

MXene-Based Tailoring of Carrier Dynamics, Defect Passivation, and Interfacial Band Alignment for Efficient Planar p–i–n Perovskite Solar Cells

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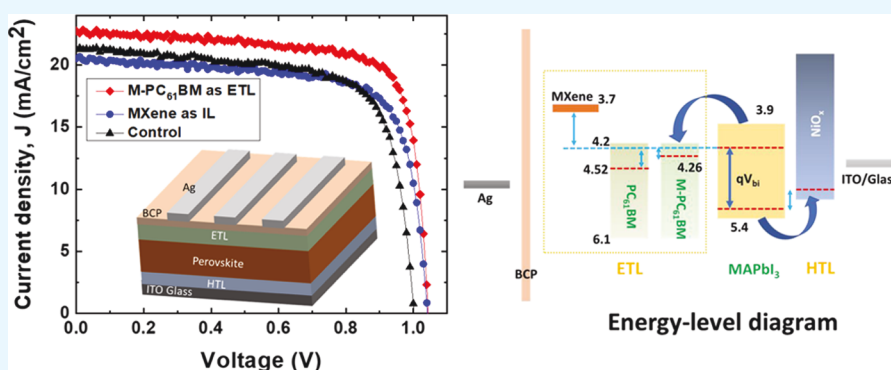
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ABSTRACT: Defect passivation and tailoring of perovskite–charge transport layer interfaces are critical strategies to minimize the recombination losses and improve the power conversion efficiency (PCE) in perovskite solar cells (PSCs). Herein, we use titanium carbide MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) to tailor the electronic properties of the electron transport layer (ETL) and ETL/perovskite interface in inverted (p–i–n) PSCs and correlate them to the observed PCE. MXene doping in a [6,6]-phenyl- C_{61} -butyric acid methyl ester (M- PC_{61}BM)-based ETL results in an improved electrical conductivity and ETL/perovskite interface band alignment. A red shift in the $A_g(2)$ peak in the Raman spectrum and a localized upshift of the Fermi level calculated using scanning Kelvin probe force microscopy (SKPFM) confirm the n-doping of PC_{61}BM . Consequently, PSC devices with M- PC_{61}BM as the ETL show a higher PCE of 18% than PC_{61}BM ETL-based control devices (PCE = 15.2%). Importantly, our study proves that the improvement in the open-circuit voltage (V_{OC}) and fill factor (FF) depends on how MXene is integrated into the PSC, i.e., as a dopant in the PC_{61}BM ETL, an interfacial layer between the perovskite and ETL, or a standalone ETL. Through comprehensive photoluminescence, electrochemical impedance spectroscopy, space-charge limited current, and scanning Kelvin probe force microscopy-based analyses, we establish that the introduction of MXene in PSCs has multiple benefits, including improvement in carrier transport, passivation and trap state reduction, and better interfacial energy alignment. Further, we unravel the most prominent factor influencing device performance in each mode of MXene introduction. Hence, the study reinforces the potential of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as a versatile material for high-performance electronic and optoelectronic devices.

KEYWORDS: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, perovskite solar cells, electron transport layer (ETL), scanning Kelvin probe force microscopy (SKPFM), interface engineering, defect passivation

1. INTRODUCTION

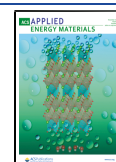
Organic–inorganic hybrid perovskites have shown great promise for applications including solar cells, light-emitting diodes (LEDs), photodetectors, and transistors.^{1,2} Methylammonium lead iodide (MAPI, $\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite owing to its excellent material properties, including direct band gap, tunable absorption in the visible and near-infrared region, ambipolar transport, long diffusion lengths, high absorption coefficient, low exciton binding energy, and high carrier mobilities catalyzed the development of high-efficiency perovskite solar cells (PSCs).^{3–6} Despite the rapid progress, the

power conversion efficiencies (PCE) of PSCs are still below the thermodynamic limit. A major reason for the less than ideal PCE in PSCs lies in nonradiative recombination losses caused

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by defects present in perovskite films and various interfaces in the PSC device structure.^{7,8} While improving the crystal quality, smoothness, and uniformity of perovskite films can alleviate recombination losses within the perovskite film, careful engineering of energy-level alignment and the electronic properties at the perovskite–charge transport layer (CTL) interfaces are required to curtail the interfacial recombination and associated PCE losses.^{9,10} In spite of significant research efforts to enhance extraction of photo-generated charge carriers (i.e., electrons and holes) by idealizing the electron transport layer (ETL) and hole transport layer (HTL) properties, resolving the electronic energy-level misalignment at the interfaces in planar PSCs is still a major research challenge.

Optimizing the interfacial structure and ensuring the best energy alignment at the interfaces is also critical for minimizing or eliminating hysteresis effects, which is a significant concern for the long-term reliability of PSCs.^{11,12} Adopting advanced materials-based ETL and HTL with tunable charge transport properties can reduce hysteresis effects. For example, the application of fullerenes-based [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as ETL in PSCs can suppress the hysteresis compared to traditional metal oxides (e.g., TiO₂, SnO₂)-based ETLs.^{13,14} The ability of PC₆₁BM to passivate dangling bonds/grain boundaries in the MAPI film, together with the feasibility for low-temperature solution processing, made PC₆₁BM a prominent ETL candidate in inverted PSCs. However, the poor intrinsic electron mobility and conductivity of PC₆₁BM films are shown to be responsible for higher series resistance and a decrease in the fill factor (FF), open-circuit voltage (*V*_{OC}), and PCE of p–i–n PSCs.¹⁵ Also, the inferior charge extraction ability of PC₆₁BM leads to unbalanced charge transport compared to the HTL (e.g., NiO_x), further diminishing the *V*_{OC}.^{16,17} Doping of PC₆₁BM films has been employed as a successful strategy in inverted PSCs to enhance the PCE by improving the conductivity of PC₆₁BM and minimizing the charge-transfer resistance via improving the surface morphology of PC₆₁BM films.^{15,18} Hence, to further improve the PCE of PC₆₁BM-based inverted PSCs, it is important to use novel dopant materials that can help optimize the electronic properties (i.e., electronic conductivity and Fermi level) of PC₆₁BM and passivate the underlying perovskite film simultaneously.

Two-dimensional (2D) materials (e.g., graphene, MoS₂, WS₂, etc.), with dimensionally confined charge transport and resultant highly superior and configurable properties, are employed in PSCs as ETLs, HTLs, and electrodes to improve the device performance.^{19–23} As a comparatively newer member of the 2D family, “MXenes” with highly controllable electronic properties can play a critical role in developing planar PSCs. The MXenes are a family of layered two-dimensional materials with a general formula of M_{*n*+1}X_{*n*}T_{*x*}, where M is an early transition metal, X is either carbon or nitrogen, and T_{*x*} are surface terminal groups (typically –OH, –O, and –F). The most famous member of the MXene family is Ti₃C₂T_{*x*} with a strong interlayer van der Waals bonding and very high electrical conductivity.^{24,25} The first-principles calculations predicted that the work function (WF) of Ti₃C₂T_{*x*} MXene could be tailored over a broad range (between 2 and 6 eV), through careful control over the type of surface terminal groups.²⁶ Subsequently, the modulation of MXene WF values between 3.7 and 5.4 eV was experimentally demonstrated.^{27,28} In addition to their tunable WF, the

MXenes can form stable dispersions in polar and nonorganic polar organic solvents (e.g., dimethyl sulfoxide (DMSO), dimethylformamide (DMF), chlorobenzene, etc.), which is critical for its application in solution-processed PSCs.^{29,30} In the case of PSCs, the application of MXenes is particularly attractive as it can offer several advantages, including high electrical conductivity, tunable WF, and passivation of perovskite films.^{21,28,31–37} Especially, the application of MXene as a dopant in PC₆₁BM to enhance the conductivity of PC₆₁BM and improve the energy-level alignment at the PC₆₁BM/perovskite interface can provide new opportunities to tailor the performance of PSCs. Moreover, a detailed understanding of the impact of MXene on individual photovoltaic parameters, including *V*_{OC}, FF, and *J*_{sc}, can help engineer the device architecture and achieve higher PCE.

