Article

Cesium-doped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for efficient and thermally stable perovskite solar cells

High efficiency coupled with excellent stability are urgent requirements for commercializing perovskite solar cells. Bati et al. demonstrate that, by functionalizing MXene nanosheets with cesium ions and incorporating them as additives into the perovskite layer, devices with improved efficiency and enhanced thermal stability can be obtained.

Abdulaziz S.R. Bati, Albertus A. Sutanto, Mengmeng Hao, ..., Yun Wang, Mohammad Khaja Nazeeruddin, Joseph G. Shapter

yun.wang@griffith.edu.au (Y.W.)
mdkhaja.nazeeruddin@epfl.ch (M.K.N.)
j.shapter@uq.edu.au (J.G.S.)

Highlights

Perovskite solar cells with a two-step sequential deposition method are fabricated

Cs-functionalized MXene is used as an additive for perovskite films

Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ hinders the nucleation of perovskite, leading to large grain sizes

The resulting devices exhibit improved efficiency and thermal stability

Article

Cesium-doped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for efficient and thermally stable perovskite solar cells

Abdulaziz S.R. Bati,^{1,2} Albertus A. Sutanto,³ Mengmeng Hao,^{1,4} Munkhbayar Batmunkh,⁵ Yusuke Yamauchi,^{1,4,6} Lianzhou Wang,^{1,4} Yun Wang,^{5,*} Mohammad Khaja Nazeeruddin,^{3,*} and Joseph G. Shapter^{1,7,*}

SUMMARY

$\text{Ti}_3\text{C}_2\text{T}_x$ MXenes have been shown to be promising candidates for use in various applications. Herein, we prepare functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets doped with cesium (Cs) and introduce them into a lead iodide (PbI_2) precursor solution for perovskite solar cells (PSCs) through a two-step deposition method, combining the advantages of both additives. Our theoretical and experimental analysis reveal that cesium plays an important role in improving perovskite crystallization and thus leads to enlarged crystal grains, long-lived carrier lifetimes, and reduced charge recombination compared with the devices fabricated without and with undoped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. PSCs integrated with cesium-doped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene deliver high photovoltaic efficiency of up to 21.57% with excellent thermal stability. The incorporation of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ paves the way to further improve the photovoltaic performance and thermal stability of PSCs by indirectly introducing dopants.

INTRODUCTION

In the past few years, the performance of organic-inorganic metal halide perovskite solar cells (PSCs) has seen exceptional progress; therefore, these PSCs are considered promising candidates to replace some state-of-the-art energy-harvesting technologies in the photovoltaic (PV), market such as gallium arsenide (GaAs) and silicon (Si) solar cells. Perovskite absorbers exhibit outstanding properties, such as a tunable band gap, low exciton binding energy, long carrier diffusion length, high charge carrier mobility, and high absorption coefficient, making them ideal light-harvesting materials for efficient and low-cost PV applications.^{1–5} Indeed, the rapid development of PSCs has led to the fabrication of highly efficient devices with certified power conversion efficiency (PCE) exceeding 25%.⁶

In PSCs, the perovskite film is the central component that plays a critical role in affecting the light absorption capability, charge transport characteristics, and recombination dynamics and hence the overall efficiency and stability of the devices.^{7,8} Therefore, obtaining high-quality perovskite films is essential to realize high-performance PSCs. For example, the origin of photocurrent hysteresis and the poor reproducibility of the fabricated devices have been found to strongly correlate with defect formation and ion migration in the perovskite film, which are concerns for accurately determining actual device performance.⁹ Such defects can act as nonradiative recombination centers and therefore severely affect the performance and stability of PSCs.¹⁰ Clearly, inhibiting ion migration and reducing the surface and/or grain boundary defects of perovskite films by improving their uniformity

¹Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

²Centre for Organic Photonics & Electronics, School of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

³Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, EPFL Valais Wallis, Rue de l'Industrie 17, 1951 Sion, Switzerland

⁴School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

⁵Centre for Catalysis and Clean Energy, School of Environment and Science Griffith University Gold Coast, QLD 4222, Australia

⁶JST-ERATO Yamauchi Materials Space-Tectonics Project and International Center for Materials Nanoarchitectonics (WPI-MANA) National Institute for Materials Science (NIMS) 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

⁷Lead contact

*Correspondence: yun.wang@griffith.edu.au (Y.W.), mdkhaja.nazeeruddin@epfl.ch (M.K.N.), j.shapter@uq.edu.au (J.G.S.)
<https://doi.org/10.1016/j.xcrp.2021.100598>

and crystallinity are promising approaches to fabricating high-performance devices with a decent lifetime and reduced hysteresis. To date, several strategies have been developed to passivate perovskite defects, such as additive engineering, interface engineering, and compositional engineering.^{11–14}

Compositional modifications of perovskite absorbers have shown great promise in improving the long-term stability, reproducibility, and efficiency of the PSCs.¹⁵ For instance, the incorporation of cesium cations (Cs^+) into perovskite films has been demonstrated to effectively reduce the defect density at the surface/grain boundaries, which resulted in enhanced PV performance, reproducibility, and stability of the devices.^{16–24} Zhao et al.²⁵ and Li et al.,²⁶ in two subsequent studies, explored the addition of Cs cations into FAPbI_3 -based perovskite films via a sequential two-step deposition method using perovskite seed crystals and CsCl as cesium sources, demonstrating a high level of control over perovskite nucleation and crystallization and achieving large-grain perovskite films with low trap density. The corresponding devices showed considerably enhanced efficiency and excellent operational stability. Later, Yi et al.²⁷ proposed the incorporation of CsF into lead iodide (PbI_2) of FAPbI_3 -based perovskite films via a two-step method. They have proven the positive impact of Cs on perovskite crystallization, which led to the fabrication of PSCs with improved device performance and enhanced thermal, light, and humidity stability. The two-step method is preferred over the anti-solvent dropping-based one-step deposition method due to better control of nucleation and growth during perovskite crystallization formation, which is critical to achieving reproducible devices.²⁸ However, in the two-step deposition method, the direct addition of Cs sources such as CsCl to either the PbI_2 precursor solution or the mixed organic halide salts solution is a major challenge. Upon the incorporation of Cs sources into the PbI_2 solution, the nonperovskite phase (δ - FAPbI_3) can be formed, whereas Cs salts are poorly soluble in the halide salts solution (isopropanol [IPA]).²⁷

In addition to tailoring the perovskite composition, additive engineering is considered a simple and feasible approach to effectively passivate perovskite films.²⁹ In this regard, two-dimensional (2D) materials with their unique combination of properties have shown great potential as additives to enlarge the grain size of perovskite film and reduce its grain boundary, enabling efficient and stable PSCs.^{30,31} To date, additives such as graphene, transition metal dichalcogenides (TMDs), and phosphorene have been successfully reported to aid in healing the perovskite defects.^{32–34} Recently, a new family of 2D materials, known as MXene nanosheets, have emerged as promising candidates for various applications due to outstanding properties such as high electronic conductivity, high mobility, and high charge carrier density coupled with their hydrophilic surfaces.^{35–39} Few-layer MXene nanosheets with the formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ (where M represents a transition metal, X stands for carbon and/or nitrogen, and T_x consists of the termination groups) can be obtained by selectively etching the A layer from raw MAX using hydrofluoric acid (HF) or lithium fluoride/hydrochloric acid ($\text{LiF} + \text{HCl}$).^{40–42} MXenes have attracted a great deal of attention for use in PSCs.^{21,43–45} For instance, Guo et al.⁴⁶ achieved a relative 12% enhancement in efficiency after introducing MXene as an additive into the perovskite precursor. Later, Agresti et al.⁴⁷ showed that MXene can help enhance the PCE of PSCs by 26% and reduce hysteresis when employed as a dopant or an interlayer. These studies clearly indicate the potential of MXenes as dopants for PSCs. In these studies, however, MXene additives were incorporated into perovskite film fabricated using the one-step deposition method, and to our knowledge, no attempts have been made to study the effect of integrating MXene into perovskite film prepared via the two-step method.

