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SnO$_2$-$\text{Ti}_3\text{C}_2$ MXene electron transport layers for perovskite solar cells

Lin Yang$^a$, Yohan Dall’Agnese$^a$, Kanit Hantanasirisakul$^b$, Christopher E. Shuck$^b$, Kathleen Maleski$^b$, Mohamed Alhabeb$^b$, Gang Chen$^a$, Yu Gao$^d$, Yoshitaka Sanehira$^c$, Ajay Kumar Jena$^c$, Liang Shen$^d$, Chunxiang Dall’Agnese$^{a,*}$, Xiao-Feng Wang$^{a,*}$, Yury Gogotsi$^{a,b}$, Tsutomu Miyasaka$^c$

$^a$ Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, 2699 Qianjin Street, Changchun 130012, China

$^b$ A. J. Drexel Nanomaterials Institute, and Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104, United States

$^c$ Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8503, Japan

$^d$ State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China

Corresponding Authors

* Chunxiang Dall’Agnese, E-mail: chunxiang@dallagnese.fr

* Xiao-Feng Wang, E-mail: xf_wang@jlu.edu.cn
Abstract

MXenes, a class of two-dimensional (2D) transition metal carbides and nitrides, have a wide range of potential applications due to their unique electronic, optical, plasmonic, and other properties. Herein, we explore the use of Ti$_3$C$_2$ MXene in organic-inorganic lead halide perovskite solar cells (PSCs) due to its metallic conductivity. SnO$_2$-Ti$_3$C$_2$ MXene nanocomposites with different contents of Ti$_3$C$_2$ (0, 0.5, 1.0, 2.0, 2.5 wt.%) were used as electron transport layers (ETLs) in low-temperature processed planar-structured PSCs. Mixing SnO$_2$ with 1.0 wt.% Ti$_3$C$_2$ effectively increases the power conversion efficiency (PCE) from 17.23% to 18.34%, whereas the device prepared with pristine Ti$_3$C$_2$ as the ETL achieves a PCE of 5.28%. Photoluminescence and electrochemical impedance spectroscopy results reveal that the metallic Ti$_3$C$_2$ MXene nanosheets provide superior charge transfer paths, enhancing electron extraction, electron mobility, and decreasing the electron transfer resistance at the ETL/perovskite interface, and thus leading to higher photocurrents. This work proposes a new field of application for MXenes and a promising method to increasing efficiency of solar cells.

Keywords: Ti$_3$C$_2$ MXene, electron transport layers, charge transfer, conductivity, perovskite solar cells
Introduction

Since methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) was first reported as a light absorbing material by Miyasaka et al. in 2009, organic-inorganic lead halide perovskite solar cells (PSCs) have received widespread attention. Owing to the appropriate bandgap, high absorption coefficient, long carrier diffusion lengths, high charge carrier mobility, and low trap density, hybrid perovskites present great potential as an efficient, low-cost, large-scale, and flexible materials for photovoltaic technology. In less than a decade, the power conversion efficiency (PCE) of PSCs improved from 3.8% to above 23%, making them competitive with other solar cells that have been developed for decades and approaching the theoretical efficiency of 33.5%. Despite the high PCE, a number of challenges still remain, such as limited electron extraction ability of the electron transport layer (ETL), the intrinsic instability of perovskites against environment (e.g., moisture, air, heat and light), low-temperature processability, mass production, etc. To solve these issues and progress toward practical application of PSCs, further research is needed.

In the architecture of PSCs, the ETL plays a significant role in suppressing charge recombination and rectifying photocurrent. Many PSCs are based on meso-superstructures with mesoporous TiO$_2$ as the ETL, which requires a high-temperature sintering process (> 450°C) and restricts its applications in large-area, flexible or wearable devices in spite of the high PCE. In contrast, PSCs with the planar-heterojunction configuration has more potential owing to its relatively easy and low-cost fabrication resulting from the lack of mesoporous TiO$_2$ layer, where the perovskite
layer is sandwiched between an ETL and a hole transport layer (HTL). Recently, SnO$_2$ has emerged as a commonly used ETL in planar PSCs due to its low-temperature processability ($\leq 200^\circ$C), superior electron mobility, and good optical transparency. SnO$_2$-based PSCs also exhibit good stability in ambient environment. Moreover, combining SnO$_2$ with n-type semiconductors or high-conductivity materials has proven an effective way to further improve the ETL’s electrical conductivity and electron mobility, and thus improving the PCE, highlighting that SnO$_2$-based ETL shows great potential for high efficiency PSCs.