Hence, we focus the study on understanding the fundamentals of MXene-induced changes on individual photovoltaic parameters in inverted planar PSCs. For this, we synthesized Ti₃C₂T_{*x*} MXenes nanosheets and investigated their application as ETL, interfacial layer, or dopant in PC₆₁BM ETL in planar p–i–n PSCs. Our results show that MXene doping of the PC₆₁BM film resulted in a 2.8% improvement in the PCE relative to the control device with PC₆₁BM as ETL. Furthermore, both *V*_{OC} and FF showed an apparent enhancement compared to the control device. In contrast, the device with MXene as an interfacial layer between PC₆₁BM and perovskite showed a PCE enhancement by 0.4%, and the application of MXene (alone without PC₆₁BM) as an ETL showed a dramatically reduced PCE of 1.6%. Similar to PSCs using MXene-doped PC₆₁BM, the device with the MXene interlayer has also demonstrated an improvement in *V*_{OC} and FF. Through a myriad of spectroscopic, electronic, and device characterizations, we unravel the factors that lead to the observed changes in individual photovoltaic parameters in various test device architectures. Our analyses suggest that in MXene-modified inverted (p–i–n) PSCs, except when MXene is used as standalone ETL, leads to an enhancement both in open-circuit voltage (*V*_{OC}) and fill factor (FF).

2. EXPERIMENTAL DETAILS

2.1. Materials and Synthesis. Indium tin oxide (ITO)-coated glass was purchased from Liaoning Huite Photoelectric Technology Co., Ltd. Lead iodide (PbI₂, 99%) was bought from Tokyo Chemical Industry Co., Ltd. (TCI). PC₆₁BM (99%) and C₆₀ (99.8%) were bought from Nano C. Methylammonium iodide (CH₃NH₄I, 99.5%) was bought from GreatCell Solar. The MAX phase titanium aluminum carbide (Ti₃AlC₂) was purchased from Forsman Scientific (Beijing) Co., Ltd. All of the compounds were used as received without further purification and processing. Ti₃C₂T_{*x*} MXene was synthesized from MAX phase Ti₃AlC₂ powder using a hydrofluoric acid (HF) (purchased from Acros-Organics) etching process reported previously.³⁸ Briefly, 0.5 g of Ti₃AlC₂ powder was etched in 10 mL of HF (48%) for 8 h. Following the etching step, the etched solution was washed several times until the pH of the solution reached between 6 and 7, vacuum filtered using a 0.5 μm filter paper, and vacuum annealed at 80 °C to obtain the Ti₃C₂T_{*x*} MXene powder. Nanosheets of MXenes were obtained by DMSO intercalation into MXene powder samples followed by sonication in an Ar atmosphere.

2.2. Device Fabrication. The patterned ITO-coated glass substrates (25 mm × 15 mm) were initially cleaned with a commercial soap solution (Hellmanex) and then cleaned in an ultrasonic bath with DI water, acetone, and isopropanol, in that order, for 20 min each. The cleaned substrates were subjected to ultraviolet–ozone treatment for 30 min. A solution of 25 mg of nickel acetate dihydrate in 1 mL of ethanol and 50 μL of

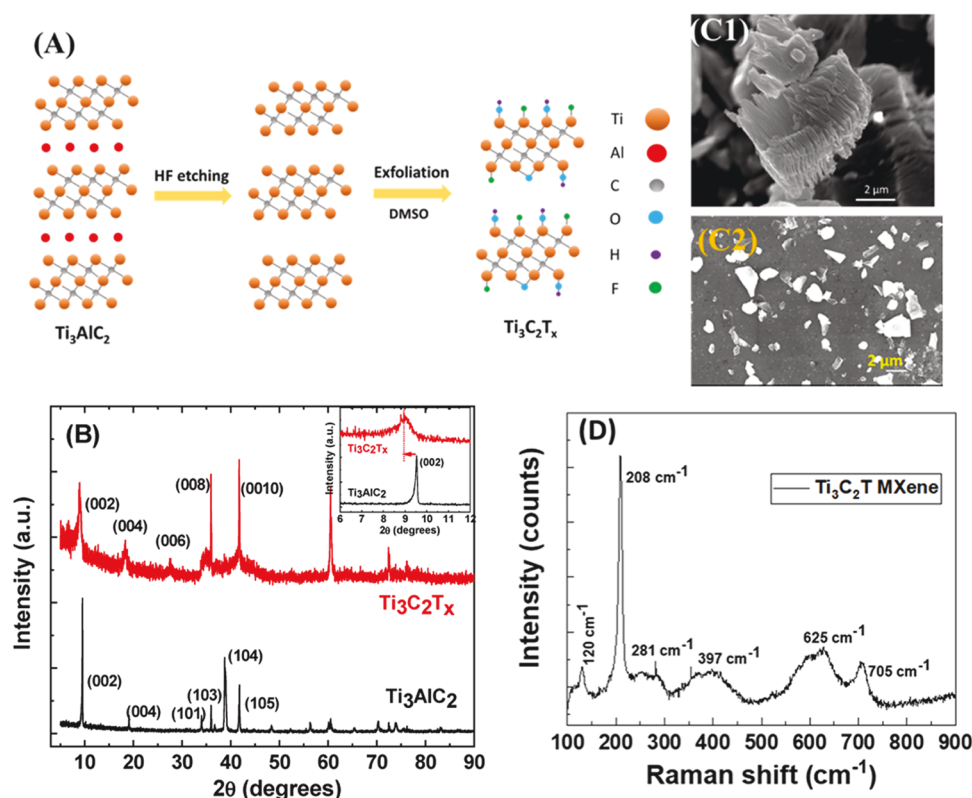


Figure 1. (A) Schematic of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene synthesis scheme from the Ti_3AlC_2 MAX phase powder. (B) XRD spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and Ti_3AlC_2 . The inset in (B) shows the relative shift in the (002) peak position for $\text{Ti}_3\text{C}_2\text{T}_x$ toward lower 2θ compared to Ti_3AlC_2 . (C1) SEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. (C2) SEM image of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. (D) Raman spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene measured under 532 nm laser excitation.

ethanolamine was prepared and stirred overnight. The resulting blue solution was filtered and spun onto the treated ITO substrates at 3000 rpm for 40 s and then heated at 350 °C for 30 min in air. The NiO_x -coated ITO substrates were transferred into a N_2 -filled glovebox, where a $\text{CH}_3\text{NH}_3\text{PbI}_3$ (1.2 M in 0.7 mL DMF and 0.3 mL DMSO) solution prepared overnight was spin-coated on the sample stage programmed to spin at 1000 rpm for 5 s and 6000 rpm for 45 s. After 10 s, in the second step, 500 μL of toluene was dripped on the sample. The spin-coated films were annealed at 100 °C for 10 min. The PC_{61}BM dissolved in chlorobenzene (20 mg/mL) was spin-coated onto the perovskite layer at 1000 rpm for 60 s and annealed at 80 °C for 15 min. Then, 1 mg/mL of BCP solution in ethanol was spun at 4000 rpm for 30 s. Finally, 100 nm thick Ag electrodes were thermally evaporated ($\sim 1 \times 10^{-6}$ Torr pressure) through a shadow mask on the surface of the BCP layer. The active area of the devices was 0.06 cm^2 . For test devices, we used as-synthesized MXene dissolved in chlorobenzene at 20 mg/mL concentration. In addition, different amounts of MXene were added to the PC_{61}BM solution for obtaining different concentrations (0.25, 0.50, 0.75, and 1.0 wt %) of MXene-doped PC_{61}BM as ETLs for exploring the device performance. It was found that 0.75 wt % MXene-doped PC_{61}BM led to the highest device performance and is represented as M- PC_{61}BM hereafter in the paper. The NiO_x HTL was replaced with a SnO_2 film deposited by spin coating the SnO_2 (20 mg/mL in chlorobenzene) solution for electron-only devices.

