

A Self-Assembled Vertical-Gradient and Well-Dispersed MXene Structure for Flexible Large-Area Perovskite Modules

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Advancing hole transport layers (HTL) to realize large-area, flexible, and high-performance perovskite solar cells (PSCs) is one of the most challenging issues for its commercialization. Here, a self-assembled gradient $\text{Ti}_3\text{C}_2\text{T}_x$ MXene incorporated PEDOT:PSS HTL is demonstrated to achieve high-performance large-area PSCs by establishing half-caramelization-based glucose-induced MXene redistribution. Through this process, the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets are spontaneously dispersed and redistributed at the top region of HTL to form the unique gradient distribution structure composed of MXene:Glucose:PEDOT:PSS (MG-PEDOT). These results show that the MG-PEDOT HTL not only offers favorable energy level alignment and efficient charge extraction, but also improves the film quality of perovskite layer featuring enlarged grain size, lower trap density, and longer carrier lifetime. Consequently, the power conversion efficiency (PCE) of the flexible device based on MG-PEDOT HTL is increased by 36% compared to that of pristine PEDOT:PSS HTL. Meanwhile, the flexible perovskite solar minimodule (15 cm^2 area) using MG-PEDOT HTL achieve a PCE of 17.06%. The encapsulated modules show remarkable long-term storage stability at 85 °C in ambient air ($\approx 90\%$ efficiency retention after 1200 h) and enhanced operational lifetime ($\approx 90\%$ efficiency retention after 200 h). This new approach shows a promising future of the self-assembled HTLs for developing optoelectronic devices.

Inverted PSCs with p-i-n inverted structure possess advantages, including low-temperature facile fabrication, low cost, and high operational stability as compared to n-i-p PSCs.^[2,3] Particularly, the hole transport layer (HTL) is of vital significance to the efficiency and durability of inverted PSCs.^[2] Various HTL materials have been investigated, such as polymers including poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA),^[4] poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS),^[5–9] and metal oxide nanocrystals including NiO_x ,^[10,11] CuSCN ,^[12] and CuO_x .^[13] The best-certified PCE of single-junction planar inverted PSCs based on PTAA is 24.3%.^[14] However, the high cost and complex process hinder the application of PTAA, especially for large-area PSCs.^[15,16] PEDOT:PSS is the widely adopted commercial polymer-based HTM in PSCs, with the advantages of high transparency, flexibility, and low-temperature solution-process adaptability.^[17] Meanwhile, PEDOT:PSS with hydrophilic properties is favorable for film fabrication by large-area printing technology. How-

ever, PEDOT:PSS faces the challenges of unsatisfactory conductivity,^[18] mismatched energy level to perovskite active layer and poor stability.^[19] These will cause low open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}).^[20]

In order to improve the electrical properties of PEDOT:PSS based HTL, different approaches including doping,^[7,8,21] bilayer

1. Introduction

While the power conversion efficiency (PCE) of single-junction perovskite solar cells (PSCs) has increased to over 25%,^[1] there are some challenges to achieve flexible large-area PSCs with a good long-term stability for practical applications.

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DOI: 10.1002/adfm.202210063

HTL,^[22,23] and other treatments,^[24] have been studied. Doping of highly conductive materials such as poly(ethylene oxide), carbon nanooxides,^[25] and silver nanowires^[26] improve J_{SC} of PSCs. V_{OC} also shows increases by doping through the suppression of chemical interaction with methylammonium iodide (MAI)^[27] and the modification of work function (WF). For instance, perfluorinated ionomer,^[28] CsI,^[29] Poly(styrenesulfonate)-Na,^[30] ammonia,^[31] MoO_x,^[32] and CuSCN^[4] have been doped into PEDOT: PSS to diminish V_{OC} loss. Notably, the self-assembled PSS upper thin layer^[33] or an insulating layer formed on the surface like glucose^[34] have been introduced to modulate WF. Considering bilayer HTL structures, a cascading band alignment between PEDOT: PSS and perovskite active layer has been demonstrated to reduce the voltage loss. Interface like SnO₂,^[35] V₂O₅,^[36] and (N,N'-Bis(1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine)^[37] are introduced to PEDOT:PSS for better band alignment. The interface non-radiative recombination and traps are also reduced by the bilayer approaches. The challenge of the two strategies of doping and bilayer structure mainly lies in the hampered conductivity due to the insulating layer or the undesirable energy-level structure with conductive dopants. Therefore, there is a trade-off between sacrificing the enhancement of J_{SC} or V_{OC} . Consequently, it is highly desirable to explore new material systems which can offer high conductivity and tunable WF to enhance J_{SC} and V_{OC} simultaneously for advancing HTL and the development of flexible large-area PSCs.