In recent years, two-dimensional (2D) materials, especially graphene, have attracted great attention and have been used in PSCs due to their unique optical and electronic properties. To date, CH$_3$NH$_3$PbI$_3$-based regular (n-i-p type) and inverted (p-i-n type) PSC containing graphene oxide (GO) as charge transport layer were reported to achieve PCEs of 18.19% and 13.8%, respectively. Reducing GO has proven an effective method to improve the conductivity of GO and Yeo et al. reported the first reduced graphene oxide (rGO)-based inverted CH$_3$NH$_3$PbI$_3$ PSC, which reached a PCE of 10.8%. Recently, Jokar et al. further improved this system to exceed 16%. Therefore, it can be seen that conductive 2D materials have great potential in PSCs.

2D materials called MXenes offer a higher conductivity than rGO, while absorbing less light in the visible range. MXenes are 2D transition metal carbides and nitrides with a composition of M$_{n+1}$X$_n$Tx, where M is an early transition metal, X is carbon and/or nitrogen, and T$_x$ indicates the surface termination (usually oxygen- and/or
fluorine-containing species). MXenes have shown outstanding performance in supercapacitor, catalysis, conducting thin films, sensors, and antennas applications due to their high electrical conductivity and hydrophilicity, which enables processing from aqueous solutions. Interestingly, MXene-based electrodes for dye-sensitized solar cells and MXene as additive in perovskite layer for perovskite solar cells were recently proposed. However, the applications of MXenes in solar cells still remain largely unexplored. Furthermore, MXenes have been reported to enhance the electrical conductivity of semiconductors. These aroused our interest in applying MXenes in ETL to enhance the electron collection in PSCs.

Herein, Ti$_3$C$_2$ (the most widely studied MXene) nanosheets were used as a conductive additive in the SnO$_2$ ETL for low-temperature-processed planar CH$_3$NH$_3$PbI$_3$ PSCs. ETL films of SnO$_2$ with different Ti$_3$C$_2$ contents (0, 0.5, 1.0, 2.0, 2.5 wt.%) were prepared by spin-coating the aqueous mixed SnO$_2$-Ti$_3$C$_2$ colloidal solutions onto indium tin oxide (ITO) substrates. Photovoltaic devices were fabricated with an ITO/ETL/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag configuration. The results reveal that the proper addition of Ti$_3$C$_2$ to the SnO$_2$ layer can increase the ETL conductivity, which is beneficial for higher short-circuit current density ($J_{sc}$) and fill factor (FF) values. Compared with the pristine SnO$_2$, the PCE of SnO$_2$-Ti$_3$C$_2$-based PSC was improved from 17.23% to 18.34%, achieved by addition of 1.0 wt.% Ti$_3$C$_2$ to the SnO$_2$ layer, under the standard AM 1.5G (100 mW cm$^{-2}$) simulated sunlight illumination. The improvement of PCE can be attributed to faster electron extraction, higher electrical conductivity and electron mobility in the ETL. In the meantime, the pristine Ti$_3$C$_2$-
based PSC can also achieve a PCE of 5.28%.

Experimental section

Materials

SnO$_2$ colloid (15 wt.%, ~5 nm) was purchased from Alfa Aesar. Methylammonium iodide (CH$_3$NH$_3$I, >99.5%), lead iodide (PbI$_2$, >99.99%), 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD, >99.8%) and lithium-bis(trifluoromethanesulfonyl) imide (Li-TFSI, >99%) were obtained from Xian Polymer Light Technology Corp. 4-tert-butyl pyridine (tBP, 96%) was purchased from Macklin. Ultradry anhydrous N,N-dimethylformamide (DMF, 99.8%) and dimethyl sulfoxide (DMSO, 99.7%) were obtained from Beijing Infinity Scientific (INFI). For MAX phase synthesis, titanium powder and aluminum powder were purchased from Aladdin. Graphite was purchased from Sigma Aldrich.