2.3. Characterization. The structural characterization of MXene powder samples was conducted using a p-XRD Empyrean 2 system. The film morphologies and energy-dispersive X-ray analysis (EDAX) spectra were recorded using a high-resolution field emission scanning electron microscope (FESEM, HITACHI, S-4800) equipped with an EDAX detector. The Raman spectral characteristics of the MXene, PC_{61}BM , and M- PC_{61}BM samples were characterized using an NTEGRA Spectra II (NT-MDT system), equipped with a 532 nm laser source and a charge-coupled device (CCD) detector. The UV–

vis absorbance spectra were recorded using a VWR UV1600 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were conducted using Kratos 165 ultra photoelectron spectrometer. For XPS measurements, Al $K\alpha$ radiation (energy = 1100 eV) was used, and He–I (energy = 21.22 eV) radiation was used for UPS measurements. During the UPS measurements, a 10 V bias was applied to the sample. Atomic force microscopy (AFM) and scanning Kelvin probe force microscopy (SKPFM) measurements were conducted using an NTEGRA Spectra-II (NT-MDT) system. The SKPFM measurements were performed in two-pass amplitude mode (AM) using a Pt-coated conductive Si probe (FMG01/Pt, resonance frequency of 56 kHz). Electrochemical impedance spectroscopy (EIS) measurements of PSC devices were conducted using a three-electrode potentiostat (CHI-660, CH Instruments) setup. The current density–voltage characteristics of fabricated solar cells were recorded using a Keithley 2400 source measure unit (SMU) under AM 1.5 spectral illumination. The external quantum efficiency (EQE) of PSCs was measured using the Bentham Instruments system. The steady-state photoluminescence (PL) spectra of thin-film samples deposited on glass were collected by exciting the sample with 550 nm wavelength light. The carrier lifetimes were estimated by recording the time-resolved photoluminescence (TRPL) spectra measured using a time-correlated single-photon counting (TCSPC) measurement setup integrated with a 550 nm excitation source.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Prepared MXene and the Surface Chemistry. The schematic in Figure 1A shows the steps involved in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene synthesis. The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene samples synthesized from HF etching of Ti_3AlC_2 were characterized using different microscopic and spectroscopic techniques. The transformation of the MAX phase

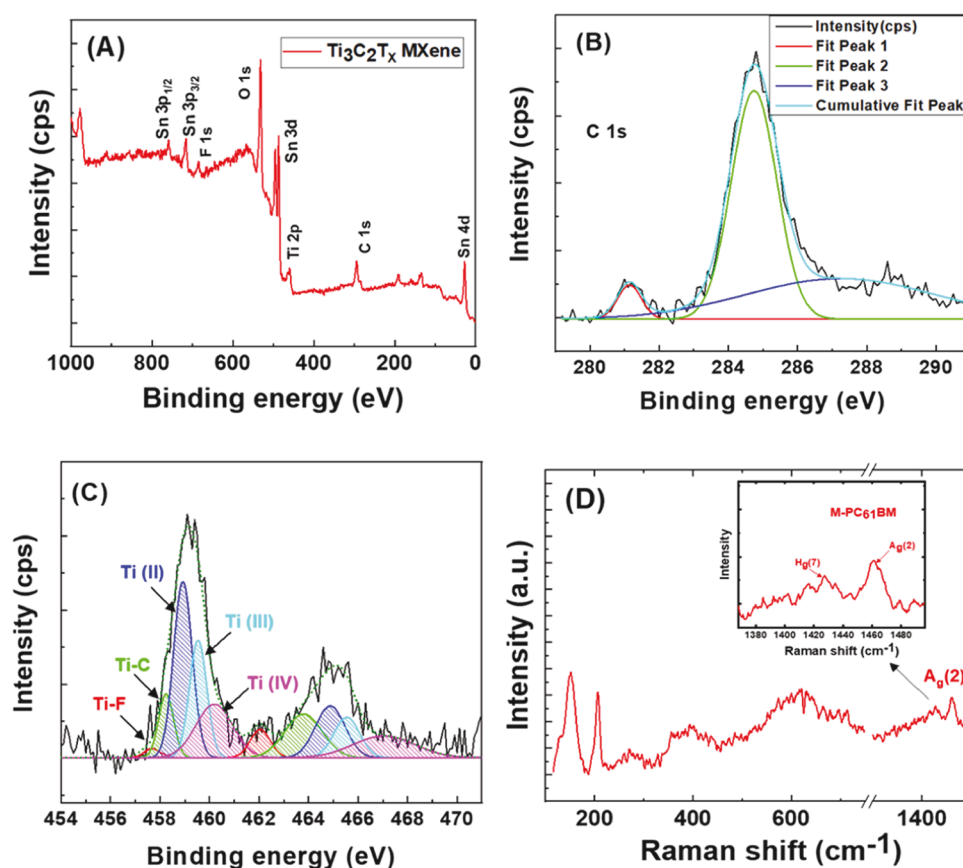


Figure 2. (A) Survey XPS spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. High-resolution XPS spectrum corresponding to C 1s (B) and Ti 2p (C). (D) Raman spectra of M-PC₆₁BM films measured under 532 nm excitation. (Inset shows a comparison of the close-up view of the Raman spectrum of M-PC₆₁BM in the 1380–1500 cm^{-1} region.)

Ti_3AlC_2 powder into $\text{Ti}_3\text{C}_2\text{T}_x$ (T_x : $-\text{O}$, $-\text{OH}$, $-\text{F}$) was confirmed by comparing their X-ray diffraction (XRD) spectra (Figure 1B). The XRD spectrum of the MAX phase Ti_3AlC_2 has a strong peak at $2\theta = 39^\circ$ that corresponds to the (104) plane, which disappears after its transformation to $\text{Ti}_3\text{C}_2\text{T}_x$.^{39,40} Also, a shift of the (002) peak to lower 2θ (from 9.5 to 8.9°) was observed in the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene sample compared to the MAX phase, indicating the increased interlayer distance due to Al etching from Ti_3AlC_2 . The XRD showed an increase in interplanar distance for exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene samples compared to the HF-etched samples (Figure S3). Figures S1 and 1C1 show the scanning electron microscopy (SEM) images of the Ti_3AlC_2 and $\text{Ti}_3\text{C}_2\text{T}_x$ samples, and the accordion-like layered structure of $\text{Ti}_3\text{C}_2\text{T}_x$ also confirms the etching of Al from the MAX phase.⁴⁰ The increased interlayer spacing achieved through Al etching helps the separation of $\text{Ti}_3\text{C}_2\text{T}_x$ layers during the intercalation and sonication steps. The SEM images of MXene flakes (sizes ranging from 0.2 to $3 \mu\text{m}$) obtained at the end of the exfoliation and sonication step are shown in Figures 1C2 and S2. The AFM topography image and the corresponding height profile (Figure S4) established that the MXene sheet has an estimated thickness of $\sim 8 \text{ nm}$, indicating an eight-layer structure.⁴¹

