Tailored Lattice “Tape” to Confine Tensile Interface for 11.08%-Efficiency All-Inorganic CsPbBr₃ Perovskite Solar Cell with an Ultrahigh Voltage of 1.702 V

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The crystal distortion such as lattice strain and defect located at the surfaces and grain boundaries induced by soft perovskite lattice highly determines the charge extraction-transfer dynamics and recombination to cause an inferior efficiency of perovskite solar cells (PSCs). Herein, the authors propose a strategy to significantly reduce the superficial lattice tensile strain by means of incorporating an inorganic 2D Cl-terminated Ti₃C₂ (Ti₃C₂Clₓ) MXene into the bulk and surface of CsPbBr₃ film. Arising from the strong interaction between Cl atoms in Ti₃C₂Clₓ and the under-coordinated Pb²⁺ in CsPbBr₃ lattice, the expanded perovskite lattice is compressed and confined to act as a lattice “tape”, in which the Pb–Cl bond plays a role of “glue” and the 2D Ti₃C₂ immobilizes the lattice. Finally, the defective surface is healed and a champion efficiency as high as 11.08% with an ultrahigh open-circuit voltage up to 1.702 V is achieved on the best all-inorganic CsPbBr₃ PSC, which is so far the highest efficiency record for this kind of PSCs. Furthermore, the unencapsulated device demonstrates nearly unchanged performance under 80% relative humidity over 100 days and 85 °C over 30 days.

1. Introduction

Organic–inorganic hybrid perovskite solar cells (PSCs) have made a forward step towards upcoming commercialization due to the rapid increase of power conversion efficiency (PCE) from initial 3.8% to reported 25.6%. However, the inherent decomposition of perovskite lattice under external stimulus such as moisture, oxygen, light and heat is still a stability burden in this way. Aiming to address this issue, all-inorganic CsPbX₃ (X = I⁻, Br⁻, or Cl⁻) perovskites have been gradually regarded as promising alternatives because of their superior environmental tolerances. Among them, tri-brominated CsPbBr₃ perovskite presents the best weatherability regardless of their large bandgap around 2.3 eV comparing to I-containing species, demonstrating a great potential in semitransparent photovoltaics or high-voltage required electronics owing to the ultrahigh theoretical voltage output around 2.0 V. Up to date, the minimum PCE loss of inorganic CsPbBr₃ PSC is still much higher than that of other devices because of the defective interfaces and grain boundaries induced open-circuit voltage (Vₒc) deficit. As is well known, the soft feature of perovskite film allows for substantial distorted lattices during the phase conversion process under high temperature, which are mainly located at the superficial region and grain boundaries. Apart from the popular positive under-coordinated Pb²⁺ ions and negative Pb–X antisites (PbX⁻), the expanded or compressed lattice (in other words, tensile or compressive strain) in this area also determines the carrier transfer and ion migration. How to heal the defective nanostructure and to realize the surface solidification undoubtedly maximize the device PCE of PSC.

Great efforts have been made to heal the perovskite surfaces by regulating the terminations. Inspired by the defect passivation in Si solar cells, many organic chemicals with functional groups such as pyridine, thiophene, and thiourea have been demonstrated to donate peripheral electrons to the under-coordinated Pb²⁺ defects for an improved efficiency and stability based on Lewis acid-base interaction. Furthermore, the fabrication of “bone-joint” configuration or soft layer by incorporating organic species with flexible chains can also effectively release the detrimental lattice strain. However, the delicate character of organic molecules and their weak secondary bonding with perovskite lattice cause an inactivation under high temperature and longstanding light irradiation, which is incompatible with the
all-inorganic concept.[26] Although inorganic passivation materials such as PbSO₄, PbS, metal halides, and oxides are employed to increase the performance of PSCs,[27] there is still no effective passivator to simultaneously reduce the above-mentioned defects and control lattice strain. How to make defect-free perovskite film by passivation-engineering and strain-engineering is of great importance to maximize the photovoltaic performances of all-inorganic CsPbBr₃ solar cells.