Preparation of Ti$_3$C$_2$ MXene

First, Ti$_3$AlC$_2$ MAX phase was prepared by mixing 7.368 g of titanium powder, 1.523 g of aluminum powder and 1.109 g of graphite together, then sintered at 1650 $^\circ$C for 2 hours under argon. Ti$_3$C$_2$ MXene was prepared by etching Ti$_3$AlC$_2$ powder (~ 400 mesh) in 12 M LiF/9 M HCl solution at room temperature, as described elsewhere. $^{34}$ Briefly, 0.8 g of LiF was added to 10 mL of 9 M HCl under continuous stirring for several minutes. Then 0.5 g Ti$_3$AlC$_2$ powder was gradually added (over 5 min) to the etchant solution and continuously reacted for 24 h at room temperature. After that, the acidic mixture was washed with deionized water by repeated centrifugation (5 min per cycle at 8000 rpm). After each cycle, the supernatant was poured out and replaced by new deionized water until its pH > 5. Finally, the slurry was placed in ultrasound for 10 min and centrifuged at 3500 rpm for 1 h. A dark-green colloid supernatant solution
containing Ti$_3$C$_2$ nanosheets was obtained. To confirm the concentration of Ti$_3$C$_2$ dispersion, 10 mL of Ti$_3$C$_2$ dispersion were filtered over a cellulose membrane (0.22 µm pore size). After drying and weighing the peeled-off Ti$_3$C$_2$ film, the concentration of Ti$_3$C$_2$ was then calculated to be 3 mg mL$^{-1}$.

**Preparation of SnO$_2$-Ti$_3$C$_2$ MXene nanocomposites**

The SnO$_2$ hydrocolloid was diluted to the concentration of 3 wt.% (30 mg mL$^{-1}$) from 15 wt.% by adding deionized water. Then the Ti$_3$C$_2$ dispersion was directly mixed with the SnO$_2$ hydrocolloid according to the experimental ratios (0, 0.5, 1.0, 2.0, 2.5 wt.%), which were stirred for 5 minutes before using. SnO$_2$-Ti$_3$C$_2$ MXene films were prepared by spin-coating 70 µL of colloids at 3000 rpm for 30 s onto the ITO substrates in air.

**Device fabrication**

The pre-patterned ITO substrates were cleaned with detergent, deionized water, acetone, alcohol, and isopropanol in ultrasonic bath for 30 min in sequence, then treated with UV ozone for 30 min. ETL was prepared via spin-coating SnO$_2$ or SnO$_2$-Ti$_3$C$_2$ nanocomposites or Ti$_3$C$_2$ hydrocolloids onto the ITO substrates at 3000 rpm for 30 s in air, followed by thermal annealing on a hot plate at 150 °C for 30 min in air and UV ozone treatment for 30 min. The samples were then moved into a glovebox filled with nitrogen, where a perovskite precursor solution was prepared by mixing 1.3 M (242 mg) PbI$_2$ and 1.3 M (83 mg) MAI in 408 µL DMF/DMSO (4:1 volume ratio) for 60 min. The perovskite layer was prepared by spin-coating its precursor solution (40 µL) at 5000 rpm for 30 s onto the ETL, and injecting chlorobenzene (350 µL) quickly onto the spinning film in 5 s during the spin-coating process. The obtained film was then heated at 100 °C for 10 min. The hole transport material, Spiro-OMeTAD, was
dissolved in chlorobenzene (80 mg mL\(^{-1}\)). Then, 10.5 mL of tBP and 15.5 mL of a Li-TFSI solution (510 mg Li-TFSI/1 mL acetonitrile) were added into Spiro-OMeTAD solution. After 5 minutes of stirring, 25 \(\mu\)L of solution was spin-coated at 4000 rpm for 30 s onto the CH\(_3\)NH\(_3\)PbI\(_3\) layer. The samples were left in the dark at room temperature overnight in dry air. Finally, 60 nm thick Ag electrode was thermally evaporated on the top of Spiro-OMeTAD to assemble a complete PSC device.