Figure 1D shows the Raman spectrum of MXene. The peaks at 203 (out-of-plane A_{1g} mode, Ti, C, O), 280 , and 370 cm^{-1} (the E_g peaks corresponding to the in-plane vibrational modes of the surface groups, both O_2 and $-\text{OH}$ groups attached to Ti atoms), 720 cm^{-1} (out-of-plane $\text{A}_{1g}(\text{C})$ vibrational mode of

carbon atoms) confirm the formation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The WF of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is controlled by the distribution of the surface terminal groups ($-\text{OH}$, $-\text{F}$, and $-\text{O}$) formed on the Ti outer layer, which depends on the procedure employed for the synthesis. Hence, we used XPS to confirm the MXene formation and identify the surface terminal groups on the prepared MXene samples. The XPS survey spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Figure 2A) displayed features corresponding to carbon, titanium, oxygen, and fluorine. The apparent absence of a prominent Al feature in the MXene sample confirmed the successful etching of the MAX phase and consequent formation of the MXene phase. The high-resolution XPS spectra were recorded to unravel the chemical composition of MXene, including the surface terminal groups, the local bonding environment, and the oxidation states of the elements identified in the survey spectrum. The deconvoluted high-resolution carbon 1s spectrum (Figure 2B) shows components at 281.2 , 284.8 , and 287.9 eV corresponding to Ti–C, C–C, and C–O, respectively. Similarly, the deconvoluted Ti 2p spectrum (Figure 2C) provided insights about Ti bonds with C, O, and F atoms. As shown, the deconvoluted Ti 2p spectrum displays a prominent doublet feature corresponding to $2p_{3/2}$ (459 eV) and $2p_{1/2}$ (464.7 eV) of Ti–C bonds.^{27,42} In addition, deconvoluted spectra reveal components corresponding to Ti(II), Ti(III), Ti(IV) (oxides such as TiO_2), and Ti–F. Thus, XPS analysis indicated that Ti in MXene exists as a combination of oxides, including mixed oxides (TiO_xF_y) and carboxides (TiC_xO_y). The deconvoluted O 1s spectrum (Figure S5A) with peaks at 530 eV (TiO_2), 531

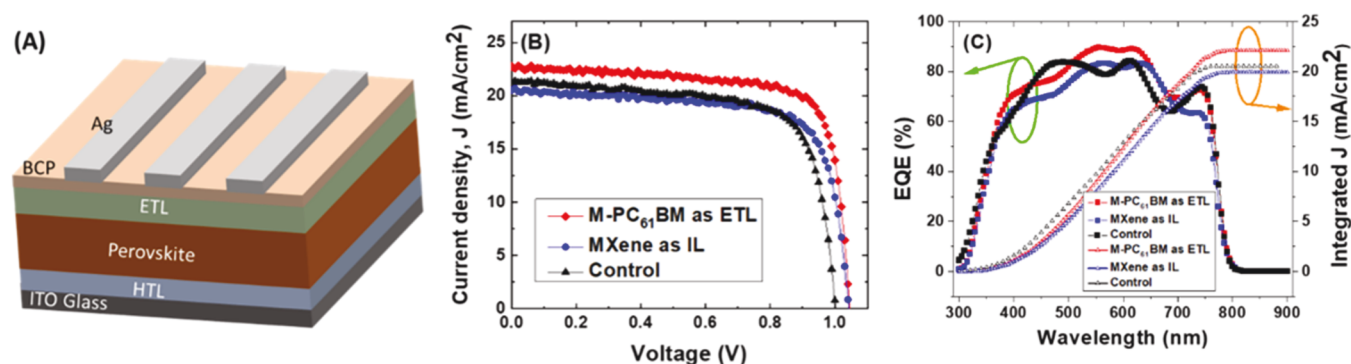


Figure 3. (A) Schematic of a cross-sectional view of a planar p-i-n perovskite solar cell device. (B) Current density (J)–voltage (V) curves (reverse scan) of devices with different ETLs or ETL/perovskite interfacial configurations including M-PC₆₁BM ETL (device A), MXene as an interfacial layer between PC₆₁BM and perovskite (device B), and the control device (device D) with PC₆₁BM as ETL, measured under AM 1.5 irradiation. (C) External quantum efficiency (EQE) and integrated current density (J_{sc}) plots of the same devices as in (B).

Table 1. Comparison of Photovoltaic Parameters of Devices A (M-PC₆₁BM Is ETL), B (MXene Is an Interfacial Layer between Perovskite and PC₆₁BM), C (MXene Is ETL), and D (PC₆₁BM Is ETL)

device	ETL	V_{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
A	M-PC ₆₁ BM	1.04 ± 0.02	22.75 ± 0.15	76 ± 1	17.95 ± 0.42
B	PC ₆₁ BM (MXene as an interfacial layer between PC ₆₁ BM and perovskite)	1.04 ± 0.01	20.53 ± 0.21	73 ± 1	15.53 ± 0.46
C	MXene	0.63 ± 0.09	5.15 ± 0.32	48 ± 2	1.55 ± 0.51
D	PC ₆₁ BM	1.0 ± 0.02	21.24 ± 0.29	71 ± 1	15.16 ± 0.39

eV (C–Ti–O_x), and 531.5 eV (C–Ti–(OH)_x) further confirmed the presence of mixed oxides. The peak at 534.3 eV in the O 1s spectrum could be assigned to water vapor adsorbed on the surface or –OH terminal groups. The deconvoluted F 1s spectrum (Figure S5B) showed two components at 684.5 eV (Ti–F) and 686 eV (Al–F).⁴² Note that the Al–F is a minor component and could originate from the residual Al after the etching process, as reported earlier.⁴² Our XPS analysis and quantification (Figure S6) confirmed the removal of most of the Al from the MAX phase, where MXene only retained ~0.9% of Al after the HF etch. Hence, the XPS analysis (together with other microscopic and spectroscopic results) confirmed the successful synthesis of MXene sheets with disproportionately distributed surface functional groups (i.e., –OH, –F, and –O).

3.2. Raman Spectroscopic Analysis of MXene Doping of PC₆₁BM Films. The introduction of dopants can lead to observable changes in the Raman spectrum of PC₆₁BM. Hence, we recorded the Raman spectra of both PC₆₁BM and M-PC₆₁BM films and analyzed the effect of MXene doping (Figures 2D and S7). The Raman spectrum of PC₆₁BM showed a peak at 1472 cm^{−1} corresponding to the pentagonal pinching mode ($A_g(2)$) of fullerene.⁴³ The Raman spectrum of M-PC₆₁BM displayed (Figure 2D) peaks corresponding to Ti₃C₂T_x MXene and PC₆₁BM.^{43,44} The presence of the unique breathing mode ($A_g(2)$) of fullerene in the Raman spectrum of MXene-doped PC₆₁BM (M-PC₆₁BM) confirmed that no structural changes occurred in PC₆₁BM upon doping. However, a red shift in $A_g(2)$ mode, from 1472 to 1461 cm^{−1}, was observed for M-PC₆₁BM relative to PC₆₁BM due to the doping of PC₆₁BM by MXene. A similar red shift in the Raman feature of PC₆₁BM upon n-type doping has been reported.⁴⁵ Hence, the Raman spectroscopic analysis of the M-PC₆₁BM sample indicated that the introduction of MXene into PC₆₁BM (in M-PC₆₁BM) leads to n-type doping of PC₆₁BM without any significant structural changes for PC₆₁BM. The in-plane and vertical homogeneity of MXene distribution in the

PC₆₁BM film are confirmed using EDAX mapping and power-dependent Raman spectroscopic studies (Figures S8 and S9).