Arisings from the strong electronic coupling, Cl atoms display superiority to thermodynamically stabilize the perovskite lattice and regulate the grain growth dynamics owing to the higher formation energy of Pb–Cl antisites at interface.[28] But the prevalent Cl-containing additives are always ionized, and the excess cations will destroy the perovskite lattice and induce unnecessary recombination centers. In this fashion, the cation size should be precisely controlled to avoid the size mismatch induced ionic effect. As is well known, the newly emerging MXenes are family members of the 2D transition-metal carbides/nitrides with metallic conductivity and easily regulated termination with different chemical groups. Similar to graphene, the MXenes are obtained from the ordered atom matrices with clear lattice fringes of metallic Cu(111) lattice planes of the Ti₃C₂ MXene,[12,35] respectively. Additionally, the disappearance of Al 2p signal and the appearance of a sharp peak of Cl 2p from X-ray photoelectron spectroscopy (XPS) spectra (Figure 1c and Figures S2 and S3, Supporting Information) after etching treatment indicates the functional Cl termination on the Ti₃C₂Clₓ MXene surface. The atomic ratio of Cl:Ti is determined to be 2:3 (11.69%:17.45%) based on the XPS results. The element mapping images (Figure S4, Supporting Information) also demonstrate the uniform distribution of Cl element on the surface of Ti₃C₂Clₓ MXene. Through furiously mechanical liquid phase exfoliation, the delaminated Ti₃C₂Clₓ MXene with thickness of ≈4 nm (Figure S5, Supporting Information) is obtained due to the weak interlayer van der Waals force. Arising from the ordered atom matrices with clear lattice fringes of defect-free surface (Figure S6, Supporting Information), the as-prepared Ti₃C₂Clₓ MXene undoubtedly benefits the application in solar cells as lattice “tape” to regulate the chemical state of perovskite interfaces and grain boundaries.

Subsequently, all-inorganic CsPbBr₃ PSC with a configuration of FTO/SnO₂–TiOₓClₓ-CsPbBr₃:Ti₃C₂Clₓ/Ti₃C₂Clₓ/ Ti₃C₂Clₓ/carbon (Figure 1d) is fabricated by means of doping Ti₃C₂Clₓ MXene into PbBr₂ solution and spin-coating Ti₃C₂Clₓ onto the surface of final perovskite film. From the cross-sectional scanning electron microscopy (SEM) image in Figure 1e, the device has a multilayered structure with a 60 nm SnO₂–TiOₓClₓ layer, a 500 nm monolayer-aligned perovskite overlayer and a 15 μm carbon electrode. By carefully optimizing the Ti₃C₂Clₓ MXene dosage (Figure 1f and Table S1, Supporting Information), a champion PCE of 11.08% with an ultrahigh Voc of 1.702 V, a short-circuit current density Jsc of 7.87 mA cm⁻², and a fill factor FF of 82.7% has been achieved by recording the characteristic photocurrent–voltage (J–V) curves via reverse scan under standard AM 1.5 G illumination, as shown in Figure 1f, which is much higher than that of pristine device with 9.18%-efficiency. All the increased photovoltaic data including Voc, Jsc, and FF are attributed to the reduction of charge recombination after adding Cl-terminated Ti₃C₂ MXene.[36] To the best of our knowledge, both the PCE of 11.08% and V oc of 1.702 V are till now the highest records for state-of-the-art all-inorganic CsPbBr₃ PSCs (Table S2, Supporting Information). The steady power outputs of inorganic CsPbBr₃ PSCs under bias voltage at maximum power point (Figure 1g) and incident photon-to-current efficiency (IPCE) spectra (Figure 1h) are characterized to cross-check the validity of PCE enhancement. A much higher steady efficiency of 11.0% and an increased integrated current density of 7.59 mA cm⁻² for Ti₃C₂Clₓ-tailored CsPbBr₃ PSC from 6.90 mA cm⁻² for control device demonstrate the validity of the above-mentioned conclusion, highly agreeing well with the J–V measurements. Moreover, the hysteresis factor of devices has been reduced from 21.6% to 14.6% after the modification (Figure S8 and Table S3, Supporting Information).