Herein, we prepared undoped $\text{Ti}_3\text{C}_2\text{T}_x$ (abbreviated as p- $\text{Ti}_3\text{C}_2\text{T}_x$) and Cs-doped $\text{Ti}_3\text{C}_2\text{T}_x$ (Cs- $\text{Ti}_3\text{C}_2\text{T}_x$) and employed them as additives into perovskite films via a two-step sequential deposition method. We found that the devices fabricated with Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ at the optimum concentration exhibited large-grain perovskite film, long charge carrier lifetime, and high charge recombination resistance. As a result, PSCs with more than 21% PCE and enhanced thermal stability were achieved.

RESULTS AND DISCUSSION

Delamination and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets

In this work, few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were prepared according to the established method reported in our previous work.³⁵ The as-prepared MXene was doped by selective adsorption of Cs^+ (see [Experimental procedures](#) for details). The negatively charged surface of MXene facilitates the adsorption of cesium cations because of the electrostatic attraction between them. To obtain uniform and stable MXene dispersion in N,N-dimethylformamide (DMF), a solvent exchange process was employed, as depicted in [Figure 1A](#). The morphology of the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes was examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), as shown in [Figures 1B–1D](#). It can be observed that the lateral size of the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes is large ($>1\ \mu\text{m}$) with a uniform thickness of $<2\ \text{nm}$, which is similar to that of p- $\text{Ti}_3\text{C}_2\text{T}_x$ ([Figure S1](#)), suggesting that the morphology was not altered by doping.

To investigate the effect of the Cs doping process on the crystal structure of MXene, X-ray diffraction (XRD) patterns were obtained. [Figure 1E](#) confirms the successful exfoliation of MXene with the full disappearance of the peaks due to Ti_3AlC_2 crystal phases (e.g., (104) at 38.9°). The interlayer spacing of p- $\text{Ti}_3\text{C}_2\text{T}_x$ was calculated to be $12.25\ \text{\AA}$. However, after Cs^+ was introduced, a shift in the (002) peak from 7.20° of p- $\text{Ti}_3\text{C}_2\text{T}_x$ to 6.73° of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ can be observed, which corresponds to an increase in the d -spacing from 12.25 to $13.11\ \text{\AA}$. The results confirm that Cs^+ , which has an ionic radius of $1.67\ \text{\AA}$, can easily diffuse into the MXene layers and hence can enhance the interaction between perovskite and MXene.⁴⁸ In addition, the absence of the (101) plane of anatase TiO_2 around 25.5° reveals that no oxidation of MXene occurred during either the doping process or the solvent exchange procedure.

[Figure 1F](#) shows the Raman spectra of p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$. The Raman peaks at ~ 200 , 268 , 385 , 574 , and $620\ \text{cm}^{-1}$ are consistent with the typical peaks of MXene.⁴⁹ MXene commonly features two Raman bands of $\sim 1,364$ and $1,549\ \text{cm}^{-1}$, which are assigned to D (disordered) and G (graphitic carbon) bands, respectively.⁵⁰ The nearly unchanged D band intensity before and after Cs doping suggests that no crystal structure defects were caused by the doping process. Moreover, no TiO_2 peak can be observed at $144\ \text{cm}^{-1}$, indicating that the Cs doping and solvent exchange protocols were successfully implemented without incurring undesirable surface oxidation, which is in excellent agreement with the XRD results.

To confirm the successful selective adsorption of Cs in the Cs-doped MXene, X-ray photoelectron spectroscopy (XPS) spectra were collected ([Figure 2A](#)). The typical peaks for $\text{Ti}_3\text{C}_2\text{T}_x$ exfoliated by LiF-HCl etchant (Ti, C, O, Cl, and F) were detected in both p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$. Compared with the XPS spectrum of p- $\text{Ti}_3\text{C}_2\text{T}_x$, two peaks at 724 and $738\ \text{eV}$, corresponding to Cs $3d_{3/2}$ and Cs $3d_{5/2}$, respectively, were clearly observed in the Cs-modified $\text{Ti}_3\text{C}_2\text{T}_x$ film ([Figure 2B](#)). Further analysis of

Figure 1. Preparation and characterization of $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ dopants

(A) Schematic illustrating the dispersion process of Cs-doped MXene in DMF.

(B) SEM.

(C and D) TEM image (C) and AFM image (D) of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$.

(E) XRD patterns of Ti_3AlC_2 , $\text{p-Ti}_3\text{C}_2\text{T}_x$, and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$.

(F) Raman spectra of $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$.

the high-resolution Ti 2p for $\text{Ti}_3\text{C}_2\text{T}_x$ before and after Cs doping suggests that MXene quality was preserved with no obvious difference in the TiO_2 content, indicating the successful incorporation of Cs without inducing surface oxidation, which is in excellent agreement with the XRD and Raman results (Figures S2A and S3A). Furthermore, high-resolution XPS spectra of F 1s, O 1s, and C 1s for both $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ reveal no significant changes (Figures S2B–S2D and S3B–S3D). The surface composition of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ was further investigated using energy-dispersive spectroscopy (EDS) mapping (Figure 2C). The uniform distribution of Cs with the other elements (Ti, F, N, and Cl) can be easily identified. N comes from the residual of DMF. It can be concluded that Cs doping has been successfully introduced without affecting the morphology and crystallinity of $\text{Ti}_3\text{C}_2\text{T}_x$.

Figure 2. Chemical composition of p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$
(A) XPS survey spectrum of the as-received Ti_3AlC_2 , p- $\text{Ti}_3\text{C}_2\text{T}_x$, and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$.
(B) High-resolution Cs 3d spectra of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$.
(C) Elemental distribution (EDS mapping) of Ti, Cs, F, N, and Cl.

Effect of doping on the morphology and optoelectronic properties of perovskite films

To study the feasibility of p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ as additives in PSCs, perovskite films were prepared via a two-step sequential deposition method. First, PbI_2 with and without p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ was deposited on a SnO_2 -coated indium-doped tin oxide (ITO) glass substrate, followed by short annealing. Then, the as-prepared formamidinium iodide (FAI)/methylamine bromide (MABr)/methylammonium chloride (MACl) mixed solution was spin-coated onto the PbI_2 layer, followed by another annealing step in air with controlled humidity to form the perovskite film.