**Thin film characterization**

UV/Vis absorption spectra of ETLs on the ITO were recorded using a Shimadzu UV-3100 spectrophotometer over the 300–900 nm wavelength range. Steady-state photoluminescence (PL) were measured on a Shimadzu RF-5301PC spectrophotometer with excitation at 403 nm and the light from the perovskite surface. Time-resolved photoluminescence (TPL) spectra were obtained on a PL spectrometer (Edinburgh Instruments, FLS 920). The X-ray diffraction (XRD) patterns were recorded on Brucker D8 X-ray diffractometer with CuK\(\alpha\) radiation (\(\lambda = 1.5418\) Å) at 25 °C. The data were collected with a 0.02° step size (2\(\theta\)) for 0.2 s. The highest occupied molecular orbital (HOMO) energy levels of SnO\(_2\) and SnO\(_2\)-Ti\(_3\)C\(_2\) (1.0 wt.\%) were measured by an integrated ultrahigh vacuum system equipped with multi-technique surface analysis system (VG Scienta R3000) with an excitation energy of 21.218 eV, and were determined by ultraviolet photoelectron spectroscopy (UPS). A field emission scanning electron microscope (Hitachi SU8000) was used to acquire top-view and cross-sectional scanning electron microscope (SEM) images. The transmission electron microscope (TEM) image of SnO\(_2\)-Ti\(_3\)C\(_2\) (1.0 wt.\%) nanocomposite was recorded using a JEM-2200FS (JEOL).

**Device characterization**
The current density-voltage ($J-V$) characteristics of solar cells were measured by a computer-controlled Keithley 2400 source meter measurement system with an AM 1.5G filter at an illumination intensity of 100 mW cm$^{-2}$, as calibrated by a reference monocrystalline silicon solar cell (91150 V Oriel Instruments). The effective area of the cell was defined to be 0.04 cm$^2$ using a non-reflective metal mask. The external quantum efficiency (EQE) spectra were measured in air under short-circuit conditions using Crowntech QTest Station 1000AD equipped with a 100 W Xe arc lamp, a filter wheel, and a monochromator. Monochromated light was chopped at a frequency of 80 Hz and photocurrents were measured using a lock-in amplifier. The setup was calibrated using a certified silicon reference diode of known spectral response. The electrochemical impedance spectroscopy (EIS) measurements on the devices were carried out by a VSP multi-channel potentiostat (Biologic, France), under the standard AM 1.5G (100 mW cm$^{-2}$) simulated sunlight illumination at open-circuit potential with the frequency ranging between 1 MHz and 10 Hz. Z-View Analyst software was used to model the Nyquist plots obtained from the impedance measurements.

Results and Discussion

Characterizations of Ti$_3$C$_2$ nanosheets and films of SnO$_2$, SnO$_2$-Ti$_3$C$_2$ and Ti$_3$C$_2$

The Ti$_3$C$_2$ MXene nanosheets were synthesized by etching the Al layers from Ti$_3$AlC$_2$ MAX phase, as represented in Figure 1a. Figure 1b shows the XRD patterns of Ti$_3$AlC$_2$ before and after 24 hours of etching. The most intense peak of Ti$_3$AlC$_2$ (104) at 38.9° 20 disappeared, furthermore the (002) peak at 9.5° shifted to about 7°, confirming the topochemical synthesis of Ti$_3$C$_2$. Etching of Al layers and delamination leads to formation of Ti$_3$C$_2$ 2D nanosheets, as shown in SEM and TEM images in Figure 1c and 1d respectively.
Figure 1. (a) Schematic representation of Ti$_3$C$_2$ synthesis, (b) XRD patterns of Ti$_3$AlC$_2$ powder and dried Ti$_3$C$_2$ film, (c) top-view SEM image of freeze-dried Ti$_3$C$_2$, and (d) TEM image of a typical Ti$_3$C$_2$ nanosheet.

