An Interlayer with Strong Pb-Cl Bond Delivers Ultraviolet-Filter-Free, Efficient, and Photostable Perovskite Solar Cells

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HIGHLIGHTS
The intrinsic mechanism of PSCs degradation under UV photocatalysis has been revealed
An interlayer with strong Pb-Cl bond has been prepared through ion-exchange
The UV-filter-free, efficient, and photostable PSCs have been achieved

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An Interlayer with Strong Pb-Cl Bond Delivers Ultraviolet-Filter-Free, Efficient, and Photostable Perovskite Solar Cells

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SUMMARY

The inorganic metal oxides (IMOs), including titanium dioxide (TiO2) and tin dioxide (SnO2), inevitably induce decomposition of perovskite under UV illumination owing to their photocatalytic activity, and the use of a UV filter will add extra cost and reduce the effective power output. Here, we first reveal that the weak Pb-I bond in I-based perovskite is prone to breakage under UV photocatalysis, leading to serious degradation of the SnO2/perovskite interface. We introduced a chlorine-rich mixed-halide perovskite interlayer (ClMPI), which possesses an excellent tolerance to photocatalysis owing to the strong Pb-Cl bond, between the SnO2 and I-based perovskite. The ClMPI-based device achieves an enhanced efficiency of up to 21.01% (certified 20.17%). Most importantly, the resultant devices can maintain >94% of their initial performance after 180 h under outdoor solar irradiation, >80% after 500 h under UV irradiation, and 500 h under continuous full spectrum illumination at their maximum power points.

INTRODUCTION

Organic-inorganic metal halide perovskites have attracted extensive attention as solution-processed and low-cost photovoltaic materials owing to their excellent properties, such as strong light absorption, high charge carrier mobility, long intrinsic carrier lifetime, and low-temperature processability (Kojima et al., 2009; Kim et al., 2012; Lee et al., 2012; Zhou et al., 2014; Bi et al., 2016; Yang et al., 2017; Liu et al., 2019). The highest certification efficiency of perovskite solar cells (PSCs) has been achieved up to 25.2% (National Renewable Energy Laboratory, n.d.), which can keep up with that of present commercial solar cells, such as silicon solar panels, copper indium gallium selenide (CIGS). Unfortunately, the device stability is still far from industrial standards, which generally require that the solar cell can deliver greater than 25 years of outdoor operation (Wang et al., 2017b). The elements in organic-inorganic halide perovskite materials, such as halogen (I, Br, Cl), methylammonium (MA+), and Pb2+, are mostly mobile, polarized, and unstable (Wang et al., 2019); thus the PSCs are vulnerable under various aging stresses such as oxygen (Aristidou et al., 2015; Pearson et al., 2016), moisture (Pearson et al., 2016; Wang et al., 2017c; Xie et al., 2016), and high temperature (Misra et al., 2015). By encapsulation, the device lifetime can be prolonged by excluding most of these external environmental factors (Han et al., 2015).

At present, the inorganic metal oxides (IMOs), including titanium dioxide (TiO2) (Yang et al., 2017; Jeon et al., 2018) and tin dioxide (SnO2) (Jiang et al., 2017a; Turren-Cruzet et al., 2018; Shi et al., 2019), are generally used as electron transport layers (ETLs) in the conventional device architecture PSCs to achieve high performance and stability. However, the PSCs stability suffers accelerating degradation owing to the well-known intrinsic photocatalysis of IMOs under the exposure of UV light (Leijtens et al., 2013; Ito et al., 2014). Such instability cannot be avoided during device operation, even if they are well encapsulated. Previous reports have shown that the degradation is most prone to occur at the interface between IMOs and perovskite (Lira-Cantu´, 2017; Li et al., 2016; Jiang et al., 2019). For example, the MAPbI3 layer can be decomposed to PbI2 with losing CH3NH2 and HI at the TiO2/MAPbI3 interface (Ito et al., 2014). To eliminate the UV effect, various methods have been reported to improve the photo-stability, such as inserting an interfacial layers (Ito et al., 2014; Zhang et al., 2016a, 2016b), using inferior UV photocatalysis materials as ETLs (Luo et al., 2017; Shin et al., 2017), and introducing a down-converting layer (Bella et al., 2016; Q. Wang et al., 2017; S. H. Wang et al., 2017; Wang et al., 2017d). It is worthy to note that most of the reported top-level photo-stability of PSCs is always carried out by completely eliminating the UV light using a UV filter or adopting a white LED illumination light without UV range (Jeon et al., 2018; Tan et al., 2017).
These additional processes either damage the device performance or increase the cost, which hinders the commercialization of PSCs (Leijtens et al., 2013). Thus, improving the intrinsic stability of perovskite active layer against UV photocatalysis is an essential approach to achieve low-cost and photo-stable PSCs.

Here, we first demonstrate that the serious degradation of I-based perovskite under UV photocatalysis is mainly caused by the breakage of weak Pb-I bonds, whereas the Cl-based perovskite possesses the best tolerance for the photocatalysis compared with the Br-based and I-based perovskite owing to the strong Pb-Cl bonds. We introduced a chlorine-rich mixed-halide perovskite (MAPb\textsubscript{1-x}Cl\textsubscript{x}) interlayer (ClMPI) between the SnO\textsubscript{2} and I-based perovskite layer through halide exchange to improve the interfacial contact and protect the I-based perovskite layer from damage by the SnO\textsubscript{2} photocatalysis. Such ClMPI could largely mitigate the interfacial recombination, and thus our device achieves an enhanced efficiency of up to 21.01% (certified 20.17%) with reduced hysteresis phenomenon. More importantly, without using any UV filter, the ClMPI-based PSCs show greatly enhanced photo-stability compared with the control ones under different conditions, including outdoor solar irradiation, high-intensity UV irradiation, and 1-sun full spectrum illumination (including UV light). Our work reveals the intrinsic mechanism for the performance degradation in I-based PSCs under UV photocatalysis and provides a fundamental approach for achieving UV-filter-free, photostable, and low-cost PSCs.