2. Results and Discussion

Cl-terminated Ti₃C₂Clₓ MXene is synthesized using a redox-controlled Al etching of precursor Ti₃AlCₓ MAX-phase in Lewis acidic CdCl₃ melts combined with exfoliation and ultrasonication,[32] the details can be found in the Supporting Information. As schematically shown in Figure 1a, the unit cell of Ti₃AlCₓ MAX-phase is composed of Ti₃C octahedrons interleaveed with layers of Al elements.[33] Upon selectively removing Al atoms from interlayers with CdCl₃ melts, an accordion-like microstructure (Figure S1, Supporting Information) demonstrates the formation of 2D MXene, which can be cross-checked by X-ray diffraction (XRD) patterns.[14] As shown in Figure 1b, most of the diffraction peaks of Ti₃AlCₓ MAX-phase disappear in the final product, the characteristic diffraction peaks centered at 7.95°, 16.04°, 40.71°, and 57.98° correspond to the (002), (004), (101), and
MXene (the optimized concentration is controlled at 0.02 mg mL\(^{-1}\), see Figure S11 and Table S4, Supporting Information). Taking the labile surface bonding of Cl/Br-terminated MXene into consideration, versatile synthons for further chemical transformations provide multi-possibilities to heal the defective surface of CsPbBr\(_3\) perovskite.

To reveal the intrinsic mechanism behind the efficiency enhancement, we first explore the effect of Ti\(_3\)C\(_2\)Cl\(_x\) on the film quality. As shown in Figure 2a,b and Figure S12, Supporting Information, the Ti\(_3\)C\(_2\)Cl\(_x\)-tailored PbBr\(_2\) film with larger porosity is formed during the solvent volatilization.\(^{[37]}\) These nanoholes undoubtedly provide enough pathways for subsequent CsBr diffusion and match pre-expanded volume for perovskite grain growth.\(^{[38]}\) helping make a high-quality CsPbBr\(_3\) film with enlarged grain size and compact grain boundary (Figure 2c,d), which is accordance with the increased XRD peak intensities (Figure 2e) and enhanced light absorption ability (Figures S13 and S14, Supporting Information). The mechanism behind the regulated film growth dynamics is attributed to the stronger electronic coupling between Pb and Cl atoms (Figure S15, Supporting Information) than that with Br atoms. Upon introducing the Ti\(_3\)C\(_2\)Cl\(_x\) into the perovskite precursor, partial PbBr\(_2\) lattice will
bond with the dangling Cl atoms in Ti₃C₂Clₓ to spatially retard the nucleation around the additives. [39,40] In the following phase conversion process from PbBr₂ to CsPbBr₃, the homogeneously distributed Ti₃C₂Clₓ additives (Figures S16 and S17, Supporting Information) will play a role of “reservoir” to slow down the intercalation of Cs⁺ into underlying PbBr₂ frameworks. Furthermore, the strong electron-withdrawing properties of Cl atoms cause the binding energy of Pb ⁴f to shift up by 0.26 eV for Ti₃C₂Clₓ-tailored CsPbBr₃ (Figure 2f), [41] in other words, the electron cloud over under-coordinated Pb²⁺ defect will be efficiently delocalized and redistributed over the whole lattice evenly, which in turn regulates the binding energies of Cs and Br elements (Figure S18, Supporting Information). Similarly, the slight shifts of Cs 3d, Pb 4f, and Br 3d for the case of only Ti₃C₂Clₓ surface modification also indicate the formation of Pb–Cl bonds at the CsPbBr₃/Ti₃C₂Clₓ interface (Figure S19, Supporting Information). Combined with the current results, we propose a concept of full defect passivation strategy here, as illustrated in Figure 2g, the strong binding interaction between under-coordinated Pb²⁺ ions (V₃d) and Cl atoms is responsible for the reduction of halide ions deficiency or excess induced defects due to the higher formation energy of Pb–Cl antisites at interfaces. [44] It is worthy to mention that the underlying surface of perovskite film is passivated by the electron transfer layer SnO₂/TiOₓCl₄−(Cl₂)x according to our previous report. [45]  