SnO$_2$ hydrocolloids containing different amounts of Ti$_3$C$_2$ and pristine Ti$_3$C$_2$ dispersions are shown in Figure 2a. Because the surfaces of both Ti$_3$C$_2$ nanosheets and SnO$_2$ nanoparticles are negatively charged,$^{35,36}$ they do not interact or self-assemble during mixing, and hence, the mixture forms a colloidal suspension in the aqueous medium. Obviously, the color of the colloids became darker along with increasing the concentration of Ti$_3$C$_2$ although the amount of Ti$_3$C$_2$ is very low (0.5-2.5 wt.%). For the device fabrication, each suspension was spin-coated at 3000 rpm for 30 s onto ITO-coated glass substrates, followed by thermal annealing at 150 °C for 30 min in air to accomplish ETLs. To investigate the crystal structures, XRD patterns of films spin-
coated from SnO$_2$, SnO$_2$–Ti$_3$C$_2$ and Ti$_3$C$_2$ suspensions on glass were collected (Figure 2b). Because the concentrations of Ti$_3$C$_2$ in the nanocomposite samples were too low (1.0 wt.%o) to expect visible peaks, the concentration of Ti$_3$C$_2$ was increased 30 times to increase the signal. As shown in Figure 2b, Ti$_3$C$_2$ presents a peak at about 7°, corresponding to the (002) diffraction plane. This peak appeared in the SnO$_2$–Ti$_3$C$_2$ diffraction pattern along with all peaks attributed to SnO$_2$, confirming that the crystal structures of both, Ti$_3$C$_2$ and SnO$_2$, were maintained. This evidenced that the two materials do not undergo any chemical or structural change in the process and coexist in the composite film. Moreover, the high-resolution transmission electron microscope image of SnO$_2$–Ti$_3$C$_2$ (1.0 wt.%o) nanocomposites was shown in Figure S1. SnO$_2$ nanoparticles can easily to be observed on the surface of Ti$_3$C$_2$ nanosheets, indicating successful mixing of SnO$_2$ and Ti$_3$C$_2$.

Figure 2. (a) A digital photo of SnO$_2$ hydrocolloid with different contents of Ti$_3$C$_2$ (0, 0.5, 1.0, 2.0, 2.5 wt.%o) and Ti$_3$C$_2$ dispersion, (b) the XRD patterns of SnO$_2$, SnO$_2$–Ti$_3$C$_2$ (1.0 wt.%o×30) and Ti$_3$C$_2$ films deposited on bare glass substrates.
Photovoltaic characterization

In order to determine the potential of Ti$_3$C$_2$ to improve the performance of PSCs, devices with architecture of ITO/ETL/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag were fabricated, as presented in Figure 3a. Figure 3b shows a cross-sectional SEM image of the PSC device with the planar architecture. Figure 3c provides the schematic energy-level diagram of each layer, where the HOMO and lowest unoccupied molecular orbital (LUMO) of SnO$_2$ and SnO$_2$-Ti$_3$C$_2$ nanocomposites are determined by UPS and UV-vis absorption data (see Figure S2 and Table S1). Figure 4a displays the $J$–$V$ curves obtained for PSCs with SnO$_2$, SnO$_2$-Ti$_3$C$_2$, or Ti$_3$C$_2$ as ETls. Table 1 summarizes the corresponding photovoltaic parameters. Figure S3 shows the PCE histogram of SnO$_2$-based and SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%)-based cells, where $J$–$V$ parameters display small standard deviation, indicating good reproducibility of devices. It is clear that, with the increase of Ti$_3$C$_2$ loading, $J_{sc}$ value continuously increases from 22.83 to 23.56 mA cm$^{-2}$, accompanied by positive effect on the open-circuit voltage ($V_{oc}$) and FF in some cases. The optimum performance was obtained with the Ti$_3$C$_2$ concentration of 1.0 wt.%o, where $V_{oc}$ and FF reached a maximum, and the PCE went above 18%. We think that metallic Ti$_3$C$_2$ flakes function like conductive wires in the composite ETL and offer better electron transport paths, giving rise to more efficient electron collection. As a result, the $J_{sc}$ increases continuously. However, despite $J_{sc}$ kept on increasing, the PCE dropped for higher concentration of Ti$_3$C$_2$ (> 1.0 wt.%o), which was apparently due to reduced $V_{oc}$ and FF. In addition, the device with pristine Ti$_3$C$_2$ as the ETL demonstrated only 5.28% PCE.
The EQE spectra and integrated currents calculated from them for various ETLs (Figure 4b) are in line with the changes in $J_{sc}$. The integrated current density from EQE curves for the pristine SnO$_2$-based cell is 19.62 mA cm$^{-2}$, and it is increased to 20.2 mA cm$^{-2}$ for the device containing 1.0 wt.% Ti$_3$C$_2$. The deviation between integrated current from EQE and the actual measured $J_{sc}$ values (Table 1) is about 10%, indicating good accuracy of our $J$-$V$ measured values. Besides, the hysteresis of reverse and forward scans of $J$-$V$ curves is reduced from 17.4% for the device based on pristine SnO$_2$ to 8.4% for that based on SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%)(Figure S4).