RESULTS AND DISCUSSION

In this work, the planar N-I-P PSCs with a structure of ITO/SnO\textsubscript{2}/perovskite/spiro-OMeTAD/Au were adopted; the SnO\textsubscript{2} was used as an ETL owing to its high electron mobility, wide band gap, and low-temperature preparation (Xie et al., 2017; Jiang et al., 2017a; Baena et al., 2015). Although the SnO\textsubscript{2} is considered as a material with less photocatalytic activity compared with conventional TiO\textsubscript{2}, it indeed seriously degrades the perovskite under the UV illumination (see later discussion) (Roose et al., 2016). To investigate the tolerance of perovskite for photocatalysis generated by SnO\textsubscript{2}, we grew three types of high-quality perovskite single crystals, including MAPbI\textsubscript{3}, MAPbBr\textsubscript{3}, and MAPbCl\textsubscript{3}, as shown in Figure 1A. After grinding the perovskite single crystals into powder, we uniformly mixed these powder and SnO\textsubscript{2} nanoparticles with a molar ratio of 1:1 together and then exposed these mixtures to continuous UV illumination for several days. All the operations were carried out in a N\textsubscript{2} glove box, ruling out the effects of moisture and O\textsubscript{2}.

As shown in Figure 1A, the MAPbI\textsubscript{3}:SnO\textsubscript{2} mixtures gradually turned from black to yellow in 48 h and finally became gray within 120 h, whereas the bare perovskite powder remained black at the same condition (Figure S1). It illustrates that SnO\textsubscript{2} indeed induces the accelerated degradation of MAPbI\textsubscript{3} under UV illumination. In comparison, the MAPbBr\textsubscript{3}:SnO\textsubscript{2} mixtures remained red with little gray products and the MAPbCl\textsubscript{3}:SnO\textsubscript{2} mixtures showed no obvious change at the same UV illumination time. The components of these samples were traced by X-ray diffraction (XRD) measurements, as shown in Figures 1B–1D and S2. In the MAPbI\textsubscript{3}:SnO\textsubscript{2} case, the perovskite peak was largely reduced and a strong PbI\textsubscript{2} (12.7\textdegree) characteristic peak appeared in the spectrum after 120 h UV illumination, whereas there was no PbI\textsubscript{2} peak in the case of pure MAPbI\textsubscript{3} (Jo et al., 2016; Zhao et al., 2016; Zhang et al., 2016a, 2016b). In comparison, the MAPbBr\textsubscript{3}:SnO\textsubscript{2} showed a weak PbBr\textsubscript{2} characteristic peak after 72 h UV exposure and it further increased after 120 h aging (Figures 1C and S2), whereas the PbCl\textsubscript{2} characteristic peak appeared until UV aging for 120 h (Figures 1D and S2). Furthermore, we performed the X-ray photoelectron spectroscopy (XPS) analysis to elucidate the effect of photocatalysis for the stability of different type perovskite. As shown in Figure S3, the binding energy (BE) at around 142.8 and 137.9 eV is assigned to 4f\textsuperscript{5/2}, 4f\textsuperscript{7/2} of divalent Pb\textsuperscript{2+}, respectively, and another two peaks at around 141.3 and 136.4 eV are associated with metallic Pb\textsuperscript{0} (Wang et al., 2019; Raga et al., 2015). It was observed that the Pb\textsuperscript{0} peak in MAPbI\textsubscript{3}:SnO\textsubscript{2} case increased much faster than those in MAPbBr\textsubscript{3}:SnO\textsubscript{2} and MAPbCl\textsubscript{3}:SnO\textsubscript{2} cases. We calculated the intensity ratio of ΔPb\textsuperscript{0}/Pb\textsubscript{sum} (Pb\textsubscript{sum} = Pb\textsuperscript{0} + Pb\textsuperscript{2+}) for three mixture samples based on different type perovskite after exposure to 0, 24, 48, 72, and 120 h UV illumination, as shown in Figure 1E. The ΔPb\textsuperscript{0}/Pb\textsubscript{sum} in the MAPbI\textsubscript{3}/SnO\textsubscript{2} showed a rapid increase and reached 5.42% after exposure to 120 h UV illumination. The gray one we observed corresponds to the color of Pb metal as a decomposition product of MAPbI\textsubscript{3}. At the same condition, the ΔPb\textsuperscript{0}/Pb\textsubscript{sum} in MAPbBr\textsubscript{3}/SnO\textsubscript{2} and MAPbCl\textsubscript{3}/SnO\textsubscript{2} reached 2.86% and 0.98%, respectively.