The surface lattices suffer from distortion to cause the formation of residual stress in perovskite film owing to the soft feature of perovskite, which is detrimental to device performance. Taking the stronger binding energy of Pb–Cl (301 kJ mol⁻¹) in comparison to 248 kJ mol⁻¹ for Pb–Br into consideration, the Cl terminated Ti₃C₂ MXene can drag the adjacent perovskite grains closer (reduced grain gap as shown in Figure 2d), anchoring the Pb atoms and confining the perovskite lattice without deformation owing to the immovable 2D Ti₃C₂ substrate. Following this line of thoughts, the Ti₃C₂Clₓ is expected to be surface lattice “tape” to hinder the lattice expansion or contraction and reduce the residual stress. To deeply understand the strain evolution, we have characterized the Raman mapping images in Figure 3a,b. In theory, the vibrational mode around 309 cm⁻¹ in Raman spectra presents the reorientation of Cs⁺ in CsPbBr₃ lattice influenced by the PbBr₆ octahedral framework, which is strongly dependent on the lattice strain. [46,47] The enlarged lattice allows for a blue shift of Raman peak under the presence of tensile strain. [48] Therefore, the pristine CsPbBr₃ perovskite film suffers from a serious tensile strain owing to the lower average wavenumber around 295 cm⁻¹ for Cs⁺ vibrational mode
Figure 3. Raman mapping images of CsPbBr$_3$ perovskite films a) without and b) with Ti$_3$C$_2$Cl$_x$ MXene, and c) the corresponding distribution statistics of Raman peak for different perovskite films. GIXRD patterns of CsPbBr$_3$ (100) plane for the perovskite films d) without and e) with Ti$_3$C$_2$Cl$_x$ modification. f) d-spacing values obtained from the GIXRD patterns as a function of the incidence angle. g) Schematic diagram of residual strain in the pristine CsPbBr$_3$ grains, and h) schematic diagram of released strain in the reinforced CsPbBr$_3$ grains with Ti$_3$C$_2$Cl$_x$ MXene.

in Figure 3c, which is mainly formed during the annealing process owing to the different thermal expansion coefficients of adjacent layers in the PSC devices.$^{[49]}$ Higher tensile strain results in more serious lattice distortion, larger charge transfer barrier, and lower ions migration energy.$^{[50]}$ Upon introducing Ti$_3$C$_2$Cl$_x$ MXene into the CsPbBr$_3$ film, homogeneously distributed Raman peak for Cs$^+$ vibrational mode is closer to 309 cm$^{-1}$ (Figure 3b,c), this is a clear indicator of the released tensile strain in the perovskite film. We have further investigated the strain distribution by depth-dependent grazing incident X-ray diffraction (GIXRD) measurement to better highlight the lattice distortion in CsPbBr$_3$ films. As shown in Figure 3d and Figure S20, Supporting Information, the obvious shift of the characteristic peaks for pristine perovskite film to lower angles along with increasing the incidence angle demonstrates gradually increased crystal plane distance along the perpendicular direction to substrate according to Bragg's Law, in other words, the pristine film suffers from a serious tensile strain. In contrast, the CsPbBr$_3$ perovskite film with Ti$_3$C$_2$Cl$_x$ modification delivers a significantly reduced shift of diffraction peaks (Figure 3e and Figure S20, Supporting Information). The plots of d-spacing values for (100) planes as a function of incident angle demonstrate the lattices across whole film especially in bottom region are contracted, as shown in Figure 3f. Owing to the strong electron-withdrawing property of terminated Cl atoms to bond with under-coordinated Pb$^{2+}$ ion in the perovskite, 2D Ti$_3$C$_2$Cl$_x$ MXene can tightly adhere to the surface of CsPbBr$_3$ grains, like a lattice "tape" to heal the soft perovskite lattice and to relieve the lattice expansion (Figure 3g,h).