![Figure 3.](image)

**Figure 3.** (a) Device architecture of ITO/ETL/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag based on representative SnO$_2$-Ti$_3$C$_2$ as ETL, (b) cross-sectional SEM image of the PSC device, and (c) schematic energy-level diagram of each layer.
Figure 4. (a) $J-V$ curves of PSCs based on SnO$_2$, SnO$_2$-Ti$_3$C$_2$ (prepared with different concentrations of Ti$_3$C$_2$) and Ti$_3$C$_2$ as ETLs under AM 1.5G simulated illumination, (b) EQE spectra and the corresponding integrated current densities for the representative PSCs fabricated with SnO$_2$, SnO$_2$- Ti$_3$C$_2$ (1.0 wt.%o) and Ti$_3$C$_2$ respectively.

Table 1. The photovoltaic performance parameters of PSCs based on ETLs under different conditions.

<table>
<thead>
<tr>
<th>ETL</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>1.05±0.01</td>
<td>22.83±0.21</td>
<td>72±0.88</td>
<td>17.23±0.55</td>
</tr>
<tr>
<td>SnO$_2$-Ti$_3$C$_2$ (0.5 wt.%o)</td>
<td>1.05±0.01</td>
<td>22.99±0.23</td>
<td>73±0.98</td>
<td>17.56±0.51</td>
</tr>
<tr>
<td>SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%o)</td>
<td>1.06±0.01</td>
<td>23.14±0.30</td>
<td>75±0.86</td>
<td>18.34±0.50</td>
</tr>
<tr>
<td>SnO$_2$-Ti$_3$C$_2$ (2.0 wt.%o)</td>
<td>1.04±0.01</td>
<td>23.20±0.31</td>
<td>71±0.90</td>
<td>17.22±0.54</td>
</tr>
<tr>
<td>SnO$_2$-Ti$_3$C$_2$ (2.5 wt.%o)</td>
<td>1.02±0.01</td>
<td>23.56±0.30</td>
<td>68±0.91</td>
<td>16.34±0.60</td>
</tr>
<tr>
<td>Ti$_3$C$_2$</td>
<td>0.93±0.02</td>
<td>13.69±0.48</td>
<td>41±1.32</td>
<td>5.28±0.54</td>
</tr>
</tbody>
</table>

To gain insight into the possible reasons for the improvement of PCE upon adding...
little amount of Ti$_3$C$_2$, CH$_3$NH$_3$PbI$_3$ films or devices based on SnO$_2$, SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%), and Ti$_3$C$_2$ were selected and further investigated. The XRD patterns of CH$_3$NH$_3$PbI$_3$ films were recorded and shown in Figure S5a. Here, the CH$_3$NH$_3$PbI$_3$ films were prepared on ETL films according to previously reported one-step deposition method, as detailed in the experimental section (see Supporting Information). The XRD result is similar to that previously reported. Figure S5b-d show the SEM images of perovskite layer based on ITO/SnO$_2$, ITO/SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%), and ITO/Ti$_3$C$_2$, respectively. All the films were pinhole-free with smooth surface and large grains, which are the basis for good performance devices. Indeed, this implied that there was no significant effect of perovskite layer on the device performance difference. The enhancement in cell performance must be related to the ETL instead of perovskite.

Figure S6a displays photographs of SnO$_2$, SnO$_2$–Ti$_3$C$_2$ (1.0 wt.%) and Ti$_3$C$_2$ films fabricated by spin-coating onto ITO. Both films of SnO$_2$ and SnO$_2$–Ti$_3$C$_2$ are transparent and there is a little change of the color between them. The film of Ti$_3$C$_2$ obviously became dark compared to that of SnO$_2$ and SnO$_2$–Ti$_3$C$_2$, as expected from the color of their suspensions. Figure S6b-d show their magnified SEM images. The morphologies of the SnO$_2$–Ti$_3$C$_2$ is similar to that of SnO$_2$, both films are flat, uniform, and pinhole-free, suggesting the corresponding PSCs are likely of the planar-heterojunction configuration. The results are in coherence with the UV-vis absorption spectra of the various films shown in Figure 5a. Precisely, the curves of SnO$_2$ and SnO$_2$–Ti$_3$C$_2$ films are almost the same, while the Ti$_3$C$_2$ curve has a slightly stronger absorption in the UV region ($\lambda = 330$ nm), indicating that the addition of Ti$_3$C$_2$ to SnO$_2$ layer does
not affect the transmission of light.