Based on these findings, we propose the degradation procedure of MAPbI\textsubscript{3} under SnO\textsubscript{2} photocatalysis expressed as the following:

\[
\text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2
\]  
(Equation 1)
In the first stage of degradation (Equation 1), the moderate PbI$_2$ product might not be harmful for the stability and efficiency of solar cells. Instead, many reports show that excess PbI$_2$ at the grain boundary or ETL/perovskite interface can be beneficial to the PSCs performance (Jiang et al., 2017b; Matsui et al., 2017; Jacobsson et al., 2016; Zhao et al., 2019). However, as the decomposed products of PbI$_2$, both Pb$^0$ and I$_2$ severely degrade the performance of PSCs, as well as their long-term photo-stability (Wang et al., 2017a, 2019; Adinolfi et al., 2016). As the decomposed product of MAPbI$_3$, PbI$_2$ is thermodynamically

$$PbI_2 \rightarrow Pb^0 + I_2$$  \hspace{1cm} (Equation 2)
stable since it has a negative standard molar Gibbs formation energy ($\Delta G^\circ$) of $-173.6$ kJ/mol (Macdonald and Lide, 2003), as shown in Figure 1F. However, actually, the PbI$_2$ can be decomposed through interfacial redox reactions of electron-hole pairs, which are generated upon band gap excitation when SnO$_2$ is exposed to UV light. The schematic diagram of a possible reaction process is shown in Figure 1F. Owing to the stronger bond strength of Pb-Cl (301 kJ/mol) and Pb-Br (248 kJ/mol) than that of Pb-I (194 kJ/mol) (Luo, 2017), the $\Delta G^\circ$ of PbCl$_2$ and PbBr$_2$ are $-314.1$ and $-261.9$ kJ/mol (Macdonald and Lide, 2003), respectively, both much more negative than that of PbI$_2$ ($-173.6$ kJ/mol). The standard redox potentials of the decomposition reactions of PbI$_2$, PbBr$_2$, and PbCl$_2$ are $-1.8$, $-2.7$, and $-3.3$ V, respectively, according to the Nernst equation $\Delta G^* = -nF \Delta E^*$ ($\Delta G^* = -\Delta G^\circ$) (Rubi and Kjelstrup, 2003). It means that much bigger thermodynamic barriers need to be overcome for decomposing the PbCl$_2$ compared with PbBr$_2$ and PbI$_2$. Thus, we systematically studied the tolerance of PbX$_2$ (I, Br, Cl) for photocatalysis and the operations were similar to the pervious MAPbX$_3$:SnO$_2$ cases (Figure S4). As shown in Figure 1G, it was observed that the Pb$^0$ peak in the PbI$_2$:SnO$_2$ case was more notable than those in the PbBr$_2$:SnO$_2$ and PbCl$_2$:SnO$_2$ cases after UV illumination. Furthermore, combining the color change and XRD measurements of the samples, we confirmed that the PbCl$_2$ is much more stable than PbBr$_2$ and PbI$_2$ under photocatalysis, which is consistent with the thermodynamic analysis (Figures S4 and S5). The above-mentioned results illustrate that the strong Pb-Cl bond leads to the suppression of the decomposition of MAPbCl$_3$ and PbCl$_2$ under SnO$_2$ photocatalysis. Although the MAPbCl$_3$ shows the best tolerance for the photocatalysis, it is not suitable to be used as a light absorption layer for the efficient PSCs owing to its broad band gap.

Then, we devised a means to achieve efficient and UV-stable I-based PSC through preparing a ClMPI between the MAPbI$_3$ and SnO$_2$ against the photocatalysis. The procedure includes two steps: (1) the preparation of a uniform NH$_4$Cl film on the SnO$_2$ through precipitation and (2) the formation of a ClMPI at the MAPbI$_3$/SnO$_2$ interface through halide exchange between MAPbI$_3$ and NH$_4$Cl, as shown in Figure 2A. We give the detailed process as following. First, we added a small amount of ammonium hydroxide (NH$_4$OH) into SnCl$_2$ precursor solution and then spin coated the prepared precursor on the ITO substrate. After treating the films at a temperature of 180°C in air, it is expected that the NH$_4$Cl can be separated out during the annealing and homogeneously distributed on the surface of the SnO$_2$. The NH$_4$Cl can be generated according to reaction (3):

$$2SnCl_2 + 4NH_4OH = 4NH_4Cl + SnO_2 + 2H_2O$$  \hspace{1cm} \text{(Equation 3)}

From the surface top view atomic force microscopy (AFM) images (Figure 2B), we found that the modified SnO$_2$ (M-SnO$_2$) surface was covered by a uniform NH$_4$Cl layer. Thus, the root-mean-square roughness of the M-SnO$_2$ surface is 3.3 nm, which is much smaller than that of bare SnO$_2$ (26.1 nm). As shown in Figure 2C, it was found that a spectral peak of N 1s appears at around 401.8 eV for the M-SnO$_2$ film, whereas the peak of N 1s is lacking for the bare SnO$_2$ film. The strong spectral peaks of Cl 2p can be also found in the M-SnO$_2$ film, whereas a very weak signal of Cl 2p that appeared in the bare SnO$_2$ film might be due to the incomplete oxidation of SnCl$_2$ (Figure 2D). Figure 2E shows the surface top view EDS mappings of the M-SnO$_2$, showing that the NH$_4$Cl is uniformly distributed on the surface of M-SnO$_2$. To clarify the existence of NH$_4$Cl, Raman spectra of pure NH$_4$Cl, SnO$_2$, M-SnO$_2$ films were conducted. As shown in Figure 2E, the sharpest peak at around 3,051 cm$^{-1}$ corresponding to the characteristic peak of ammonium chloride can be observed in the M-SnO$_2$ but cannot be found in the bare SnO$_2$. Furthermore, another Raman spectra measurement shows that the NH$_4$Cl on the surface of SnO$_2$ can be well retained after treatment by the DMF/DMSO mixed solvent (Figure 2E).