Under light irradiation, the defects and strain in perovskite film will undoubtedly cause a carrier loss during the transfer process, as illustrated in Figure 4a, leaving less holes accumulated on the perovskite top surface. In this fashion, there will be more holes to call for a larger photovoltage upon healing and solidifying the defective surfaces and grain boundaries (Figure 4b). Aiming to visually distinguish the surface charge, we have further carried out transient surface photovoltage (TSPV) measurement and the schematic setup is provided in Figure S21, Supporting Information. As shown in Figure 4c, the higher positive signal of 7.36 V under pulse laser stimuli for Ti$_3$C$_2$Cl$_x$-tailed perovskite film suggests an increased hole concentration,$^{[51]}$ which can be cross-checked by the higher contact potential difference (CPD) than that of pristine perovskite film obtained from Kelvin probe.
force microscopy (KPFM) images (Figure 4d,e), therefore, the defects located at skin layer induced by dangling bonds and tensile strain are healed. We then quantitatively evaluated the defect-state density \((n_t)\) in the perovskite films using a hole-only device according to the space-charge-limited-current (SCLC) model.\(^{[52]}\) As shown in Figure 4f, the reduced trap-filled limit voltage \((V_{TPL})\) from 0.78 to 0.56 V for Ti\(_3\)C\(_2\)Cl\(_x\) passivated perovskite film means a significantly reduced \(n_t\) from \(5.93 \times 10^{15}\) to \(1.92 \times 10^{15}\) cm\(^{-3}\), which can be cross-checked by the increased photoluminescence (PL) peak intensity (Figure S22, Supporting Information) because PL behavior of perovskite film is highly dependent on the defect density.\(^{[53]}\) When assembled into a PSC, the nonradiative recombination is suppressed to produce a prolonged lifetime from 1.083 to 2.169 ns (Figure 4g and Table S5, Supporting Information) for a voltage and efficiency enhancement. As shown in Figure 4h, the reverse current density of optimized device under dark condition is over one order of magnitude lower than that of reference device, demonstrating that more photogenerated carriers pass through the device rather than direct shunting along with the defect-assisted channels.\(^{[54]}\) By further recording capacitance–voltage curves in the dark according to the Mott–Schottky relationship (Figure 4i), a higher built-in electric field \((V_{bi})\) for the Ti\(_3\)C\(_2\)Cl\(_x\)-tailored PSC implies an enhanced driving force for charge separation (improved electron lifetime, see Figure S23, Supporting Information) and an extended depletion region for suppressing charge recombination (enlarged recombination resistance, see Figure S24, Supporting Information)\(^{[55,56]}\), which is one main origin for the ultrahigh \(V_{oc}\). Apart from the reduced defect and the released strain, we have further characterized the band structure of MXene. As shown in Figure S25, Supporting Information, the work function of Ti\(_3\)C\(_2\)Cl\(_x\)-MXene obtained from ultraviolet photoelectron spectroscopy (UPS) is determined to be \(-4.62\) eV, which will upward bend the valence and conduction band of CsPbBr\(_3\) at the interface, accelerating the charge extraction.\(^{[57]}\)

Finally, the long-term stability of all-inorganic CsPbBr\(_3\) PSCs is evaluated under persistent moisture or thermal attacks. As shown in Figure 5a, the Ti\(_3\)C\(_2\)Cl\(_x\)-repaired PSC device free of encapsulation delivers a stabilized PCE performance under 25 °C and 80% relative humidity (RH) in air over 100 days, which is mainly attributed to the reduced defect and contracted lattice to trigger unwanted phase attenuation and the protection of hydrophobic Ti\(_3\)C\(_2\)Cl\(_x\) encapsulant (enlarged contact angle from 50.9° to 92.1°).\(^{[58]}\) Owing to the absence of damageable organic
species, both two PSCs present excellent thermal stability. As shown in Figure 5b, there is nearly no PCE degradation after 30 days storage under 85 °C, 40% RH condition, demonstrating the advantages of functionalized Ti3C2 as lattice “tape” to enhance the performance of highly-efficient PSCs. It is worthy to note that the performance improvement behavior of PSC device in stability test is related to the film quality improvement after storage for a few days under controlled ambient atmosphere.

3. Conclusions

In summary, we have demonstrated a novel strategy to simultaneously realize defect passivation and strain release by incorporating Cl-terminated Ti3C2 MXene into the bulk and surface of perovskite film for stable and efficient all-inorganic CsPbBr3 PSCs. Arising from the formation of Pb–Cl bond between the interfacial under-coordinated Pb2+ ions in perovskite lattice and terminated Cl atoms in Ti3C2Clx MXene, the defects and expanded lattices located at the interfaces and grain boundaries in perovskite film are significantly healed, playing a role of surface lattice “tape”, in which the Pb–Cl bond represents “glue” and Ti3C2 immobilizes the lattice. As a result, the best all-inorganic CsPbBr3 solar cells were fabricated through molten salt-based etching of Ti3AlC2 MAX phase and subsequent multi-step substitution/elimination reactions in a N2-filled glovebox. 0.5 g of Ti3AlC2 was first mixed with 3.768 g of CdCl2 (molar ratio of 1:8). The resultant mixture was then heated in an alumina crucible at 610 °C for 7 h, which involved the following reactions.