MXene materials offer many glaring merits including high conductivity and tunable WF, which facilitate their application for optoelectronic devices.^[38] The first use of Ti₃C₂T_x MXene in PSCs is as an additive of a perovskite absorber layer.^[39] Incorporating MXene into nanoparticles like SnO₂^[40] and TiO₂,^[41] was reported to be a useful approach to form effective electron transport layer (ETL) of PSCs.^[41–43] Besides the use in ETL and HTL,^[44] Ti₃C₂ MXenes have also been used in PSCs as an interlayer in perovskite solar cells.^[45] Overall, there are rooms to simultaneously improve the conductivity and interfacial properties. In addition, similar to other two-dimensional (2D) materials, MXenes typically tend to stack and aggregate due to the strong van der Waals forces,^[46,47] which will lead to penetration into adjacent layers and current leakage, and thus need to be addressed for further use in devices.

In this work, we demonstrate a self-promoted vertical-gradient Ti₃C₂T_x MXene structure-based PEDOT:PSS HTL. The unique gradient HTL is realized via a glucose-assisted Ti₃C₂T_x MXene self-dispersion strategy in which the addition of glucose and its half-caramelization process make the aggregated Ti₃C₂T_x MXene nanosheets spontaneously exfoliate and redistribute on the top surface. Our results show that the self-organized MXene/glucose-rich composite concurrently tailors electrical properties of PEDOT:PSS, and promotes the quality and crystallization of perovskite film deposited on top of it. With the optimized gradient MXene HTL, we have fabricated different sizes of flexible PSCs based on MAPbI₃ and Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})₃ (FA = formamidinium; MA = methylammonium) perovskites. The power conversion efficiency (PCE) of the flexible device with the new HTL is increased by 36% compared to that of pristine PEDOT:PSS HTL. Finally, we assemble the flexible PSCs into a module

with 15 cm² in size and obtain a PCE of 17.06%. Meanwhile, the encapsulated perovskite solar modules (PSMs) show remarkable long-term storage stability at 85 °C in ambient air (≈90% efficiency retention after 1200 h) and enhanced operational lifetime (≈90% efficiency retention after 200 h). The work shows a promising future with the possibility of the synergistic self-assembled HTL for applications in photovoltaic devices.

2. Results and Discussion

2.1. Formation of Well-Dispersed and Vertical-Gradient PEDOT:PSS-Ti₃C₂T_x:Glucose Nanocomposites

The accordion-like multilayers of Ti₃C₂T_x MXene are prepared via the minimally intensive layer delamination method,^[48] which are then delaminated into a small number of layers of Ti₃C₂T_x MXene nanosheets (Figure S1, Supporting Information). Glucose have been reported to assist the exfoliation of layered nanomaterials, as graphene, MoS₂, and WS₂.^[49] For glucose, the caramelization is a process which removes the water contents with heating. It has been reported that with the addition of glucose into PEDOT:PSS, a partial caramelized glucose layer forms atop of PEDOT:PSS after annealing.^[34] To obtain the hybrid MXene:glucose:PEDOT:PSS composite via the half-caramelization process of glucose, hereinafter referred as MG-PEDOT, we firstly mixed PEDOT:PSS with a dispersion of MXene in water to form PEDOT:PSS/MXene (M-PEDOT) mixed solutions. The glucose powder was lastly incorporated into the M-PEDOT dispersion to obtain the MG-PEDOT composite, as shown in **Figure 1**. We also added only glucose powder to PEDOT:PSS solution as a reference and named as G-PEDOT. The dispersion of Ti₃C₂T_x MXene nanosheets and the morphologies of the nanocomposite films are investigated by atomic force microscope (AFM), scanning electron microscope (SEM), and transmission electron microscopes (TEM) characterizations. As shown in **Figure 2a,b**, with the incorporation of MXene into the PEDOT:PSS, there is large aggregation in the M-PEDOT film. Besides, according to the AFM results, the root-mean-square (RMS) roughness of M-PEDOT layer is high at ≈9.1 nm (Figure 2a), while the RMS roughness of MG-PEDOT film substantially reduces to 3.9 nm (Figure 2d). Such smooth HTL would benefit the deposition of perovskite layer, resulting in compact interfacial contact between HTL and perovskite layer. **Figure 2c** depicts the TEM images of stacked Ti₃C₂T_x MXene nanosheets, which is the large aggregation in M-PEDOT. Differently, the MG-PEDOT film has a considerable smoother surface, with a more uniform distribution of Ti₃C₂T_x MXene nanosheets as shown in **Figure 2d,e**. The inserted TEM image in **Figure 2f** shows the edge of oligo layers MXene in higher resolution figure, indicating that oligo-layer Ti₃C₂T_x MXene nanosheets were obtained with the addition of glucose in the MG-PEDOT thin film. The hydrophilic edges of Ti₃C₂T_x MXene nanosheets and the glucose hydroxyl groups favor the dispersion in PEDOT:PSS polymer matrix.^[49] Overall, by introducing glucose into M-PEDOT, the interaction of MXene and glucose causes the stacked Ti₃C₂T_x MXene nanosheets in the PEDOT:PSS polymer matrix to be dispersed into oligo-layer MXenes and disperse well to form MG-PEDOT films.