The MAPbI$_3$ film was deposited on the M-SnO$_2$ surface through spin coating and then annealed at 100°C for 10 min. During the annealing, it is expected that the CIMP will be formed through halide exchange between MAPbI$_3$ and NH$_4$Cl, which can be described as:

$$\text{MAPbI}_3 + 3\text{NH}_4\text{Cl} \rightarrow \text{MAPbCl}_3 + 3\text{NH}_4\text{I}$$  \hspace{1cm} \text{(Equation 4)}

However, as shown in Figure 2F, it is hard to detect the MAPbCl$_3$ phase by XRD measurement in CIMP-based sample mostly because of the trace amounts of Cl and the weakened signal by the thick MAPbI$_3$ films. Thus, we spin-coated the diluted perovskite solution on a thicker NH$_4$Cl film; after annealing, an obvious peak at around 15.6° corresponding to MAPbCl$_3$ perovskite (100) appeared in the XRD spectra (Figure S7).
of perovskite film (for detailed information see the experimental section). In a double-checked test, we mixed the single-crystal MAPbI₃ and NH₄Cl powder uniformly and then treated the mixtures at 100 °C for 1 h in inert atmosphere. The color of the MAPbI₃/NH₄Cl mixture turned from black to a bit gray after annealing, whereas the color of bare MAPbI₃ showed no obvious change under the same conditions, as shown in Figure S8. The XRD results show that the diffraction peaks at 15.6° ascribed to the MAPbCl₃ perovskite also appeared after annealing, confirming that the halide exchange between MAPbI₃ and NH₄Cl indeed exists (Figure S9). To investigate the distribution of ClMPI in the device, we performed time-of-flight secondary-ion mass spectrometry (ToF-SIMS) to probe the chemical composition throughout the ITO/M-SnO₂/perovskite film, as shown in Figure 2G. The result shows that the Cl is mainly accumulated at the perovskite/SnO₂ interface in ClMPI-based sample. In addition, the distribution of I and Cl at the SnO₂ side indicates that the ClMPI could be considered a mixed component of MAPbIXCl₃-X (X = 0–3); we suggest that the concentration of Cl will gradually decrease from the SnO₂ surface toward the MAPbI₃ active layer. As shown in Figures 2F and S10, the ClMPI perovskite film achieves an enhanced crystal quality and increased grain size, which will be beneficial to improve the performance of the device. It could be related to the facilitation effect of the trace amounts of product NH₄I on perovskite crystallization, which can be supported by previous reports (Si et al., 2017; Zhang et al., 2018).

Figure 2. Preparation and Characterization of the NH₄Cl and CIMPI
(A) Schematic diagram of the preparation process of CIMPI.
(B) AFM images of the bare SnO₂ film and M-SnO₂ film.
(C and D) XPS spectra of the N 1s (C) and Cl 2p (D) of SnO₂ and M-SnO₂ films.
(E) Raman spectra of the pure NH₄Cl, SnO₂, M-SnO₂, and M-SnO₂ after DMF/DMSO treatment.
(F) XRD patterns of the bare MAPbI₃ film and CIMPI-based MAPbI₃ film.
(G) The normalized ToF-SIMS results of a CIMPI-based device with a structure of ITO/SnO₂/CIMPI-based MAPbI₃.
Performance of Devices

The cross-sectional scanning electron microscope (SEM) image of the optimized device is displayed in Figure 3A, which determined the thickness of ClMPI-based perovskite layer. Although it is hard to distinguish the ClMPI in SEM, its thickness can be estimated at 10 nm according to the full width at half maximum (FWHM) of SnO$_2$ and Cl in ToF-SIMS (Figure 2G) and the thickness of SnO$_2$ (around 25 nm, Figure 3A). We systematically optimized the processing parameters for the ClMPI-based devices, and the best photovoltaic performance was attained with a molar ratio of 1:4 for NH$_4$OH:SnCl$_2$, as shown in Figure S11. Figure 3B gives the J–V curves of the champion devices with and without ClMPI. It can be found that overall photovoltaic parameters have been improved for the ClMPI-based devices and the highest power conversion efficiency (PCE) of the devices increases from 18.08% to 21.01%, with obvious reduction of hysteresis. This is consistent with a rapid increase in stabilized power efficiency to a value of 20.9%, compared with a slower increase to 18% for the control one (Figure 3C and Table 1). As presented in Figure 3D, the histogram with GaussAmp fitting of over 20 devices exhibits an average PCE of 20.2% for the ClMPI-based devices compared with 16.45% for the control devices. The integrated current densities extracted from the typical EQE spectra of ClMPI-based and control devices (Figure S12) are 21.15 and 22.35 mA cm$^{-2}$, respectively, which are closed to the measured values. To verify our device efficiency measurements, we sent one of our unsealed devices to the National Institute of Metrology, China, for independent certification and obtained a PCE of 20.17% ($V_{OC} = 1.13$ V, $J_{SC} = 23.2$ mA cm$^{-2}$, and FF = 77%), as shown in Figure S13.

The perovskite layer based on M-SnO$_2$ exhibits stronger photoluminescence (PL) quenching and faster time-resolved photoluminescence (TRPL) compared with that based on SnO$_2$, indicating the better charge extraction from perovskite to ETLs (Figure S14 and Table S1). In addition, the lower $R_S$ in the ClMPI device also indicates better charge transfer through the ClMPI layer under operation conditions and accounts for the enhanced fill factor, as shown in Figure S15. We attribute the better charge extraction at interface to the improved crystal quality and higher carrier concentration of M-SnO$_2$ (Figures S16 and S17), which are beneficial to the improvement of conductivity. Previous reports demonstrated that the weak alkaline solution is more favorable to the crystallization of SnO$_2$ (Hiratsuka et al., 1990; Jin et al., 2015; Lupan et al., 2009). The

Figure 3. Photovoltaic Performance of the Control and ClMPI-Based Devices

(A) Cross-sectional SEM image of the ClMPI-based device with the structure of ITO/SnO$_2$/ClMPI/MAPbI$_3$/Spiro-OMeTAD/Au.

(B) J–V curves of the champion control device and ClMPI-based device under forward and reverse scan directions.