We first investigated the influence of these dopants on the morphology, crystallinity, optical properties, and carrier transport dynamics. Figure 3 displays top-view SEM images of the films prepared without MXene; with Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ at various concentrations of 0.001, 0.002, 0.003, 0.005, 0.01, and 0.02 wt %; and with p- $\text{Ti}_3\text{C}_2\text{T}_x$ at concentrations of 0.001 and 0.003 wt %. It can be observed that increasing the concentration of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ in the PbI_2 precursor solution leads to a considerable increase in perovskite grain size, with the largest grain size obtained at 0.003 wt %. Based on the statistics shown in Figure S4, the average grain size substantially increased from 0.55 μm for the control film to 4.75 μm for the 0.003 wt % Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ -based film (dimensions quoted are average lateral sizes). However, with further increases in the concentration, the grain size started to decrease, reaching an average of 0.73 μm with 0.02 wt % Cs- $\text{Ti}_3\text{C}_2\text{T}_x$. Interestingly, no noticeable changes were observed with the films prepared with 0.001 and 0.003 wt % p- $\text{Ti}_3\text{C}_2\text{T}_x$, obtaining average grain sizes of 0.81 and 0.75 μm , respectively. It is well established that a perovskite film with a large grain size is critical to obtaining high-quality films with a reduced density of grain boundaries and defects that act as charge carrier trap centers, leading to charge recombination, degradation, and hysteresis.^{15,51} The presence of Cs alongside the termination groups of $\text{Ti}_3\text{C}_2\text{T}_x$ is believed to reduce the density of nucleation sites, retard perovskite growth, and improve perovskite crystallization, hence enlarging the grains of perovskite films.^{25,46,52}

XRD patterns of the control film (without MXene), the p- $\text{Ti}_3\text{C}_2\text{T}_x$ films, and the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ films are shown in Figure S5A. It is clear that the PbI_2 peak around 12.70° can be observed in all films. However, the films with Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ exhibited lower PbI_2 peak intensity compared with the control and p- $\text{Ti}_3\text{C}_2\text{T}_x$ films. This indicates that

Figure 3. Morphological characterization of perovskite films prepared with p- $\text{Ti}_3\text{C}_2\text{T}_x$ and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$

(A–G) Top-view SEM images of perovskite films prepared with various concentrations of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ of (A) 0 wt %, (B) 0.001 wt %, (C) 0.002 wt %, (D) 0.003 wt %, (E) 0.005 wt %, (F) 0.01 wt %, and (G) 0.02 wt %.

(H and I) Surface morphology of perovskite films with 0.001 (H) and 0.003 (I) p- $\text{Ti}_3\text{C}_2\text{T}_x$.

Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ can suppress the formation of PbI_2 . Excessive PbI_2 has been found to passivate the perovskite layer.⁵³ However, very high residual PbI_2 content can adversely affect the device's efficiency, hysteresis, and stability.⁵⁴ In addition to PbI_2 , the higher (001) plane peak intensity of the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ film around 13.9° suggests enhanced crystallinity of the perovskite film compared with the control and p- $\text{Ti}_3\text{C}_2\text{T}_x$ films. Furthermore, although the full width at half-maximum (FWHM) value of the (001) diffraction peak of the control and p- $\text{Ti}_3\text{C}_2\text{T}_x$ films is almost identical (0.132), the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ -doped film exhibit a narrower peak (0.112), which suggests preferred perovskite crystal orientation in the film with Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ incorporated (Figure S5B).⁵⁵ This observation is consistent with the increased grain size revealed by SEM (Figure 3).

The absorption spectra of the control, p- $\text{Ti}_3\text{C}_2\text{T}_x$, and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ films are depicted in Figure 4A. There is a negligible difference in light absorption in the wavelength ranging from 550 to 900 nm. However, for the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ film at 0.003 wt %, there is slightly stronger absorption in the wavelength between 500 and 550 nm, which might be ascribed to the improved crystallinity and enlarged grain size.⁵⁶ To further study the effect of p- $\text{Ti}_3\text{C}_2\text{T}_x$, and Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ dopants on trap passivation of the perovskite film, photoluminescence (PL) and time-resolved PL (TRPL) were measured. As shown in Figure 4B, the PL peak intensity of the perovskite film was enhanced considerably after Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ doping, indicating the effective suppression of nonradiative charge recombination in the perovskite film.⁵⁷ Surprisingly, the perovskite

Figure 4. Spectral characterization of films with and without dopants

(A) Absorption spectra of the control, $\text{Cs-Ti}_3\text{C}_2\text{T}_x$, and $\text{p-Ti}_3\text{C}_2\text{T}_x$ films.

(B) Steady-state photoluminescence (PL) spectra.

(C) Time-resolved photoluminescence (TRPL) spectra.

(D) Nyquist plots with different dopants measured in the dark at a 1 V bias. The inset shows the equivalent circuit used for curve fitting.

film with the $\text{p-Ti}_3\text{C}_2\text{T}_x$ dopant showed lower peak intensity than the control and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ films. In addition to the improved peak intensity, a blue shift in the PL peak of the Cs-doped film can be observed from 794 nm for the control and $\text{p-Ti}_3\text{C}_2\text{T}_x$ films to 790 nm for the $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ -doped film. This shift can be attributed to the presence of Cs, which leads to a reduction in the lattice constant.²⁶ Time-resolved PL decay spectra in Figure 4C confirm the considerably increased charge carrier lifetime from 1,081.8 ns (control film) to 1,428.7 ns ($\text{Cs-Ti}_3\text{C}_2\text{T}_x$ film), whereas the film based on $\text{p-Ti}_3\text{C}_2\text{T}_x$ displayed the shortest carrier lifetime of 859 ns.

Interactions between $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and perovskite

To understand the origin of the improved charge carrier lifetime after the introduction of Cs^+ , density functional theory (DFT) calculations were conducted by using the MAPbI_3 (001) surface and $\text{Ti}_3\text{C}_2\text{O}_2$ as model systems.⁵⁸ Our previous studies suggest that the change of A cations has a negligible impact on the interaction between the passivation materials and the perovskite surface.⁵⁹ This is because the passivation layer mainly interacts with the Pb-I framework. Moreover, only small amounts of Br^- and Cl^- were used for the synthesis. As such, only the MAPbI_3 (100) surface was considered here. The DFT results reveal that the Cs^+ can strongly interact with the MA vacancy of perovskite. The binding energy is -5.13 eV, which is 104% stronger than the binding energy between Cs^+ and MXene (-2.52 eV). The binding energy of Cs^+ at the FA vacancy of the FAPbI_3 surface was also calculated and determined to be -5.55 eV, which is similar to that for the MAPbI_3 surface. This supports that the change of A cations has a minor effect on the adsorption properties of MXene

Figure 5. Photovoltaic performance comparison of PSC

(A–D) Photovoltaic statistical distribution of (A) V_{oc} , (B) J_{sc} , (C) FF, and (D) PCE of the devices assembled without and with $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ at different concentrations. The box represents the values between 25% and 75% with median line and mean open square, while the whiskers define the minimum and maximum values.

on perovskite. It also suggests that introduction of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ can greatly prohibit the generation of surface vacancies in the perovskite. The surface vacancy often plays a detrimental role as a charge recombination center. As such, the highest PL density was observed in Figure 4B after the introduction of Cs^+ . However, p-MXene has a considerably strong interaction with perovskite film, as evidenced by the interaction energy of $-0.013 \text{ eV } \text{\AA}^{-2}$. It indicates that the interaction between p-MXene and perovskite film can prohibit the passivation of the surface vacancy, which leads to the lowest PL intensity. Moreover, the passivation of the surface vacancy by Cs^+ can remove shallow defect states. This explains the improved light absorption at relatively short wavelengths (Figure 4A). The reduced charge recombination in the $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ film is further proven by the electrochemical impedance spectroscopy (EIS) results shown in Figure 4D. The measurement was carried out in the dark at a bias voltage of 1 V. It can be found that the Cs-doped device exhibit relatively larger recombination resistance compared with the control film and p- $\text{Ti}_3\text{C}_2\text{T}_x$.

