cl) with the PbI₂ pre-coating and (b) MAPbI₃(Cl) without PbI₂. (c) MAPbI₃ perovskite with the PbI₂ pre-coating. Circle (purple) symbols are I 5s, 4d, 4p, 4s, 3d₃/2, 3d₅/2, 3p₃/2, 3p₁/2, MnN (Auger), and 3s peaks (in sequence from low to high binding energies). Diamonds (dark yellow) are Pb 4f₇/2, 4f₅/2, 5s, 4d₃/2, 4d₅/2, 4p₃/2, 4p₁/2, and 4s peaks (from low to high energies). Triangle (black) represents the C 1s peak.