(C) Stabilized performance measured by maximum power point tracking of the control and ClMPI-based devices under AM 1.5G illumination.

(D) Performance distribution of the control and ClMPI-based devices.

(E) log($J$)–log($V$) plots for the electron only devices. The inset shows the device structure of ITO/SnO$_2$/with or without ClMPI/MAPbI$_3$/PCBM/Ag.

(F) Mott-Schottky plots of control and ClMPI-based devices.
band alignment between M-SnO2 (or SnO2) and ClMPI-based perovskite (or perovskite) was determined from UV photoelectron spectroscopy and absorption measurements (Figures S18 and S19). The better match in conduction band between M-SnO2 and perovskite allowed larger quasi-Fermi level splitting, which is helpful to improve the V_OC of the device (Figure S20). The trap density (n_t) is evaluated through space-charge-limited current measurement based on a device structure of ITO/SnO2/MAPbI3 or ClMPI-based MAPbI3/PCBM/Ag. As shown in Figure 3E, it can be attained that n_t decreases from 3.98 × 10^{15} to 3.29 × 10^{15} cm^-3 after the introduction of ClMPI according to Equation S1. Figure 3F gives the Mott-Schottky plots 1/C^2 versus voltage attained by EIS measurements for the control and ClMPI-based device. By fitting the voltage dependence of the 1/C^2 curves, we found that the slope of the ClMPI-based device is larger than that of the control device, indicating the reduced interfacial charge density. In addition, these details also demonstrate the higher flat-band potential of the ClMPI-based device is larger than that of the control device, indicating the reduced interfacial charge density. By fitting the voltage dependence of the 1/C^2 curves, we found that the slope of the ClMPI-based device is larger than that of the control device, indicating the reduced interfacial charge density. In addition, these details also demonstrate the higher flat-band potential of the ClMPI-based device compared with the control device, which is related to an improvement in V_OC. Owing to the easy breakage of weak Pb-I bond at interface, the undercoordinated Pb and I vacancies will generate in perovskite materials during the device preparation and aging process (Wang et al., 2019). Encouragingly, in the ClMPI device, Cl at the interface can result in a stronger binding at the SnO2/perovskite interface for PbCl2-terminated perovskite. Thus, we attribute the improved interface contact (or reduced interface defects) at SnO2/perovskite to the introduction of ClMPI, which possesses a strong Pb-Cl bond and results in the suppression of formation of defects.

### Photo-Stability Test

To explore the effect of UV filters on the efficiency, we give the J-V of an efficient ClMPI-based device before and after using a UV filter, as shown in Figure 4A. The results show that the PCE is reduced from 20.03% to 16.01% mainly owing to the serious decrease of J_SC (from 23.23 to 19.02 mA/cm^2). It can be confirmed by the stabilized power efficiency of 19.88% for the device without eliminating UV, compared with just 16.26% when a 420-nm UV filter is added, showing around 20% efficiency loss (Figure 4B). The image in the inset is the transmittances of ITO/M-SnO2 with and without a UV filter, showing that the UV filter not only absorbs all the light of UV region (<420 nm), but also leads to ~10% transmittances loss of visible light from 420 nm to 800 nm. These results show that the application of UV filter not only increases the additional cost, but also seriously reduces the effective output when the device is in operation.

We tested the devices stabilities under different conditions without using any UV filter. The first test was designed to verify the stability of the devices under real outdoor atmospheric conditions, where the UV light was really encountered. It is known that UV radiation is present in sunlight and contributes about 3% of the total light output of the Sun at ground level. Several encapsulated devices (to exclude the damage of moisture and oxygen) were exposed on the roof of our laboratory building in Zhejiang University, Hangzhou city, China. These PSCs were subjected to sunlight without UV filters; we provided the statistics of solar irradiation hours during 2 months from November to December 2018, and the stabilities of devices are shown in Figure 4C. The ClMPI-based devices remarkably retained 94% of their initial PCE after 180 h. However, the control device was almost completely degraded within 168 h. In the second test, we exposed the control and ClMPI-based devices to 365-nm UV light with a high power of 100 mW/cm^2 for 500 h (Figure 4D). The results show that the PCE of the control device showed a constant drop during the UV-induced aging test and reduced to <10% of its original value within 100 h. Encouragingly, the ClMPI-based device still retained over 82% of the original highest value after 500 h.

In actual applications, the PSCs should continuously be operated at their maximum power point (MPP) for a long time. Thus, in our last test, the unencapsulated device stability was measured under AM1.5 G Sun illumination at MPP tracking in a N_2 glove box (Figure 4E). Here, we confirm that our simulator of solar

| Scan Direction | J_SC (mA cm^-2) | V_OC (V) | FF (%) | PCE (%) |
|----------------|----------------|---------|--------|---------|
| Control        |                |         |        |         |
| Reverse        | 22.41          | 1.087   | 74.2   | 18.08   |
| Forward        | 22.43          | 1.096   | 66.1   | 16.25   |
| ClMPI          |                |         |        |         |
| Reverse        | 23.42          | 1.146   | 78.2   | 21.01   |
| Forward        | 23.28          | 1.137   | 75.5   | 19.98   |

| Table 1. Photovoltaic Parameters of the Champion Control and ClMPI-Based Device |
irradiation emits the full spectra light, including the UV region, and the detailed data are shown in Figure S21. To better exhibit the effect of UV light on the stability of PSCs, a 420-nm UV filter was used within the initial 200 h illumination (the first test stage) and then we removed the UV filter in the next 500 h illumination (the second test stage). We found that the control and ClMPI-based devices had a similar stability in the first test stage: the control and ClMPI-based device can maintain 90% and 95% of their initial photovoltaic performances, respectively. Such stabilities can be comparable with those of previous works under UV-free test condition (Turren-Cruz et al., 2018; Tan et al., 2017; Jung et al., 2019). However, after removing the UV filter, the stability of the control device showed a rapid drop and the PCE decreases to <50% of its original value within only 10 h. In comparison, the ClMPI-based device can maintain >90% of the original PCE after 200 h continuous 1-sun illumination and >80% after 500 h. By calculation, the SPO t80 lifetime of the