Device fabrication and performance

To examine the effect of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and p- $\text{Ti}_3\text{C}_2\text{T}_x$ on the PV performance of the devices, PSCs with a layered structure of ITO/ SnO_2 /perovskite/2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD)/Au and an active area of 0.2 cm^2 were fabricated. A cross-sectional SEM image of the devices is displayed in Figure S6. We began our investigation by optimizing the concentration of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ in the PbI_2 precursor solution. The details of varying the concentrations can be found in the Supplemental information. Figure 5 summarizes the device performance

Figure 6. Computational studies on the interaction between perovskite and MXene

(A and B) The atomic structures of the interface between the MAPbI_3 (100) surface and the $\text{Ti}_3\text{C}_2\text{O}_2$ MXene (A) without Cs^+ and (B) with Cs^+ . The binding energy between two components (ΔE_b) is also provided. Purple, I; dark gray, Pb; brown, C; blue, N; red, O; light blue, Ti; pink, H.

parameters, including short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE. The reference devices without the MXene additive showed an average PCE of 18.32% with J_{sc} of 24.44 mA cm^{-2} , V_{oc} of 1.05 V, and FF of 0.71. With increasing concentration of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ in the PbI_2 solution, the average PCE increased to 19.80% with V_{oc} of 1.09 V, J_{sc} of 24.16 mA cm^{-2} , and FF of 0.75 at 0.003 wt %. It is clear that the considerable PCE enhancement primarily originated from the improved V_{oc} and FF.

The increased V_{oc} can be ascribed to the removal of the shallow state after Cs^+ filled the surface defects, as demonstrated by our DFT results. After Cs^+ incorporates into the surface MA^+ vacancy, the conduction band maximum (CBM) also returns to the energy level without surface defects (Figure S7). Moreover, the introduction of Cs^+ can increase the interaction strength between MXene and perovskite film. The corresponding binding energy of $-0.016 \text{ eV/\AA}^2$ is 23% higher than that without Cs^+ (Figure 6). This has resulted in highly crystallized and improved morphology of the perovskite film, which in turn can effectively reduce the defect density. The stronger interaction can benefit the charge transfer and enhance FF values, as observed in Figure 5. However, an excessive amount of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ can lead to aggregation in the perovskite film and a dramatic increase in the nucleation sites and hence lead to decreased grain sizes and consequently reduced FF and V_{oc} (Figure 3).

To elucidate the role of Cs, devices with $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ were constructed. The detailed PV parameters of these devices are presented in Table 1. It is seen that with low dopant concentration of 0.001 wt %, both $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ showed similar improvement compared with the control device, which might result from the small amount of Cs present in the solution to observe an actual effect. However, when the concentration increased to 0.003 wt %, the devices with $\text{p-Ti}_3\text{C}_2\text{T}_x$ exhibited a reduction in FF compared with that of the control and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$. FF was further decreased after increasing the content of $\text{p-Ti}_3\text{C}_2\text{T}_x$ to 0.02 wt %, whereas a slight decrease in FF was observed after the addition of a similar concentration of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$. These results imply that the presence of Cs is favorable for improving perovskite crystallization. In addition, similar to other 2D materials, MXene sheets tend to restack because of van der Waals forces, which might cause severe aggregation in the perovskite film.⁶⁰ Preventing the restacking of the delaminated MXene nanosheets using an interlayer spacer such as ions is an effective strategy that has been demonstrated to stabilize the MXene structure.^{60,61} As such, we hypothesize that the existence of Cs within the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets not only improves the interaction between the perovskite and the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes but also helps minimize their aggregation.

Table 1. Photovoltaic parameters of PSCs fabricated without and with $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ at three concentrations of 0.001, 0.003, and 0.02 wt %.

Concentration	Dopant	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
0 wt %	none	1.05 ± 0.03	24.44 ± 0.47	0.71 ± 0.02	18.32 ± 0.45
		1.07^a	25.02^a	0.71^a	19.03^a
0.001 wt %	$\text{p-Ti}_3\text{C}_2\text{T}_x$	1.07 ± 0.01	24.39 ± 0.32	0.71 ± 0.01	18.50 ± 0.43
		1.08^a	24.78^a	0.72^a	19.19^a
	$\text{Cs-Ti}_3\text{C}_2\text{T}_x$	1.06 ± 0.03	24.59 ± 0.41	0.73 ± 0.02	18.93 ± 0.39
		1.06^a	24.94^a	0.74^a	19.73^a
0.003 wt %	$\text{p-Ti}_3\text{C}_2\text{T}_x$	1.08 ± 0.01	24.09 ± 1.03	0.70 ± 0.02	18.21 ± 0.47
		1.10^a	24.12^a	0.71^a	18.89^a
	$\text{Cs-Ti}_3\text{C}_2\text{T}_x$	1.09 ± 0.01	24.16 ± 0.66	0.75 ± 0.02	19.80 ± 0.65
		1.10^a	26.00^a	0.76^a	21.57^a
0.02 wt %	$\text{p-Ti}_3\text{C}_2\text{T}_x$	1.00 ± 0.01	24.21 ± 0.48	0.62 ± 0.04	14.99 ± 1.07
		0.98^a	24.82^a	0.67^a	16.42^a
	$\text{Cs-Ti}_3\text{C}_2\text{T}_x$	1.04 ± 0.02	24.24 ± 0.26	0.70 ± 0.02	17.51 ± 0.40
		1.04^a	24.51^a	0.71^a	18.05^a

^aThe best devices.

This might explain the good performance of the devices fabricated at even high $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ loadings compared with the inferior performance of the PSCs based on $\text{p-Ti}_3\text{C}_2\text{T}_x$. External quantum efficiencies (EQEs) of the control, 0.003 wt % $\text{p-Ti}_3\text{C}_2\text{T}_x$, and 0.003 wt % $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ are displayed in Figure 7A. The integrated current densities from the EQE spectra are 23.57, 23.21, and 24.60 mA cm^{-2} for the control, $\text{p-Ti}_3\text{C}_2\text{T}_x$, and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$, respectively, which is in good agreement with the J_{sc} values obtained from the current density-voltage (J-V) measurements (within 10%). Figure 7B depicts the J-V characteristics of the best-performing devices without MXene and with $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$.

Device thermal stability

Finally, we studied the thermal stability of the devices without MXene and with $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ by annealing them at 85°C inside a glove box without encapsulation (Figure 8). A clear drop in the PCE of the control device can be observed, showing almost 0% efficiency after 200 h. Interestingly, the PSCs with $\text{p-Ti}_3\text{C}_2\text{T}_x$ and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ preserved about 40% and 65%, respectively, of their initial efficiencies over the same period. This improved thermal stability can be ascribed to several reasons. First, the incorporation of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ into perovskite films led to a reduction in the PbI_2 content, as demonstrated by the XRD results. Excessive unreacted PbI_2 has been found to be detrimental to the stability of PSCs.⁶² Second, the inactive δ phase can be largely suppressed in the presence of Cs, leading to more homogeneous, compact, and stable perovskite film.¹⁶ Third, the existence of chlorine within $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ can prevent the formation of vacancies via strain relaxation, which can reduce the defect density that induces degradation.⁶³ Furthermore, doping the perovskite lattice with fluoride has been found to be effective for defect passivation via the formation of strong hydrogen bonds ($\text{N-H} \cdots \text{F}$) with MA/FA ions and strong ionic bonds with lead in the perovskite films.⁶⁴ Lastly, the fast degradation of PSCs at high temperatures has been correlated with the iodine migration from the perovskite layer and its interaction with Spiro-OMeTAD, causing significantly reduced hole extraction.¹⁰ As such, $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ might inhibit ion diffusion, improving the stability of the devices.