To know the electron extraction abilities of different ETLs, the PL spectra of perovskite absorber layer spin-coated onto ITO/SnO$_2$, ITO/SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%$\%$) and ITO/Ti$_3$C$_2$ substrates were measured, as shown in Figure 5b. The PL quenching is originated from the electron extraction across the interface of CH$_3$NH$_3$PbI$_3$/ETL. The PL signal at about 780 nm is assigned to the emission from CH$_3$NH$_3$PbI$_3$. ITO/Ti$_3$C$_2$/perovskite shows the highest PL intensity, indicating the hole blocking ability of Ti$_3$C$_2$ is less good, thus there is more carrier recombination happening in this device. This can be attributed to the metallic nature of Ti$_3$C$_2$ whose work function is higher than the valence band edge of CH$_3$NH$_3$PbI$_3$ (Figure 3c). The lowest PL intensity is obtained with the ITO/SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%$\%$)/perovskite sample. It is lower than that of ITO/SnO$_2$/perovskite, indicating the addition of Ti$_3$C$_2$ successfully enhanced the electron extraction from perovskite to ETL and suppressed carrier recombination. Figure 5c gives the TPL spectra of perovskites based on different ETLs. The lifetimes of PL decay of SnO$_2$, SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%$\%$) and Ti$_3$C$_2$–based perovskites are 40.3 ns, 33.8 ns, and 42.7 ns, respectively. This is consistent with the steady-state PL results, further supporting the results from $J$–$V$ curves and EQE spectra, and demonstrating that the addition of Ti$_3$C$_2$ to SnO$_2$ significantly enhances the $J_{sc}$.

To investigate the changes in FF, which is related to charge collection and conductivity, determined by interfacial charge transfer, EIS characterization was done on the devices with the architecture of ITO/ETL/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag,
where the ETL is either SnO$_2$, SnO$_2$–Ti$_3$C$_2$ (1.0 wt.‰) or Ti$_3$C$_2$, under the standard AM 1.5G (100 mW cm$^{-2}$) simulated sunlight illumination at 0 V relative to the open-circuit potential with the frequency ranging from 1 MHz to 10 Hz. Figure 5d shows the Nyquist plots of the three devices which present semi-circles corresponding to the equivalent circuit model proposed. Here, $R_s$ is the series resistance largely associated with wires and the ITO substrate. The observed major semi-circle represents the charge recombination resistance ($R_{\text{rec}}$) and interfacial capacitance (C) at the ETL/perovskite interface.$^{38}$ $R_{\text{rec}}$ is inversely proportional to charge recombination, in other words, higher $R_{\text{rec}}$ suggests lower carrier recombination (better hole blocking ability). The values fitted to the equivalent circuit are tabulated in Table S2. The value of $R_{\text{rec}}$ follows the order SnO$_2$ > SnO$_2$–Ti$_3$C$_2$ > Ti$_3$C$_2$, where the larger resistance is favorable to higher electron collection. Ti$_3$C$_2$-based PSC has the lowest $R_{\text{rec}}$, indicating the most charge recombination occurred at the interface, and thus resulting in the lowest FF. This is consistent with $J$-$V$ results. Despite that the PSC based on SnO$_2$–Ti$_3$C$_2$ has lower charge recombination resistance compared to SnO$_2$, its $J_{\text{sc}}$ and FF are larger than the SnO$_2$-based device. This can be partly attributed to the better electron extraction due to the addition of Ti$_3$C$_2$, as reflected in the steady-state PL spectra.

Electron mobility of the ETL was evaluated by the method of space charge-limited current (SCLC) on electron-only devices with the structure of ITO/TiO$_2$/ETL/BCP/Ag under dark (Figure S7). The highest electron mobility among the three ETLs was determined as 2.23×10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for Ti$_3$C$_2$, almost triple that of SnO$_2$ (7.52×10$^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$). Despite of the high electron mobility of Ti$_3$C$_2$, it showed the least efficient
electron extraction and the most charge recombination, as demonstrated by the steady-state PL and EIS results, resulting in its lowest $J_{sc}$ and FF, and thus the lowest PCE. As Ti$_3$C$_2$ nanosheets have good conductivity, it is coherent that after introducing Ti$_3$C$_2$ in SnO$_2$ layer, the electron mobility was increased to $1.23 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the SnO$_2$-Ti$_3$C$_2$ sample, which is about ten times higher than that of TiO$_2$. The mobility results also effectively explain the increase in $J_{sc}$ and FF values in the device based on SnO$_2$-Ti$_3$C$_2$ compared to the one based on SnO$_2$.