Figure 4. Long-Term Stability Tests and the Effect of UV Filter on Efficiency
(A) J-V curves of the ClMPI-based device with efficiency of 20% with and without a UV filter. The inset is the transparency of M-SnO2 films with and without a 425-nm UV filter.
(B) Stabilized performance measured by MPP tracking of the ClMPI-based device. The second 100 s is operated with a 425-nm UV filter.
(C) Photo-stability of control and ClMPI-based PSCs with encapsulation operated under the outdoor solar irradiation. The test time is from 8:00 am to 6:00 pm when the weather is sunny; otherwise, the devices were stored in the indoor drawer. The surface temperature is < 50° C.
(D) 100 mW/cm² pure UV light aging test of control and ClMPI-based PSCs for 500 h.
(E) Continuous maximum power point tracking for 200 h of PSCs in a nitrogen glove box under 1-sun illumination with a 420-nm cutoff UV filter and 500 h without any filter.
ClMPI-based device was 500 h, showing two orders of magnitude improvement compared with the control devices with an SPO Te lifetime of only 4 h. The resultant stability of our devices is among the best results reported so far in IMO-based PSCs under similar test conditions (without a UV filter) (Bai et al., 2019; Shin et al., 2017; Wang et al., 2017c; Li et al., 2018). We measured the elements distribution of the aged ClMPI device by ToF-SIMS (Figure S22), confirming that the ClMPI still presented. In addition, we directly compared the stability of the control device using a UV filter with that of ClMPI device without UV filter (Figure S23). The ClMPI and control devices showed near linear loss of PCE with relative −0.31% per 10 h and −0.29% per 10 h, respectively, illustrating that our strategy can prevent the PSCs degradation well under UV light.

Conclusion
In summary, we reveal that the weak Pb-I bond in I-based perovskite is prone to breakage under photocatalysis, leading to serious degradation of the SnO2/perovskite interface. It has been demonstrated that the chlorine-based perovskite possesses the best tolerance for photocatalysis compared with the bromine-based and iodine-based perovskite owing to the strong Pb-Cl bond. We introduced a ClMPI between the SnO2 and I-based perovskite, which not only improved the interface contact but also protected the I-based perovskite light absorption layer from damage by photocatalysis. As a result, the device with an enhanced PCE of up to 21.01% (certified 20.17%) with reduced hysteresis phenomenon is achieved. Most importantly, the ClMPI-based device shows enormous enhancement for the photo-stability compared with the control one under different conditions, including outdoor solar irradiation, high-intensity UV irradiation, and 1-sun full spectrum illumination (including UV light). Our work provides a simple and effective method for achieving UV-filter-free, efficient, and photo-stable PSCs.

Limitations of the Study
In this study, we proposed the degradation procedure of MAPbI3 under SnO2 photocatalysis, as expressed in Equations 1 and 2. However, we did not detect the MAI phase through XRD measurements. We are not sure whether the MAI will be decomposed further. More studies are needed to reveal the exact final product of MAPbI3 under photocatalysis.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

DATA AND CODE AVAILABILITY
All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplemental Information. Additional data related to this paper may be requested from Y.X. (yuxuegong@zju.edu.cn).

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.10.021.

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AUTHOR CONTRIBUTIONS
X.Y. and J.X. supervised the whole project. P.H. and J.X. conceived the idea. J.X. and P.H. designed the experiments and drafted the manuscript. P.H. and G.L. conducted most of experiments. Y.W. contributed to the PL and TRPL tests. D.F. and Y.Y. contributed to the synthesis of single crystals. D.X. and C.C. conducted the XRD and AFM measurements. X.Y. and D.Y. revised the manuscript. All authors contributed to the discussion of the paper. P.H. and J.X. contributed equally.

DECLARATION OF INTERESTS
The authors declare that they have no competing financial interests.
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Supplemental Information

An Interlayer with Strong Pb-Cl Bond Delivers Ultraviolet-Filter-Free, Efficient, and Photostable Perovskite Solar Cells

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Supplemental Information

Transparent Methods

Materials. All the materials were purchased from Sigma-Aldrich unless the following material.
ITO glasses were purchased from Hangzhou Hongshi Electronic Technology Co., Ltd. MAI, MABr, MACl, PbI₂, PbBr₂ and PbCl₂ were purchased from Xi’an Polymer Light technology Corp. Spiro-OMeTAD and PCBM were purchased from Luminescence Technology Corp. SnO₂ nanoparticles were purchased from Alfa-Aesar.

Synthesis of perovskite single crystal. CH₃NH₃PbX₃ (X = I, Br, Cl) single crystal was synthesized followed by the previous work (Liu et al., 2015). For MAPbI₃ single crystal, equimolar mixture of MAI and PbI₂ were dissolved in GBL with the concentration at 1.3 M. The solution was kept into a blast drying oven for 1-2 days to grow seed crystals. By placing the seeds into a fresh solution, then keeping it at ~100 °C for some days, the original seeds grew into a larger one. For MAPbBr₃ single crystal, equimolar mixture of MABr and PbBr₂ were dissolved in DMF with the concentration at 0.7 M to form the fresh solution. For MAPbCl₃ single crystal, equimolar mixture of MACl and PbCl₂ were dissolved in DMSO with the concentration at 2 M to form the fresh solution. The seed crystal preparation and large crystal growth were the same as MAPbI₃ single crystal growth. These single crystals were ground into powder in a glove box and mixed with SnO₂ nanocrystals at a molar ratio of 1:1 to prepare for the aging test. Likewise, the same molar ratio for lead halide and SnO₂ nanocrystal mixtures were prepared.