3.3. Perovskite Solar Cell Device Characterization.

After confirming the successful synthesis of MXene nanosheets and the doping effect of MXene on PC₆₁BM, we investigated the application of MXene nanosheets in inverted planar (p-i-n) PSCs. Our goal was to examine the influence of MXene nanosheets in controlling PC₆₁BM ETL properties and tuning the band alignment at the perovskite–ETL interface. To study this, we fabricated p-i-n PSCs with different ETL combinations (based on where MXene was introduced in the device structure). The fabricated devices had the following structures: glass/ITO/NiO_x/MAPI/M-PC₆₁BM/BCP/Ag (device A, MXene used as a dopant to modify the electronic properties of PC₆₁BM), glass/ITO/NiO_x/MAPI/MXene/PC₆₁BM/BCP/Ag (device B, MXene used as an interfacial layer between the MAPI perovskite film and PC₆₁BM), and glass/ITO/NiO_x/MAPI/MXene/BCP/Ag (device C, MXene nanosheets alone used as ETL). A control device: glass/ITO/NiO_x/MAPI/PC₆₁BM/BCP/Ag (device D, with only PC₆₁BM as ETL) was also fabricated. A schematic of the cross-sectional view of the control device structure is shown in Figure 3A. In all of the devices, NiO_x was used as the HTL. The current density–voltage (J – V) and EQE characterization results of the test (A–C) and control (D) devices are presented in Figures 3B,C and S10. Table 1 shows a summary of the photovoltaic parameters of the devices tested in this study. The integrated current density (J_{sc}) from EQE spectra of each PSC device is consistent with the J – V measurement results. These J – V and EQE results suggest that device A (with M-PC₆₁BM as ETL), with a PCE = 18%, is the best configuration among all four device configurations investigated. The photovoltaic parameters of device A (with M-PC₆₁BM as ETL) were J_{sc} = 22.8 mA/cm², FF = 0.76, and V_{OC} = 1.04 V. Compared to device A, all other devices illustrated inferior performance with lower PCEs of 15.7, 1.6, and 15% for devices B, C, and D, respectively. To monitor the hysteresis in these devices, forward and reverse

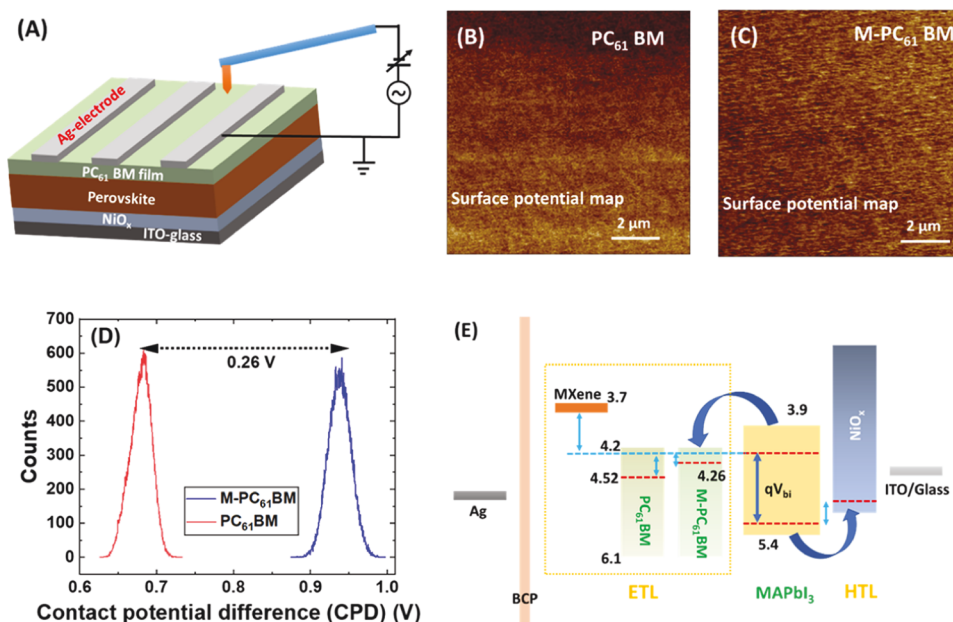


Figure 4. (A) Schematic of a scanning Kelvin probe force microscope (SKPFM) measurement setup. Contact potential difference (CPD) maps of PC₆₁BM (B) and M-PC₆₁BM (C) samples were recorded using SKPFM (scan size: 10 $\mu\text{m} \times 10 \mu\text{m}$). (D) Histogram of CPD values obtained from the SKPFM mapping for PC₆₁BM and M-PC₆₁BM samples shown in (B) and (C). As shown, the difference between the average CPD of PC₆₁BM and M-PC₆₁BM is 0.26 V, and this represents the shift in the Fermi level in M-PC₆₁BM relative to PC₆₁BM. (E) Energy-level band diagram.

$J_{\text{sc}}-V$ studies are recorded on both control and M-PC₆₁BM ETL devices (Figure S11). When compared to a control device, the M-PC₆₁BM device showed better hysteresis characteristics, and this can be attributed to passivation of perovskite by the M-PC₆₁BM ETL film. The M-PC₆₁BM ETL device stability data (Figure S12) indicates that these devices can retain >50% of their maximum PCE even after 3 weeks. Table S1 shows the optimized device PCE results for MXene doping of PC₆₁BM.

Understanding the fundamentals behind the observed superior performance of device A compared to control device (D) and devices B and C is critical for the practical application of MXene in PSCs. While our Raman results indicated that mixing MXene with PC₆₁BM leads to n-doping of PC₆₁BM, which may improve the conductivity of the M-PC₆₁BM film, a comprehensive understanding of the influence of MXene in all devices (A–C) is required to optimize the application of MXene in p–i–n PSCs. We used SKPFM, PL, TRPL, space-charge limited current (SCLC), and EIS studies to unravel the basis of the impact of MXene on interfacial charge dynamics in p–i–n PSCs. Further, the data was correlated with the device performance to delineate the effect of MXene on the photovoltaic parameters for devices A–C.

3.4. Electronic Energy-Level Characterization. Optimal alignment of energy levels (i.e., highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of CTLs, i.e., ETL and HTL, present on either side of the MAPI perovskite film, is critical for efficient separation and collection of photogenerated charge carriers (i.e., electrons and holes). Therefore, we employed UV–visible absorption spectroscopy, UPS, and SKPFM to obtain the band gap (E_{g}), HOMO, and LUMO values of the MAPI, PC₆₁BM, M-PC₆₁BM films, and Ti₃C₂T_x MXene nanosheets. The optical band gaps of PC₆₁BM and M-PC₆₁BM were estimated to be equal to 1.9 eV, from the UV–vis absorbance results (Figure S13A). The optical band gap of MAPI perovskite was

estimated to be 1.5 eV from the corresponding UV–vis absorbance spectrum (Figure S13A). The WF (Φ) values of pristine MXene and perovskite deposited on the conducting ITO glass substrate were estimated, from the UPS measurements, to be $\Phi_{\text{MXene}} = 3.7$ eV and $\Phi_{\text{MAPI}} = 4.2$ eV, respectively (Figure S13B). The HOMO, LUMO, and the band gap values of 3.9, 5.4, and 1.5 eV for the MAPI are estimated from the UPS and the UV–vis absorbance (Figure S13A,B) measurements.