**Figure 5.** (a) UV-vis absorption spectra of SnO$_2$, SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%), and Ti$_3$C$_2$ films fabricated by spin-coating onto the ITO substrates, (b) PL (excitation at 403 nm) and (c) TPL spectra of ITO/SnO$_2$/CH$_3$NH$_3$PbI$_3$, ITO/SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%)/CH$_3$NH$_3$PbI$_3$, ITO/Ti$_3$C$_2$/CH$_3$NH$_3$PbI$_3$, (d) Nyquist plots of the PSCs with SnO$_2$, SnO$_2$-Ti$_3$C$_2$ (1.0 wt.%), or Ti$_3$C$_2$ as ETLs under one sun illumination, where the
scattered points are experimental data and the solid lines are the fitted curves according to the equivalent circuit.

Apart from the increase of PCE, the effects of adding Ti$_3$C$_2$ to SnO$_2$ ETL on the device stability were also studied. Figure S8 shows the stability results of PSCs based on SnO$_2$, SnO$_2$–Ti$_3$C$_2$ (1.0 wt.%) and Ti$_3$C$_2$ as ETLs in ambient air (relative humidity ≈ 20 %) without encapsulation at 25 °C, which were tested under the standard AM 1.5G (100 mW cm$^{-2}$) simulated sunlight illumination. Despite the pristine Ti$_3$C$_2$-based PSC showing a good stability within the first 192 h, an obvious reduction of the PCE occurred after 192 h. On the contrary, PSCs based on SnO$_2$–Ti$_3$C$_2$ and SnO$_2$ exhibited similar good stability trends for 768 h. SnO$_2$–Ti$_3$C$_2$-based PSC just showed slightly increased and less fluctuating stability compared to the SnO$_2$-based one, indicating that the addition of Ti$_3$C$_2$ had no negative impact on the device stability. Moreover, after 700 hours of storage, the SnO$_2$–Ti$_3$C$_2$-based PSC retained about 80% of the initial PCE, demonstrating the excellent stability of this device.

**Conclusion**

Conductive Ti$_3$C$_2$ MXene nanosheets were prepared and nanocomposites of Ti$_3$C$_2$ and SnO$_2$ were used as the electron transport layers for perovskite solar cells. Flat, uniform and pinhole-free films of SnO$_2$ containing different amounts of Ti$_3$C$_2$ (0, 0.5, 1.0, 2.0, 2.5 wt.%) were prepared by spin-coating. A relatively high PCE of 18.34% was achieved using SnO$_2$–Ti$_3$C$_2$ (1.0 wt.%) as the ETL with a device architecture of ITO/ETL/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag. The variation of efficiency from cell to
cell is smaller than that of graphene-based CH$_3$NH$_3$PbI$_3$ PSCs with regular configuration (15.42±0.54%),\textsuperscript{22} highlighting the potential application of MXenes toward the development of low-cost solar cells. This high efficiency originated from an excellent electron extraction, electron mobility and low interfacial charge transfer resistance of the SnO$_2$-Ti$_3$C$_2$ layer, thanks to the good conductivity of Ti$_3$C$_2$ MXene which provides charge transfer paths, as evidenced by the steady-state PL spectra, SCLC and EIS results. A PCE of only 5.28\% was achieved using pristine Ti$_3$C$_2$ as the ETL. This work sets a milestone for incorporation of 2D MXenes into solar cells. Moreover, the fabrication of low-temperature and solution-processed ETL offers prospective applications for flexible photovoltaic devices.

**Conflict of Interest**

The authors declare no conflict of interest.

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**Supporting Information**

SEM and TEM images, UPS analysis, optoelectronic parameters of SnO$_2$ and SnO$_2$-Ti$_3$C$_2$ (1.0 wt.\%), device reproducibility results, XRD analysis, SCLC results, EIS
fitting parameters, and device stability. This material is available from website at http://...... or from the author.

References


Addition of Ti$_3$C$_2$ MXene in SnO$_2$ enhanced the power conversion efficiency due to the good conductivity of Ti$_3$C$_2$ nanosheets.