In summary, we have systematically investigated the crystallization, grain orientation, and charge transfer dynamic of perovskite film before and after the addition

Figure 7. Evaluation of device performance

(A) EQE spectra of the control, $\text{p-Ti}_3\text{C}_2\text{T}_x$, and $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ devices.

(B) J-V curves of the control, $\text{Cs-Ti}_3\text{C}_2\text{T}_x$, and $\text{p-Ti}_3\text{C}_2\text{T}_x$ measured in the reverse scan direction.

of $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ and $\text{p-Ti}_3\text{C}_2\text{T}_x$ to the PbI_2 precursor solution via a two-step method in planar-structure PSCs. It has been shown that $\text{Cs-Ti}_3\text{C}_2\text{T}_x$ can retard the nucleation of the perovskite, leading to large grains. This, in turn, can result in a few grain boundaries, reduced defect density, and less nonradiative recombination. As a result, efficient and thermally stable PSCs were realized with an efficiency exceeding 21%. The simple and versatile strategy reported in this work demonstrates the feasibility of MXene to host some monovalent cations such as Cs in perovskite, which might help in using the most striking benefit of 2D materials to design various additive combinations to enhance efficiency and stability not only in PSCs but also in other photoelectronic applications.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Joseph G. Shapter (j.shapter@uq.edu.au).

Materials availability

This study did not generate new unique materials.

Data and code availability

The published article includes all data analyzed and necessary to reach the conclusions of this study in the figures and tables of the main text and [supplemental information](#). Further information and requests for additional data should be directed to the lead contact.

Materials

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich. Ti_3AlC_2 was purchased from Carbon-Ukraine, Ukraine. ITO-coated glass substrates were purchased from Xin Yan Technology. SnO_2 colloidal solution (15 wt % in water) and PbI_2 were purchased from Alfa Aesar. FAI, MABr, and FK 209 Co(III) TFSI salt were purchased from Greatcell Solar. MACl and Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology.

Preparation of MXene and Cs-MXene

MXene was synthesized according to a method reported in our previous work.³⁵ To prepare $\text{Cs-Ti}_3\text{C}_2\text{T}_x$, CsCl (1 mg mL^{-1}) was dissolved in deionized water, followed by

Figure 8. Stability assessment of the cells

Thermal aging test at 85°C for 200 h under a nitrogen environment without encapsulation.

bath sonication for 10 min. Subsequently, 10 mg of the as-synthesized MXene was dissolved in 10 mL of CsCl solution and was then shaken on a flask shaker for 30 min. To prepare p- $\text{Ti}_3\text{C}_2\text{T}_x$, 10 mg of the as-synthesized MXene was dissolved in 10 mL of deionized water. The prepared MXene dispersions were then bath sonicated for 10 min under Ar flow to avoid oxidation, followed by centrifugation at 3,500 rpm for 30 min. The supernatant was disposed of and the pellet at the bottom was redispersed in DMF at the same concentration. This step was repeated three times to remove residual water. Finally, all samples were sonicated for 5 min under Ar flow. All dispersions were then degassed with Ar for 10 min and stored in a fridge ($\sim 4^\circ\text{C}$) for later use.

Device fabrication

ITO substrates were cleaned with a detergent, distilled water, acetone, and IPA for 15 min, each using ultrasonication. Then, the ITO glasses were treated with ultraviolet (UV) ozone for 15 min. The diluted SnO_2 solution (2.67% in water) was spin-coated onto the ITO at 3,000 rpm for 30 s, followed by annealing at 150°C for 30 min in air. After cooling, the substrates were treated with UV ozone for 10 min before being transferred into a nitrogen-filled glove box.

The perovskite was deposited by a two-step sequential deposition method. First, 599.3 mg of PbI_2 in DMF:DMSO (9:1) solvent was spin-coated onto SnO_2 at 1,500 rpm for 30 s and then annealed at 70°C for 1 min. For the Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ - and p- $\text{Ti}_3\text{C}_2\text{T}_x$ -based devices, different amounts of Cs- $\text{Ti}_3\text{C}_2\text{T}_x$ and p- $\text{Ti}_3\text{C}_2\text{T}_x$ solutions were added into the PbI_2 precursor solution. The total concentration of PbI_2 precursor solution was maintained by reducing the volume of DMF used to dissolve the PbI_2 beads. After cooling to room temperature, a solution of FAI:MABr:MACl (60:6:6 mg in 1 mL of IPA) was spin-coated onto the samples at 1,500 rpm for 30 s, followed by transferring the films into ambient with a controlled humidity of 30%–40% and annealing at 150°C for 15 min. After the annealing process, the substrates were quickly transferred to a nitrogen-filled glove box. Then, hole transporting material (HTM) solution was spin-coated at 3,000 rpm for 30 s. The HTM solution was prepared by dissolving the following in 704 μL of chlorobenzene: 55 mg of Spiro-OMeTAD, 22 μL of 4-tert-butylpyridine (tBP), 13 μL of bis (trifluoromethylsulphonyl) imide (Li-TFSI) predissolved as 520 mg mL^{-1} in acetonitrile, and 10 μL of FK209 Co(III) TFSI salt predissolved as 99 mg in 263 μL of acetonitrile. The devices were then left inside a desiccator overnight. Finally, a 70-nm-thick gold top electrode was deposited by a thermal evaporator under a high vacuum.

Materials characterization

The optical absorbance spectra were measured using a ultraviolet-visible (UV-vis)-NIR spectrometer (Shimadzu UV-2600). The cross-sectional SEM images of the device and the top-view SEM images were obtained using a field emission scanning electron microscope (JOEL JSM-7001). AFM was performed in air using Asylum Research Cypher S with Asylum Research software, operating in the standard tapping mode configuration using the AIR cantilever holder. Raman spectra were acquired using a WITec alpha300 RA + S with a 40 $\times$ objective. Data from TEM (HT7700) were acquired using 120 kV of beam energy. XPS data were acquired using a Kratos Axis Ultra x-ray photoelectron spectrometer incorporating a 165-mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al $K\alpha$ X-rays (1,486.6 eV) at 225 W (15 kV, 15 mA). Base pressure in the analysis chamber was 1.0×10^{-9} torr and during sample analysis was 1.0×10^{-8} torr.

Photovoltaic characterization

The J-V characteristics of the devices were measured in a N_2 -filled glove box using a Keithley 2400 source measure unit (SMU) and with simulated air mass index 1.5 global light with an intensity of 100 mW cm^{-2} . The system was calibrated with a National Renewable Energy Laboratory (NREL)-certified, spectral mismatch-corrected standard silicon photodiode. The J-V measurements were carried out in reverse scan direction from +1.2 to -0.1 V . The active area of the devices was 0.2 cm^2 . The EQE spectra were measured by a light source (xenon lamp) coupled with a monochromator. A calibrated silicon photodiode (Newport) was used as a reference device to calibrate the EQE response. The scan was taken within the range of 300 to 900 nm at an interval of 10 nm. EIS was performed on a full cell configuration using an Autolab PGSTAT128N system at a bias of (1 V) in dark conditions. Fits of the obtained impedance spectra were done using NOVA software with an appropriate equivalent circuit. The steady-state PL emissions were measured at 450-nm light source excitation using a monochromatized Xe lamp, and the TRPL decay studies were carried out with a 377-nm pulsed diode laser excitation source on a fluorescence spectrophotometer (FLSP-900, Edinburgh Instruments). Perovskite films without and with the different dopants were deposited on bare glass following the same fabrication procedure. All measurements were performed at room temperature without encapsulation.