\[
\begin{align*}
2Ti3AlC2 + 3CdCl2 & \rightarrow 2Ti3C2 + 2AlCl3 + 3Cd \\
Ti3C2 + CdCl2 & \rightarrow Ti3C2Clx + Cd
\end{align*}
\]

After cooling to room temperature, the powders were washed by concentrated aqueous HCl (12.1 m) to remove excess CdCl2 and metallic Cd, followed by washing with deionized water for several times until pH ≈ 6.5. The resultant Cl functionalized MXene powders were dried under vacuum at 45 °C. Finally, by liquid phase exfoliation of Cl functionalized MXene powders in IPA, the 2D few-layer Cl-terminated Ti3C2Clx MXene could be obtained. In details, 0.1 g of Cl functionalized MXene powders was added to 50 mL of IPA and then ultrasonicated for 25 h at a power of 200 W. The upper dark green suspension was obtained after centrifuging at 10 000 rpm for 30 min to separate the un-exfoliated MXene. Before usage, the obtained Ti3C2Clx MXene suspension was filtered with 0.22 μm PTFE filter.

4. Experimental Section

Materials and Reagents: SnCl2·2H2O (Alfa Aesar), CH3NH3I (Macklin), TiCl4 (Aladdin), Ti3AlC2 (Mianyang Hengchuan Electrical Equipment Sales Co., Ltd.), PbBr2 (Aladdin), CsBr (Aladdin), N,N-dimethylformamide (DMF, Sinopharm), CH3OH (Sinopharm), isopropanol (IPA, Aladdin), HCl (Guangzhou Chemical Reagent Factory), FTO glass (12 Ω per square), Zn powder (Guangzhou Chemical Reagent Factory), carbon paste (Shanghai MaterWin New Materials Co., Ltd.). All materials were used as supplied without further treatment.

Figure 5. Long-term stability of the encapsulation-free devices with and without Ti3C2Clx in air under a) 25 °C, 80% RH and b) 85 °C, 40% RH conditions.
QUANTA250 and Zeiss Gemini300. The Raman mapping was recorded using an InVia Raman system (α42K864 Renishaw, InVia system) with an excitation laser wavelength of 532 nm. The film thickness of MXene was obtained by atomic force microscopy (AFM, Seiko SPA400). The surface potential was characterized by KPFM (Multimode 8, Bruker, Germany). The XRD and GIXRD patterns of perovskite and MXenes were conducted on an X-ray diffractometer (Bruker D8 Advance). PL spectra were recorded via a fluorescence spectrometer excited by a 350 nm laser and the TRPL spectra were characterized using a Horiba spectrometer with an excitation wavelength of 500 nm. The characteristic J–V curves of PSCs were recorded on an electrochemical workstation (CHI660E) under irradiation of simulated solar light (Newport, Oriel Class 3A, 91195A). The light intensity was controlled at 100 mW cm\(^{-2}\) calibrated by a standard silicon solar cell. The IPCE spectra of various devices were obtained using an IPCE kit from Enli Technology Co., Ltd. The Tafel curves of various devices were measured on CHI660E electrochemical workstation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by Guangdong Basic and Applied Basic Research Foundation (2020A1515110548), Guangzhou Basic and Applied Basic Research Foundation (202102020775), Postdoctoral Research Foundation of China (2020M683135, 2019M663179), National Natural Science Foundation of China (61774139, 62004083, U1802257), Natural Science Foundation of Guangdong Province (2019B151502061, 2020A1515111123), and the Fundamental Research Funds for the Central Universities (21620348, 21618409, 21619311).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords
all-inorganic CsPbBr\(_3\) perovskite solar cells, interface solidification, long-term stability, strain release, Ti\(_3\)C\(_2\) MXene

Received: April 7, 2021
Revised: June 1, 2021
Published online: August 8, 2021

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