To derive a localized understanding of the variation of surface roughness and associated changes in WF, we examined the PC₆₁BM samples using SKPFM, which can map WF changes with nanoscopic resolution.³² Figure 4A shows a schematic of the SKPFM measurement setup. In SKPFM, we simultaneously map the topography and contact potential difference (CPD) to understand the effect of local morphology on the surface potential and estimate the WF from the measured CPD. The topography and CPD of PC₆₁BM and M-PC₆₁BM films coated on ITO/glass substrates were characterized using a Pt-coated conducting Si tip in two-pass amplitude mode (AM)-SKPFM. As shown (Figure S14A,B), both PC₆₁BM and M-PC₆₁BM films were found to have a uniform topography with an average roughness value of ≈ 3 nm. However, in comparison with PC₆₁BM, the M-PC₆₁BM film displayed a different CPD (Figure 4B,C), suggesting a modified work function due to the doping of PC₆₁BM by MXene. Interestingly, the CPD was almost constant across the scanned region (Figure 4B,C), indicating that the WF of PC₆₁BM is uniformly modified when MXene was used as a dopant. Figure 4D shows the histogram of CPDs, from 10 $\mu\text{m} \times 10 \mu\text{m}$ sample regions shown in Figure 4B,C, each corresponding to PC₆₁BM and M-PC₆₁BM films. As shown, there is a 0.26 eV difference in the average CPD of PC₆₁BM and M-PC₆₁BM samples. Furthermore, by correlating the average CPD with the tip WF (i.e., Pt tip with a WF of 5.2 eV), we estimated $\Phi_{\text{M-PC}_{61}\text{BM}}$ and $\Phi_{\text{PC}_{61}\text{BM}}$ as 4.26 and 4.52 eV,

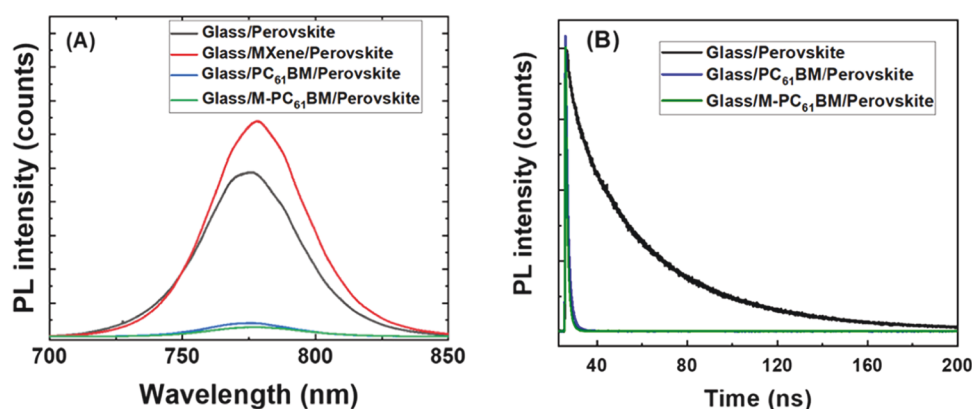


Figure 5. PL (A) and TRPL (B) spectra of perovskite/glass, perovskite/MXene/glass, perovskite/M-PC₆₁BM/glass, and perovskite/PC₆₁BM/glass samples.

respectively.^{46,47} The lower WF of M-PC₆₁BM (or upshift in the Fermi level) relative to that of PC₆₁BM is probably due to the high electron affinity of PC₆₁BM compared to MXene, resulting in an electron transfer from pristine MXene (WF = 3.7 eV) to PC₆₁BM (WF = 4.52 eV).⁴⁸ The upshift in the Fermi level for M-PC₆₁BM compared to PC₆₁BM also results in higher electrical conductivity due to increased carrier concentration (discussed later). The upshift in the M-PC₆₁BM film compared to the pristine PC₆₁BM film indicated by SKPFM agrees well with the Raman results, which suggested n-type doping for the M-PC₆₁BM film. The upshift of the Fermi level (E_F) for M-PC₆₁BM compared to pristine PC₆₁BM (i.e., $WF_{PC_{61}BM} > WF_{M-PC_{61}BM}$) can be potentially due to the dipoles formed at the interface of MXene and PC₆₁BM in M-PC₆₁BM.^{28,48} The observed reduction in WF in M-PC₆₁BM is favorable for the electron transport from MAPi to the ETL (M-PC₆₁BM), which enhances the PCE of device A.^{15,49} The energy band diagram in Figure 4E can help visualize the charge transport between different layers in devices A–D.

The upshift of the Fermi level for M-PC₆₁BM can also explain the improvement in photovoltaic parameters such as V_{OC} and FF. In general, a misalignment between the Fermi levels of the perovskite film and CTLs leads to open-circuit voltage losses due to the recombination of charge carriers (i.e., electrons and holes) at the perovskite and CTL interfaces.^{49,50} The upshift of the Fermi level by introducing MXene leads to the reduction of the energy difference between the Fermi levels of the perovskite film and ETL, leading to lower voltage losses. Therefore, tailoring the Fermi level of M-PC₆₁BM by MXene doping to align it better with the E_F of the perovskite (see the band diagram in Figure 4E) has minimized the recombination losses as indicated by enhancement in V_{OC} (Table 1).

To prove the enhancement of the electrical conductivity of M-PC₆₁BM compared to PC₆₁BM, we calculated the dc electrical conductivity using the two-probe current–voltage (I – V) measurements (Figure S16).⁵¹ The I – V characteristics of two different structures, including Ag/PC₆₁BM/ITO glass and Ag/M-PC₆₁BM/ITO glass, were measured. The estimated electrical conductivities (σ) for PC₆₁BM and M-PC₆₁BM films, with 40 nm ETL layer thickness and 0.06 cm² contact area, were 0.2 and 2.2 mS/cm, respectively. Therefore, the dc electrical I – V characteristics provided direct evidence for the enhanced electrical conductivity of M-PC₆₁BM. The higher conductivity of the M-PC₆₁BM film also agrees with the work function and band gap results, which showed that the Fermi

level is closer to the LUMO in M-PC₆₁BM compared to the Fermi level of the PC₆₁BM sample.⁵² The better proximity (or smaller separation) between LUMO and E_F for M-PC₆₁BM indicates increased electron concentration and increased conductivity for the M-PC₆₁BM film.

The very low PCE (=1.6%) of device C (with pristine MXene as ETL) (Figure S7) can also be explained based on energy-level misalignment. As shown in the band diagram, the photogenerated electrons in the perovskite encounter a potential barrier (uphill) when MXene alone is used as the ETL due to its low WF value of 3.7 eV. Moreover, the photogenerated holes do not experience any transport barrier when MXene is used as ETL, resulting in higher charge recombination, leading to low PCE.³³ The PCE of device B with MXene as an interfacial layer between MAPi and PC₆₁BM is almost similar to the PCE of the reference device D. We think that the higher conductivity of M-PC₆₁BM and better energy-level alignment results in better PCE enhancement in device A compared to device B. Although the PCE enhancement for device B is not as high as that for device A, we observed a clear improvement in V_{OC} and FF, which could be a consequence of improved passivation of the perovskite film by MXene at the interface between PC₆₁BM and the perovskite. To understand the role of MXene in perovskite passivation and charge extraction kinetics at the interface, we characterized our samples using PL, TRPL, EIS, and space-charge limited current (SCLC) measurements as discussed below.