Computational details

The first-principles DFT calculations were performed using Vienna *Ab initio* Simulation Package (VASP) code with the projector-augmented wave (PAW) method.⁶⁵ The PAW potential was used to describe the electron-ion interaction,⁶⁶ with valence electron structures of $5s^25p^66s^1$ for Cs (Cs_sv), $5d^{10}6s^26p^2$ for Pb (Pb_d), $5s^25p^5$ for I, $4s^23d^2$ for Ti, $2s^23p^4$ for O, $2s^22p^2$ for C, $2s^22p^3$ for N, and $1s^1$ for H. The exchange and correlation effects of the electron-electron were described using the Perdew-Burke-Ernzerhof (PBE) functional of a generalized gradient approximation (GGA) method.⁶⁷ The plane-wave kinetic energy cutoff was set at 520 eV to expand the smooth part of the wave functions. All calculations were carried out on the thermodynamically stable (001) surface using a (1×3) four-layer slab model with the periodic boundary condition.⁵⁸ To match the lattice constants of the perovskite surfaces, a $(4 \times 5\sqrt{3})$ MXene monolayer was employed here with a structural tolerance of less than 2%. A vacuum region of 15 Å was used to avoid interaction between slabs. The Brillouin zone was sampled using gamma-centered $(2 \times 1 \times 1)$ *k*-point mesh for all surface calculations. Because traditional DFT calculations at the PBE level cannot correctly

include nonlocal van der Waals interactions, the calculations with dispersion corrections may affect the adsorption energies of small molecules. In this regard, the optBB86b method was adopted for dispersion corrections here.^{68,69} During geometry optimizations, the bottom two layers were fixed at the bulk position, whereas the top three atomic layers and the adsorbents were fully relaxed with energy and force convergences of less than 1×10^{-4} eV and 1×10^{-3} eV $\text{\AA}^{-1}$, respectively.

The binding energy between MXene and perovskite surface (ΔE_b [eV]) was calculated according to the following equation:

$$\Delta E_b = (E_{\text{hybrid}} - E_{\text{perov}} - E_{\text{MXene}}) / A$$

where E_{hybrid} , E_{perov} , and E_{MXene} are the energies of an interface, the MAPbI_3 (001) surface, and the $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer, respectively. A is the surface area of the perovskite film and MXene.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2021.100598>.

ACKNOWLEDGMENTS

We acknowledge the facilities and the scientific and technical assistance of the Queensland node of the Australian National Fabrication Facility (ANFF) and Microscopy at the Centre for Microscopy and Microanalysis, The University of Queensland. A.S.R.B. acknowledges the Saudi Arabian Cultural Mission (SACM) and the Ministry of Education of Saudi Arabia for their financial support during his study in Australia. M.B. acknowledges the support of Griffith University internal grant 102551. The support of the Australian Research Council Discovery Program (DP 200101217) is acknowledged. This research was also undertaken on the supercomputers at the National Computational Infrastructure (NCI) in Canberra, Australia, which is supported by the Australian Commonwealth Government, and the Pawsey Supercomputing Centre in Perth, with funding from the Australian Government and the Government of Western Australia.

AUTHOR CONTRIBUTIONS

A.S.R.B., M.B., M.K.N., and J.G.S. conceived the project and designed the experiments. A.S.R.B. fabricated the devices, analyzed the data, and wrote the initial draft. A.A.S. and M.B. contributed to the experimental work. M.H. conducted PL and TRPL measurements. Y.W. carried out the computational studies. L.W. provided access to the PL and TRPL infrastructure and helped interpret the results. Y.Y. helped with the preparation of the nanomaterials required. M.K.N. and J.G.S. supervised the project. All authors contributed to revising the manuscript and approved the final version of the manuscript for submission.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: July 20, 2021