Device fabrication. ITO glasses were cleaned by cleaning fluid, acetone, ethanol and isopropanol under sonication for 5 min, respectively. And then the ITO was dried to be treated into UV-Ozone machine for 20 min. The bare SnO₂ was prepared by spin coating the precursor solution of SnCl₂-H₂O (23 mg/mL) on ITO at 3000 rpm for 30 s. The M-SnO₂ was deposited on the ITO via spin coating the SnCl₂:H₂O:K₂O precursor solution with different molar ratio (8:1, 4:1, 2:1 molar ratio) at 3000 rpm for 30 s. The films were preheated for 5 min on a hot plate at 100 °C and then annealed at 180 °C for 1 h. The films were followed by UV-Ozone treatment for 5 min. The perovskite precursor solution was prepared by mixing 461 mg PbI₂ and 159 mg MAI in a mixed solvent of DMF/DMSO (632 uL/78 uL). The precursor solution was spin coated onto the ETLs at 1000 rpm for 10 s and 5000 rpm for another 20 s. 0.6-1 ml diethyl ether was dropped 15 s before the end. Then the samples were annealed at 70 °C for 1 min and then 100°C for 10 min. For the hole transport layer, 40 µL of the precursor solution prepared by dissolving 72.3 mg Spiro-OMeTAD, 17.5 µL solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl) imide in acetonitrile and 21 µL 4-tert-butylpyridine in 1 mL chlorobenzene was spin-coated on the perovskite at 3000 rpm for 35 s. Finally, 100 nm Au was deposited under a high vacuum (<1.0×10⁻³ Pa). For the PCBM layer, 20 mg/mL PCBM chlorobenzol solution was spin coated on the substrates at 1000 rpm for 30 s. The silver was deposited using the same condition as the gold. For the thin perovskite on a thick NH₄Cl, 40 µL ammonium chloride ethanol saturated solution was spin coated on glass three times, and then 0.2 mol/L perovskite precursor solution was spin coated on the NH₄Cl film. At last, the film was annealed for 45 min at 100 °C.
Characterization. The surface and cross sectional images of perovskite and tin oxide were obtained by a S-4800 (Hitachi) field-emission scanning electron microscope. AFM images were tested by a Dimension Edge atomic force microscope (Bruker). XPS measurements were performed with an X-ray photoelectron spectrometer (Kratos, AXIS Supra) using mono-chromator Al Kα (1486.6 eV) for XPS. Raman measurements were conducted using a Laser confocal Raman spectrometer (LabRAM HR Evolution). XRD patterns of the structure of perovskites were determined by a D8 Discover (Bruker). Optical properties of SnO₂ and M-SnO₂ were examined by a UV–vis spectrometer (U-4100, Hitachi Limited). ToF-SIMS was tested by ToF-SIMS V (INNTOF GmbH, Germany). The PL and TRPL spectra of the perovskite films were obtained by PL spectrometer (Edinburgh Instruments, FLS 920). The carrier concentration was measured by Hall effect instrument (LakeShore 760474028). EQE curves were obtained using an EQE measurement system (Model QEX10, PV Measurements, Inc.) across a functional wavelength from 300 to 850 nm. Photovoltaic performances of the devices were measured by masking on the active area with a metal mask (0.0855 cm²). The J–V curves of solar cells were measured a Keithley 2400 source meter with a solar simulator (94022A, Newport) under AM 1.5 G condition at an illumination intensity of 100 mW cm⁻², calibrated by a standard Si solar cell (PVM937, Newport) with KG5 filter. The J–V curves were obtained by scanning along the reverse scan direction and the forward scan direction in the range of −0.2 V to 1.4 V. For SCLC measurements, it was measured on the electron-only device with a structure of ITO/SnO₂/MAPbI₃ or ClMPI-based MAPbI₃/PCBM/Ag. Both types of devices were kept under dark condition during the measurements. The experiments were performed using a Keithley 2400 Source Measure Unit with scanning voltage ranging between -5 to 5 V. The electron trap state density in the perovskite was calculated using the following Equation S1. All the J–V measurements were carried out in ambient air.

Stability test. For the device stability under real outdoor atmospheric conditions, the encapsulated devices were exposed on the roof of our laboratory building in Zhejiang University, Hangzhou city, China. These PSCs were subjected to sunlight without UV-filters. We tested the device from November to December 2018 and recorded solar irradiation hours. The test time is from 8:00 am to 6:00 pm when the weather is sunny; otherwise, the devices were stored in the indoor drawer. For the UV-stability test, the device was exposed under a M-Ultra violet Light Source (MUA-165) with an illumination intensity of 100 mW cm⁻². The efficiency of the aged devices was measured under ambient conditions. For the MPP tracking stability, the tests were carried in a nitrogen glove-box and the device efficiency was measured by using a Keithley 2400 Source Measure Unit under100 mW cm⁻² simulated 1.5 Global (AM 1.5 G) solar simulator (Enli Technology Co., Ltd., SS-F5-3A) without using any UV-filter. The simulator of solar irradiation emits the full spectra light including the UV region and the detailed data are shown in Figure S18.
Supplementary Text

The electron trap state density in the perovskite was calculated using the following equation:

\[ \text{Equation S1: } V_{\text{TFL}} = \frac{enL^2}{2\varepsilon \varepsilon_0} \]

where \( L \) is the thickness of perovskite layer, \( \varepsilon (= 25.7) \) is relative dielectric constant of MAPbI\(_3\) (Frost et al., 2014), \( \varepsilon_0 \) is vacuum permittivity and \( n_t \) is the trap state density.