3.5. PL and TRPL-Based Study of Charge Extraction from Perovskite by Adjacent ETL. Photoluminescence spectroscopy is a nondestructive technique that can provide information about the quality of the absorbing perovskite film, passivation effects, carrier lifetimes, and the charge extraction efficiency of CTLs. We performed steady-state PL and time-resolved PL (TRPL) measurements to unravel the impact of MXene on the radiative/nonradiative carrier recombination of photogenerated charge carriers. The PL studies were performed for samples with the following configurations: (a) glass/MAPi, (b) glass/MXene/MAPi, (c) glass/PC₆₁BM/MAPi, and (d) glass/M-PC₆₁BM/MAPi, where the pure MAPi film deposited on a glass substrate (i.e., glass/MAPi) was used as the control sample. The steady-state PL intensity (Figure 5A) was lower for the samples with PC₆₁BM films (i.e., both PC₆₁BM and M-PC₆₁BM) underneath the MAPi perovskite film compared to the other samples without PC₆₁BM or M-PC₆₁BM. The PL quenching for the samples

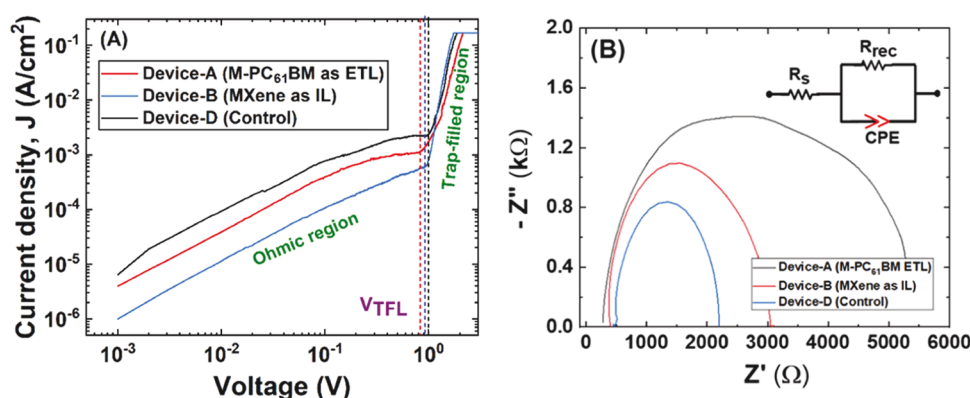


Figure 6. (A) Current density–voltage (J – V) characteristics of electron-only devices. Here, SnO₂ is used as a second ETL in devices A, C, and D. (B) Nyquist plots obtained from EIS measurements on devices A-, B-, and D-based perovskite devices measured under dark and at 0 V. The inset shows the modified Randles circuit used for fitting the Nyquist plots.

consisting of PC₆₁BM or M-PC₆₁BM is due to a more efficient electron extraction by the adjacent ETL (PC₆₁BM or M-PC₆₁BM). Interestingly, the samples with the M-PC₆₁BM film showed a more pronounced PL quenching when compared with the sample with PC₆₁BM alone. The potentially better electron extraction by M-PC₆₁BM could be due to improved energy-level alignment at the perovskite and M-PC₆₁BM interface. Notably, in the glass/MXene/MAPI sample, a very high PL intensity was observed compared to all other samples, including the control sample (glass/MAPI). We attribute the higher PL in this MXene-only sample to the passivation of undercoordinated Pb²⁺ ions present in the MAPI film by surface terminal groups present in MXene.^{28,53} We hypothesize that MXene can passivate undercoordinated Pb²⁺ ions present in the perovskite film. The interaction and passivation of undercoordinated Pb²⁺ ions present in the perovskite film were verified by investigating the high-resolution Pb 4f regions of the pristine perovskite, PC₆₁BM/perovskite, and M-PC₆₁BM/perovskite films (Figure S16). A clear shift of 4f_{7/2} and 4f_{5/2} peaks toward lower binding energy is observed for both PC₆₁BM/perovskite and M-PC₆₁BM/perovskite samples compared to the pristine perovskite sample, suggesting that surface terminal groups in MXene and PC₆₁BM can interact with Pb²⁺ in the perovskite film.⁵⁴ Further, the higher shift (0.3 eV) for the M-PC₆₁BM/perovskite sample compared to PC₆₁BM/perovskite (0.1 eV) relative to pristine perovskite confirms additional passivation effect of MXene compared to PC₆₁BM alone. The enhanced surface passivation thus resulted in suppressing nonradiative recombination at surface and grain boundary defects. Also, the lower WF of MXene (Figure S7B), compared to the LUMO level of the MAPI film, excludes the possibility of facile electron transfer from perovskite to MXene. Hence, passivation of MAPI by MXene coupled with the impeded interfacial electron abstraction from MAPI to MXene results in an increased PL intensity for the glass/MXene/MAPI sample. We expect an upshift in the E_F of perovskite films due to the passivation of grain boundaries in the perovskite film, which reduces the E_F splitting or increases the open-circuit voltage.^{49,55,56} The reduction in trap state density (n_{trap}) in the perovskite film also helps to minimize V_{OC} losses that arise due to pinning of the Fermi levels of CTLs to the trap state present in perovskites. The MXene passivation effect is evident in the measured photovoltaic data (Table 1), where both devices A and B showed significant improvement in V_{OC} values compared to the control sample. In device C (with MXene

as ETL), the poor V_{OC} could be due to improper energy alignment at the ETL/perovskite interface, as discussed previously. Therefore, in addition to the E_F shift for the M-PC₆₁BM film, the reduced Fermi level splitting for the perovskite film may have also contributed to the observed enhancement in V_{OC} .

We also conducted TRPL measurements to obtain insights into the charge-transfer kinetics for different samples and understand the effect of MXene in the charge-transfer kinetics. Figure 5B shows the TRPL spectra of the different samples investigated. The obtained TRPL spectra were fitted to a biexponential decay process, using the equation⁵⁷

$$y = A_1 \exp\left(\frac{-x}{\tau_1}\right) + A_2 \exp\left(\frac{-x}{\tau_2}\right) + y_0 \quad (1)$$

A_1 , τ_1 and A_2 , τ_2 are the amplitudes and time constants corresponding to the fast and slow decay processes, and y_0 is a constant. τ_1 is the lifetime corresponding to the carrier recombination at the interface between the perovskite and the transport layers, and τ_2 is the carrier lifetime corresponding to the carrier recombination in the perovskite film.²³ Table S2 shows the summary of the recombination time constants obtained by fitting the TRPL spectra. From the data, we can identify that the PL decay is faster for MAPI/M-PC₆₁BM/glass and MAPI/PC₆₁BM/glass samples with time constants, $\tau_{\text{M-PC}_{61}\text{BM}} = 0.8$ ns, and $\tau_{\text{PC}_{61}\text{BM}} = 1.1$ ns, respectively. In comparison, the PL decay for the MAPI/glass sample was significantly slower with $\tau_{\text{MAPI}} = 6.25$ ns. The faster decay profile observed for the samples with the ETL layer sandwiched between the MAPI perovskite film and the ITO/glass suggests a charge transfer from the MAPI to the adjacent ETL. This observation is consistent with ETL-assisted PL quenching, as discussed in steady-state PL results. The accelerated charge transport across the ETL/perovskite interface in the case of the MAPI/M-PC₆₁BM/glass sample, as indicated by a lower time constant, further confirms the importance of MXene doping in M-PC₆₁BM for enhancing the photovoltaic performance. Based on steady-state PL and TRPL results, we conclude that the enhancement in V_{OC} of PC₆₁BM ETL-based test devices (i.e., A and B) is due to the improved passivation of perovskite films and the better energy-level alignment at the interface due to MXene doping in M-PC₆₁BM.