Revised: August 23, 2021

Accepted: September 9, 2021

Published: September 30, 2021

REFERENCES

- Noh, J.H., Im, S.H., Heo, J.H., Mandal, T.N., and Seok, S.I. (2013). Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett.* 13, 1764–1769.
- Zheng, K., Zhu, Q., Abdellah, M., Messing, M.E., Zhang, W., Generalov, A., Niu, Y., Ribaud, L., Canton, S.E., and Pullerits, T. (2015). Exciton Binding Energy and the Nature of Emissive States in Organometal Halide Perovskites. *J. Phys. Chem. Lett.* 6, 2969–2975.
- Sun, S., Salim, T., Mathews, N., Duchamp, M., Boothroyd, C., Xing, G., Sum, T.C., and Lam, Y.M. (2014). The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells. *Energy Environ. Sci.* 7, 399–407.
- Xing, G., Mathews, N., Sun, S., Lim, S.S., Lam, Y.M., Grätzel, M., Mhaisalkar, S., and Sum, T.C. (2013). Long-range balanced electron- and hole-transport lengths in organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* 342, 344–347.
- Stranks, S.D., Eperon, G.E., Grancini, G., Menelaou, C., Alcocer, M.J.P., Leijtens, T., Herz, L.M., Petrozza, A., and Snaith, H.J. (2013). Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* 342, 341–344.
- National Renewable Energy Laboratory (2021). Best research-cell efficiencies. <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20200925.pdf>.
- Jeon, N.J., Noh, J.H., Yang, W.S., Kim, Y.C., Ryu, S., Seo, J., and Seok, S.I. (2015). Compositional engineering of perovskite materials for high-performance solar cells. *Nature* 517, 476–480.
- Montcada, N.F., Méndez, M., Cho, K.T., Nazeeruddin, M.K., and Palomares, E. (2018). Photo-induced dynamic processes in perovskite solar cells: the influence of perovskite composition in the charge extraction and the carrier recombination. *Nanoscale* 10, 6155–6158.
- Meloni, S., Moehl, T., Tress, W., Frankevičius, M., Saliba, M., Lee, Y.H., Rao, P., Nazeeruddin, M.K., Zakeeruddin, S.M., Grätzel, M., and Graetzel, M. (2016). Ionic polarization-induced current-voltage hysteresis in $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite solar cells. *Nat. Commun.* 7, 10334.
- Tumen-Ulzii, G., Qin, C., Matsushima, T., Leyden, M.R., Balijipalli, U., Klotz, D., and Adachi, C. (2020). Understanding the Degradation of Spiro-OMeTAD-Based Perovskite Solar Cells at High Temperature. *Sol. RRL* 4, 2000305.
- Gao, F., Zhao, Y., Zhang, X., and You, J. (2020). Recent Progresses on Defect Passivation toward Efficient Perovskite Solar Cells. *Adv. Energy Mater.* 10, 1902650.
- Akin, S., Arora, N., Zakeeruddin, S.M., Grätzel, M., Friend, R.H., and Dar, M.I. (2020). New Strategies for Defect Passivation in High-Efficiency Perovskite Solar Cells. *Adv. Energy Mater.* 10, 1903090.
- Fu, L., Li, H., Wang, L., Yin, R., Li, B., and Yin, L. (2020). Defect passivation strategies in perovskites for an enhanced photovoltaic performance. *Energy Environ. Sci.* 13, 4017–4056.
- Han, T.-H., Tan, S., Xue, J., Meng, L., Lee, J.-W., and Yang, Y. (2019). Interface and Defect Engineering for Metal Halide Perovskite Optoelectronic Devices. *Adv. Mater.* 31, e1803515.
- Wang, F., Bai, S., Tress, W., Hagfeldt, A., and Gao, F. (2018). Defects engineering for high-performance perovskite solar cells. *npj Flex. Electron.* 2, 22.
- Saliba, M., Matsui, T., Seo, J.-Y., Domanski, K., Correa-Baena, J.-P., Nazeeruddin, M.K., Zakeeruddin, S.M., Tress, W., Abate, A., Hagfeldt, A., and Grätzel, M. (2016). Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* 9, 1989–1997.
- Lee, J.-W., Kim, D.-H., Kim, H.-S., Seo, S.-W., Cho, S.M., and Park, N.-G. (2015). Formamidinium and Caesium Hybridization for Photo- and Moisture-Stable Perovskite Solar Cell. *Adv. Energy Mater.* 5, 1501310.
- Hu, Y., Hutter, E.M., Rieder, P., Grill, I., Hanisch, J., Aygüler, M.F., Hufnagel, A.G., Handloser, M., Bein, T., Hartschuh, A., et al. (2018). Understanding the Role of Caesium and Rubidium Additives in Perovskite Solar Cells: Trap States, Charge Transport, and Recombination. *Adv. Energy Mater.* 8, 1703057.
- Zhou, W., Zhao, Y., Zhou, X., Fu, R., Li, Q., Zhao, Y., Liu, K., Yu, D., and Zhao, Q. (2017). Light-Independent Ionic Transport in Inorganic Perovskite and Ultrastable Cs-Based Perovskite Solar Cells. *J. Phys. Chem. Lett.* 8, 4122–4128.
- Chen, J., Xu, J., Zhao, C., Zhang, B., Liu, X., Dai, S., and Yao, J. (2019). Enhanced Open-Circuit Voltage of Cs-Containing FAPbI₃ Perovskite Solar Cells by the Formation of a Seed Layer through a Vapor-Assisted Solution Process. *ACS Sustain. Chem. Eng.* 7, 3404–3413.
- Xu, X., Li, M., Xie, Y.-M., Ma, Y., Ma, C., Cheng, Y., Lee, C.-S., and Tsang, S.-W. (2019). Porous and Intercrossed PbI_2 -CsI Nanorod Scaffold for Inverted Planar FA-Cs Mixed-Cation Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* 11, 6126–6135.
- Cao, H., Dong, Z., Qiu, Y., Li, J., Wang, Y., Li, Z., Yang, L., and Yin, S. (2020). Precursor Engineering of Vapor-Exchange Processes for 20%-Efficient 1 cm^2 Inverted-Structure Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* 12, 41303–41311.
- Liu, P., Gong, Y., Xiao, Y., Su, M., Kong, S., Qi, F., Zhang, H., Wang, S., Sun, X., Wang, C., and Zhao, X.-Z. (2018). Highly efficient and stable air-processed hole-transport-material free carbon based perovskite solar cells with caesium incorporation. *Chem. Commun. (Camb.)* 55, 218–221.
- Matsui, T., Seo, J.-Y., Saliba, M., Zakeeruddin, S.M., and Grätzel, M. (2017). Room-Temperature Formation of Highly Crystalline Multication Perovskites for Efficient, Low-Cost Solar Cells. *Adv. Mater.* 29, 1606258.
- Zhao, Y., Tan, H., Yuan, H., Yang, Z., Fan, J.Z., Kim, J., Voznyy, O., Gong, X., Quan, L.N., Tan, C.S., et al. (2018). Perovskite seeding growth of formamidinium-lead-iodide-based perovskites for efficient and stable solar cells. *Nat. Commun.* 9, 1607.
- Li, Q., Zhao, Y., Fu, R., Zhou, W., Zhao, Y., Liu, X., Yu, D., and Zhao, Q. (2018). Efficient Perovskite Solar Cells Fabricated Through CsCl-Enhanced PbI_2 Precursor via Sequential Deposition. *Adv. Mater.* 30, e1803095.
- Yi, X., Zhang, Z., Chang, A., Mao, Y., Luan, Y., Lin, T., Wei, Y., Zhang, Y., Wang, F., Cao, S., et al. (2019). Incorporating CsF into the PbI_2 Film for Stable Mixed Cation-Halide Perovskite Solar Cells. *Adv. Energy Mater.* 9, 1901726.
- Dubey, A., Adhikari, N., Mabrouk, S., Wu, F., Chen, K., Yang, S., and Qiao, Q. (2018). A strategic review on processing routes towards highly efficient perovskite solar cells. *J. Mater. Chem. A Mater. Energy Sustain.* 6, 2406–2431.
- Mahapatra, A., Prochowicz, D., Tavakoli, M.M., Trivedi, S., Kumar, P., and Yadav, P. (2020). A review of aspects of additive engineering in perovskite solar cells. *J. Mater. Chem. A Mater. Energy Sustain.* 8, 27–54.
- Bati, A.S.R., Batmunkh, M., and Shapter, J.G. (2020). Emerging 2D Layered Materials for Perovskite Solar Cells. *Adv. Energy Mater.* 10, 1902253.
- Wang, B., Iocozzia, J., Zhang, M., Ye, M., Yan, S., Jin, H., Wang, S., Zou, Z., and Lin, Z. (2019). The charge carrier dynamics, efficiency and stability of two-dimensional material-based perovskite solar cells. *Chem. Soc. Rev.* 48, 4854–4891.
- Mahmoudi, T., Wang, Y., and Hahn, Y.-B. (2018). Graphene and its derivatives for solar cells application. *Nano Energy* 47, 51–65.
- Das, S., Pandey, D., Thomas, J., and Roy, T. (2019). The Role of Graphene and Other 2D Materials in Solar Photovoltaics. *Adv. Mater.* 31, e1802722.
- You, P., Tang, G., and Yan, F. (2019). Two-dimensional materials in perovskite solar cells. *Mater. Today Energy* 11, 128–158.
- Yu, L., Bati, A.S.R., Grace, T.S.L., Batmunkh, M., and Shapter, J.G. (2019). $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene)-Silicon Heterojunction for Efficient Photovoltaic Cells. *Adv. Energy Mater.* 9, 1901063.
- Dall'Agnese, C., Dall'Agnese, Y., Anasori, B., Sugimoto, W., and Mori, S. (2018). Oxidized Ti_3C_2 MXene nanosheets for dye-sensitized solar cells. *New J. Chem.* 42, 16446–16450.
- Fu, H.-C., Ramalingam, V., Kim, H., Lin, C.-H., Fang, X., Alshareef, H.N., and He, J.-H. (2019). MXene-Contacted Silicon Solar Cells with 11.5% Efficiency. *Adv. Energy Mater.* 9, 1900180.
- Hu, M., Zhang, H., Hu, T., Fan, B., Wang, X., and Li, Z. (2020). Emerging 2D MXenes for supercapacitors: status, challenges and prospects. *Chem. Soc. Rev.* 49, 6666–6693.
- Aslam, M.K., Niu, Y., and Xu, M. (2021). MXenes for Non-Lithium-Ion (Na, K, Ca, Mg, and Al)