![Figure S1. Photographs of bare single crystal MAPbI\(_3\) powders before and after 120 h UV aging. Related to Figure 1A.](image)

![Figure S2. XRD patterns of (A) MAPbI\(_3\):SnO\(_2\) (Control represents the bare MAPbI\(_3\) powder), (B) MAPbBr\(_3\):SnO\(_2\) and (C) MAPbCl\(_3\):SnO\(_2\) mixtures in different UV aging stages. Related to Figure 1B-1D.](image)

![Figure S3. XPS results of MAPbI\(_3\) mixtures, MAPbBr\(_3\) mixtures and MAPbCl\(_3\) mixtures in different UV aging stages. Related to Figure 1E.](image)
Figure S4. The schematic diagram of PbX₂:SnO₂ mixture powders and bare PbI₂ powders after 2 h UV aging. Related to Figure 1F.

Figure S5. XRD patterns of PbX₂:SnO₂ mixtures before and after 2 h UV aging. (A) PbI₂, (B) PbBr₂ and (C) PbCl₂. Related to Figure 1F.
Figure S6. EDS mappings of bare SnO$_2$ (A) and M-SnO$_2$ (B). Related to Figure 2.

Figure S7. XRD patterns of the bare MAPbI$_3$ film and CIPI based MAPbI$_3$ film. Related to Figure 2. The perovskite films were attained by spin-coating a diluted perovskite solution.
**Figure S8.** The photographs of bare NH$_4$Cl, MAPbI$_3$ and MAPbI$_3$:NH$_4$Cl before and after annealing, respectively. Related to Figure 2.

**Figure S9.** XRD patterns of NH$_4$Cl powder, MAPbCl$_3$ single crystals, MAPbI$_3$/NH$_4$Cl mixtures before and after heating for 1 h. Related to Figure 2.

**Figure S10.** SEM images of perovskite films on (A) ITO/SnO$_2$ and (B) ITO/M-SnO$_2$. Related to Figure 2.
Figure S11. Photovoltaic parameters of the PSCs employing SnO$_2$ with different content of NH$_4$Cl. Related to Figure 3.

Figure S12. External quantum efficiency (EQE) of the best control and CIMPI based devices and integrated short-circuit current density. Related to Figure 3B. The integrated $J_{sc}$ of black curve is 21.14 mA/cm$^2$, red curve is 22.35 mA/cm$^2$, and green curve is 22.42 mA/cm$^2$, respectively. Among them, the black and red curves were tested in our lab by a Model QEX10, PV Measurements, Inc. The green curve was tested by another EQE measurement (Omni-λmni-upZolix) in Prof. Peng Wang’s Group.
Figure S13. The Certification report of the ClMPI-based PSC by National Institute of Metrology (China) (Reverse scan, PCE = 20.17%, $V_{OC} = 1.13$ V, $I_{SC} = 1.99$ mA, and FF = 77 %). The certified active area of mask is 8.562 mm$^2$. Related to Figure 3.

Figure S14. (A) Photoluminescence (PL) spectrum of MAPbI$_3$ deposited on glass, SnO$_2$ and M-SnO$_2$, respectively. (B) Time-resolved photoluminescence (TRPL) decay of MAPbI$_3$ deposited on glass, SnO$_2$ and M-SnO$_2$, respectively. Related to Figure 3.
Figure S15. The sheet resistance calculated from J-V curves of the control and CIMPI based device under 1-Sun illumination and J-V curves shifted by the dark current measurements. Related to Figure 3.

Figure S16. XRD patterns of the SnO$_2$ and M-SnO$_2$ films deposited on glasses. Related to Figure 3.

Figure S17. Histogram of the counts (10 for each device) for carrier density based on ETLs from Hall tests. Related to Figure 3.
**Figure S18.** (A) UPS spectra of SnO$_2$ and M-SnO$_2$ films (B) UPS spectra of perovskite deposited on SnO$_2$ and M-SnO$_2$ films. The insets are enlargement part ranging from 0 to 8 eV to determine the valence band position. Related to Figure 3.

**Figure S19.** Abs spectra of (A) SnO$_2$ and M-SnO$_2$, (B) MAPbI$_3$ and CIMPI-based MAPbI$_3$ films. Related to Figure 3.

**Figure S20.** Energy band diagrams of (A) control and (B) CIMPI-based devices. Related to Figure 3.
Figure S21. Spectra of the solar simulator for MPP stability test. Related to Figure 4.

Figure S22. Normalized ToF-SIMS results of a CIMPI based device after 500 h 1-Sun illumination MPP tracking without a UV filter. Related to Figure 4. The FWHM of Cl⁻ signal peak slightly broadened, illustrating that the Cl⁻ distribution showed a little change in perovskite layer. It might be due to the Cl⁻ ion migration and/or the exchange between Cl⁻ and I⁻ ion under operation.

Figure S23. Continuous MPP tracking for 200 hours of control devices with a 420 nm UV filter and 500 hours for CIMPI-based devices without a UV filter. Related to Figure 4.
Table S1. Fitted values of TRPL of MAPbI$_3$ and ClMPI-MAPbI$_3$. Related to Figure S14B.

| Decay time | SnO$_2$/MAPbI$_3$ | SnO$_2$/ClMPI-MAPbI$_3$ |
|------------|------------------|------------------------|
| $\tau_1$ (ns) | 6.38             | 3.28                   |
| $\tau_2$ (ns) | 95.24            | 130.32                 |

Supplemental References

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