3.6. Evaluation of MXene Passivation Effects on the Trap State Density in Perovskite Films Using SCLC Study. During the crystallization of the perovskite film, it is known that surface and grain boundary defects can form deep-level traps (e.g., undercoordinated Pb^{2+} ions), and the formed traps can impede the PCE, especially V_{OC} .^{7,8} To better understand the influence of MXene in reducing the trap state density (n_t) of perovskite films, the trap state density of perovskite films with and without MXene was estimated. Space-charge limited current (SCLC) is a commonly used technique to estimate the trap state density.⁵⁸ For SCLC measurements, we considered structures similar to those used for J – V discussed previously, except a second reference SnO_2 film as ETL replaced the NiO_x HTL to form electron-only devices. Device C was not considered for this study since it showed very poor PCE due to improper energy-level misalignment. For the rest of the devices, the current–voltage (I – V) characteristics were measured in the dark (Figure 6A). As expected, the $\log(J)$ – $\log(V)$ curves displayed two distinct regions that consist of a linear current response region at low voltages and a nonlinear ($J \propto V^n$, $n > 3$) response at higher voltages. The dark currents for devices A and B were lower than for the control device (i.e., device D) with PC_{61}BM alone as ETL. The lower dark current is a signature of less leakage current or passivation of tail/surface states in perovskite films.⁵³ We estimated the trap density of the perovskite films in each device configuration from the high-voltage regime, where the current increased significantly as a function of voltage (i.e., $J \propto V^n$, $n > 3$). We identified the trap-filled voltage (V_{TFL}) as the voltage at which the device current follows $J \propto V^n$, $n > 3$.⁵⁸ From Figure 6A, the V_{TFL} for devices A, B, and D were 0.86, 0.94, and 0.98 V, respectively (Table S3).

The trap state density (n_t) was estimated using the equation⁵⁸

$$n_t = \frac{V_{\text{TFL}} 2\epsilon_0 \epsilon}{eL^2} \quad (2)$$

where ϵ is the dielectric permittivity of vacuum, ϵ_0 ($=70$) and L ($=300$ nm) are the dielectric constant, and the thickness of the perovskite film, and e is the electron charge. The calculated n_t values for perovskite films for devices A, C, and D were 7.4×10^{16} , 8.1×10^{16} , and $8.4 \times 10^{16} \text{ cm}^{-3}$, respectively. These SCLC measurement results confirm that the trap state density (n_t) is lower for perovskite films for the M- PC_{61}BM samples (device A) than for the control device (device D), and this can be attributed to the enhanced passivation of perovskite by MXene present in the M- PC_{61}BM film. The calculated lower trap density values for perovskite films for devices A and B, through MXene assisted improved perovskite passivation, substantiate the PL enhancement observed in the steady-state PL measurements. The reduced trap states in perovskite with doped M- PC_{61}BM ETL result in a narrower distribution of the density of states (DOS) of the conduction band, leading to an upshift in the Fermi level. The change in the Fermi level position leads to a lower loss in V_{OC} due to a higher Fermi level splitting within the perovskite.^{49,55} Hence, reduced trap states in perovskite confirmed via SCLC measurements also reaffirms that passivation of perovskite films by MXene plays a significant role in improving the V_{OC} and FF.

3.7. Electrochemical Impedance Spectroscopy (EIS) Analysis of Interfacial Charge Recombination at the Perovskite and ETL Interface. To further confirm the enhanced charge dynamics at the ETL–MAPI interface and

prove that MXene improves the transfer properties of PC_{61}BM -based ETLs, we investigated devices A, B, and D using electrochemical impedance spectroscopy (EIS) in the dark at 0 V.⁵⁸ The Nyquist plots (Z'' vs Z') display a semicircle in the high-frequency regime (Figure 6B). The Nyquist plots were fitted using the ZView software with a modified Randles circuit model (inset of Figure 6B), which contains physical properties of the devices, including a recombination resistance (R_{rec}), a constant phase element (CPE), and a series resistance (R_s).^{59,60} Among the three parameters, R_{rec} is most critical for optimizing ETL, as it is directly related to the charge recombination at the ETL–perovskite interface. A higher R_{rec} typically means that there is less recombination at the interface. Our data showed that R_{rec} follows the order, $R_{\text{rec}}(\text{control})$ (2.1 k Ω) < $R_{\text{rec}}(\text{MXene as IL})$ (2.6 k Ω) < $R_{\text{rec}}(\text{M-PC}_{61}\text{BM as ETL})$ (4.5 k Ω), implying reduced recombination or improved charge transport in device A.²³ A summary of the fitting results is shown in Table S4. Therefore, the estimated higher recombination resistance for devices A and B can be attributed to improved interfacial properties at the ETL/MAPI interface. The enhanced conductivity of M- PC_{61}BM for device A (as evidenced by electrical conductivity measurements) may also contribute to the enhanced performance. Thus, the EIS analysis also confirmed that the better interfacial energy-level alignment and enhanced conductivity afforded by MXene doping of PC_{61}BM in M- PC_{61}BM ETLs results in reduced recombination losses and a higher PCE (device A). Thus, through combined SKPFM, PL, TRPL, trap state density measurements, and EIS analyses, we established that the higher PCE value obtained for the device with MXene-doped PC_{61}BM (device A) is due to improved ETL conductivity, enhanced passivation of perovskite, and better energy-level alignment at the perovskite–ETL interface.

4. CONCLUSIONS

In summary, we investigated the application of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for the engineering of the interface between PC_{61}BM and perovskite in p–i–n PSCs. Three different configurations were investigated with MXene used as either a dopant in PC_{61}BM (M- PC_{61}BM), an interfacial layer between ETL and perovskite, and a standalone ETL. The device with MXene-doped PC_{61}BM (M- PC_{61}BM) as ETL displayed a PCE enhancement of 2.8% relative to the control device with pristine PC_{61}BM as ETL. Our detailed spectro-microscopic and device analyses show how the application of multifunctional MXene enhances the PCE of PSCs due to improved conductivity of M- PC_{61}BM , passivation of perovskite, and favorable energy-level alignment (via n-doping in PC_{61}BM) at the perovskite–M- PC_{61}BM interface. Though the application of MXene alone as ETL can passivate the MAPI layer, the unfavorable energy alignment at the interface inhibits electron abstraction and leads to inferior device performances. Hence, the standalone application of MXene as ETL will require more exclusive control of their work function for better carrier transport properties. Relatively lower enhancement in PCE for the device with MXene as the interfacial layer, compared to the M- PC_{61}BM device, suggests that the improvement of the ETL properties is also critical in addition to passivating the defects of perovskite to derive superior PCE. Finally, this study, using planar p–i–n perovskite solar cells as a case study, provided a fundamental understanding of how the multifunctional

Ti₃C₂T_x MXene can be leveraged for high-performance optoelectronic devices.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.1c01669>.

SEM images of the Ti₃AlC₂ MAX phase, Ti₃C₂T_x MXene; XRD results of Ti₃C₂T_x MXene at the end of exfoliation, AFM topography image of Ti₃C₂T_x MXene; high-resolution XPS spectra of O 1s and F 1s regions in Ti₃C₂T_x MXene; Raman spectrum of the pristine PC₆₁BM sample; current density–voltage characteristics of the p–i–n PSC device with MXene as ETL and NiO_x as HTL; UV–vis absorbance spectra of MXene, PC₆₁BM, and M-PC₆₁BM, UPS spectra of perovskite and MXene films; AFM topography of the PC₆₁BM and M-PC₆₁BM samples; current–voltage (*I*–*V*) measurements on PC₆₁BM and Ti₃C₂T_x MXene-doped PC₆₁BM (M-PC₆₁BM) films; time constant values obtained by fitting the TRPL data; PCE stability; hysteresis; PC₆₁BM doping optimization for optimal PCE; high-resolution XPS scans for Pb 4f in perovskite, PC₆₁BM/perovskite, and M-PC₆₁BM/perovskite samples; and distribution of *V*_{TFL} values for multiple devices, ZView fitting results of Nyquist plots (PDF)

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Notes

The authors declare no competing financial interest.

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