- Batteries and Supercapacitors. *Adv. Energy Mater.* **11**, 2000681.
40. Naguib, M., Mochalin, V.N., Barsoum, M.W., and Gogotsi, Y. (2014). 25th anniversary article: MXenes: a new family of two-dimensional materials. *Adv. Mater.* **26**, 992–1005.
41. Naguib, M., Kurtoglu, M., Presser, V., Lu, J., Niu, J., Heon, M., Hultman, L., Gogotsi, Y., and Barsoum, M.W. (2011). Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Adv. Mater.* **23**, 4248–4253.
42. Anasori, B., Lukatskaya, M.R., and Gogotsi, Y. (2017). 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2**, 16098.
43. Yang, L., Dall'Agnese, C., Dall'Agnese, Y., Chen, G., Gao, Y., Sanehira, Y., Jena, A.K., Wang, X.-F., Gogotsi, Y., and Miyasaka, T. (2019). Surface-Modified Metallic $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as Electron Transport Layer for Planar Heterojunction Perovskite Solar Cells. *Adv. Funct. Mater.* **29**, 1905694.
44. Huang, L., Zhou, X., Xue, R., Xu, P., Wang, S., Xu, C., Zeng, W., Xiong, Y., Sang, H., and Liang, D. (2020). Low-Temperature Growing Anatase $\text{TiO}_2/\text{SnO}_2$ Multi-dimensional Heterojunctions at MXene Conductive Network for High-Efficient Perovskite Solar Cells. *Nano-Micro Lett.* **12**, 44.
45. Bati, A.S.R., Hao, M., Macdonald, T.J., Batmunkh, M., Yamauchi, Y., Wang, L., and Shapter, J.G. (2021). 1D-2D Synergistic MXene-Nanotubes Hybrids for Efficient Perovskite Solar Cells. *Small* **17**, e2101925.
46. Guo, Z., Gao, L., Xu, Z., Teo, S., Zhang, C., Kamata, Y., Hayase, S., and Ma, T. (2018). High Electrical Conductivity 2D MXene Serves as Additive of Perovskite for Efficient Solar Cells. *Small* **14**, e1802738.
47. Agresti, A., Pazniak, A., Pescetelli, S., Di Vito, A., Rossi, D., Pecchia, A., Auf der Maur, M., Liedl, A., Larciprete, R., Kuznetsov, D.V., et al. (2019). Titanium-carbide MXenes for work function and interface engineering in perovskite solar cells. *Nat. Mater.* **18**, 1228–1234.
48. Seo, J.-Y., Uchida, R., Kim, H.-S., Saygili, Y., Luo, J., Moore, C., Kerrod, J., Wagstaff, A., Eklund, M., McIntyre, R., et al. (2018). Boosting the Efficiency of Perovskite Solar Cells with CsBr-Modified Mesoporous TiO_2 Beads as Electron-Selective Contact. *Adv. Funct. Mater.* **28**, 1705763.
49. Naguib, M., Mashtalir, O., Lukatskaya, M.R., Dyatkin, B., Zhang, C., Presser, V., Gogotsi, Y., and Barsoum, M.W. (2014). One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes. *Chem. Commun. (Camb.)* **50**, 7420–7423.
50. Ferrari, A.C., Meyer, J.C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K.S., Roth, S., and Geim, A.K. (2006). Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **97**, 187401.
51. Yang, Y., Wu, J., Wang, X., Guo, Q., Liu, X., Sun, W., Wei, Y., Huang, Y., Lan, Z., Huang, M., et al. (2020). Suppressing Vacancy Defects and Grain Boundaries via Ostwald Ripening for High-Performance and Stable Perovskite Solar Cells. *Adv. Mater.* **32**, e1904347.
52. Zhang, X., Ren, X., Liu, B., Munir, R., Zhu, X., Yang, D., Li, J., Liu, Y., Smilgies, D.-M., Li, R., et al. (2017). Stable high efficiency two-dimensional perovskite solar cells via caesium doping. *Energy Environ. Sci.* **10**, 2095–2102.
53. Chen, Q., Zhou, H., Song, T.-B., Luo, S., Hong, Z., Duan, H.-S., Dou, L., Liu, Y., and Yang, Y. (2014). Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells. *Nano Lett.* **14**, 4158–4163.
54. Jiang, Q., Chu, Z., Wang, P., Yang, X., Liu, H., Wang, Y., Yin, Z., Wu, J., Zhang, X., and You, J. (2017). Planar-Structure Perovskite Solar Cells with Efficiency beyond 21%. *Adv. Mater.* **29**, 1703852.
55. Li, T., Pan, Y., Wang, Z., Xia, Y., Chen, Y., and Huang, W. (2017). Additive engineering for highly efficient organic-inorganic halide perovskite solar cells: recent advances and perspectives. *J. Mater. Chem. A Mater. Energy Sustain.* **5**, 12602–12652.
56. Fei, C., Guo, L., Li, B., Zhang, R., Fu, H., Tian, J., and Cao, G. (2016). Controlled growth of textured perovskite films towards high performance solar cells. *Nano Energy* **27**, 17–26.
57. Noel, N.K., Abate, A., Stranks, S.D., Parrott, E.S., Burlakov, V.M., Goriely, A., and Snaith, H.J. (2014). Enhanced photoluminescence and solar cell performance via Lewis base passivation of organic-inorganic lead halide perovskites. *ACS Nano* **8**, 9815–9821.
58. Wang, Y., Sumpter, B.G., Huang, J., Zhang, H., Liu, P., Yang, H., and Zhao, H. (2015). Density Functional Studies of Stoichiometric Surfaces of Orthorhombic Hybrid Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *J. Phys. Chem. C* **119**, 1136–1145.
59. Liu, J., Kang, J., Chen, S., White, J.J., Yin, H., Liu, P., Zhao, H., and Wang, Y. (2020). Effects of compositional engineering and surface passivation on the properties of halide perovskites: a theoretical understanding. *Phys. Chem. Chem. Phys.* **22**, 19718–19724.
60. Wu, Z., Shang, T., Deng, Y., Tao, Y., and Yang, Q.-H. (2020). The Assembly of MXenes from 2D to 3D. *Adv. Sci. (Weinh.)* **7**, 1903077.
61. Lukatskaya, M.R., Mashtalir, O., Ren, C.E., Dall'Agnese, Y., Rozier, P., Taberna, P.L., Naguib, M., Simon, P., Barsoum, M.W., and Gogotsi, Y. (2013). Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* **341**, 1502–1505.
62. Tumen-Ulzii, G., Qin, C., Klotz, D., Leyden, M.R., Wang, P., Auffray, M., Fujihara, T., Matsushima, T., Lee, J.-W., Lee, S.-J., et al. (2020). Detrimental Effect of Unreacted PbI_2 on the Long-Term Stability of Perovskite Solar Cells. *Adv. Mater.* **32**, e1905035.
63. Saidaminov, M.I., Kim, J., Jain, A., Quintero-Bermudez, R., Tan, H., Long, G., Tan, F., Johnston, A., Zhao, Y., Voznyy, O., and Sargent, E.H. (2018). Suppression of atomic vacancies via incorporation of isovalent small ions to increase the stability of halide perovskite solar cells in ambient air. *Nat. Energy* **3**, 648–654.
64. Li, N., Tao, S., Chen, Y., Niu, X., Onwudinanti, C.K., Hu, C., Qiu, Z., Xu, Z., Zheng, G., Wang, L., et al. (2019). Cation and anion immobilization through chemical bonding enhancement with fluorides for stable halide perovskite solar cells. *Nat. Energy* **4**, 408–415.
65. Kresse, G., and Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50.
66. Kresse, G., and Hafner, J. (1994). Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements. *J. Phys. Condens. Matter* **6**, 8245–8257.
67. Perdew, J.P., Burke, K., and Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868.
68. Klimeš, J., Bowler, D.R., and Michaelides, A. (2011). Van der Waals density functionals applied to solids. *Phys. Rev. B Condens. Matter Phys.* **83**, 195131.
69. Wang, Y., Gould, T., Dobson, J.F., Zhang, H., Yang, H., Yao, X., and Zhao, H. (2014). Density functional theory analysis of structural and electronic properties of orthorhombic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Phys. Chem. Chem. Phys.* **16**, 1424–1429.