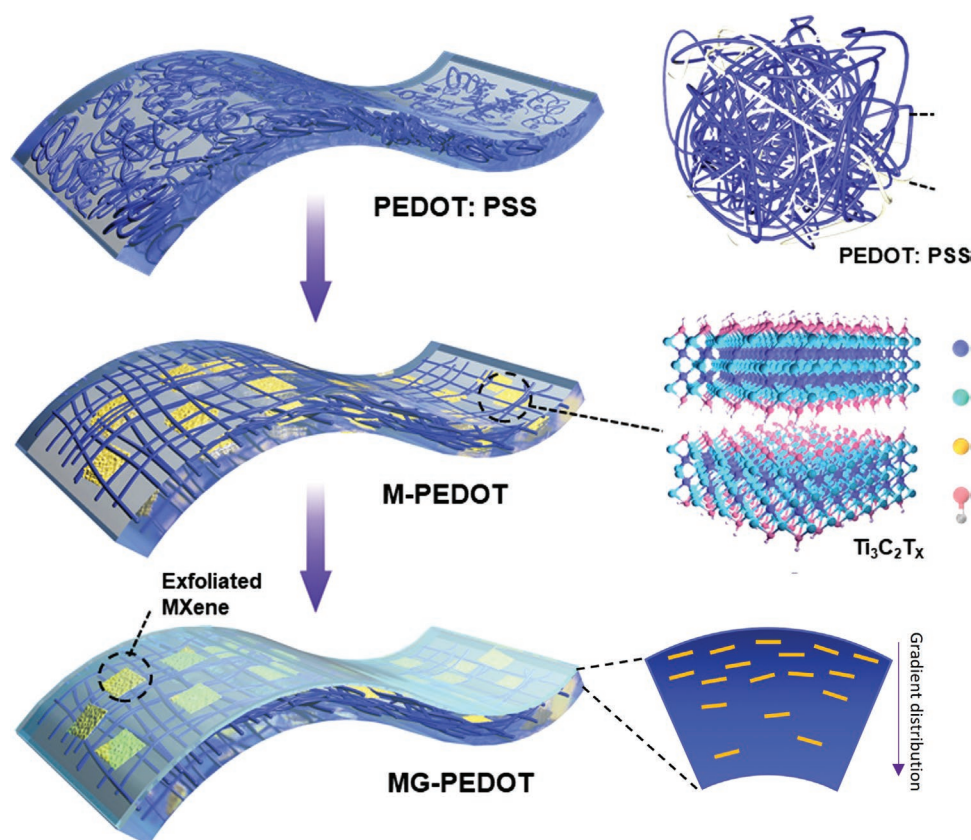


Figure 1. Schematic illustration of the nanocomposite MG-PEDOT film preparation.

To intuitively illustrate the vertical-gradient MXene distribution in MG-PEDOT film, we performed X-ray photoelectron spectroscopy (XPS) experiments. Figure S2 (Supporting Information) shows the Ti 2p peak and F 1s peak of MG-PEDOT, while there are no Ti 2p and F 1s peaks for PEDOT:PSS. Figure 3a,b and Figure S3 (Supporting Information) show the XPS depth profile analysis in the Ti 2p region and F 1s region on MG-PEDOT and M-PEDOT respectively, with the etching depth represented in terms of time. With the increase of the etching depth, the intensity of Ti 2p and F 1s peaks gradually decreased, and Ti 2p and F 1s peaks decreased to the baseline at the etching depth of 40 nm, correlating to the dispersion of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets atop of the MG-PEDOT. While for M-PEDOT, the intensity of Ti 2p and F 1s peaks do not show changes in trend with the increase of the etching depth. The intensity variation with etching depth at selected peaks of 457.7 eV for Ti 2p and 682.1 eV for F 1s are shown in Figure 3c,d. The XPS depth profiles reveal the vertical-gradient distribution of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets in the nanocomposite MG-PEDOT films. Consequently, by the half-caramelization-based glucose-induced MXene redistribution, we demonstrate vertical-gradient and well-dispersed MXene structure in the MG-PEDOT film.

Regarding the optical property of the MG-PEDOT film, the transmittance of PEDOT:PSS, M-PEDOT, and MG-PEDOT films on ITO glasses are presented in Figure S4 (Supporting Information). The three films exhibit similar transmittance between 500 and 800 nm. At wavelength less than 500 nm, the

transmittance of PEDOT:PSS and MXene added PEDOT:PSS films shows different characteristics, which could be attributed to the enhanced absorption of $\text{Ti}_3\text{C}_2\text{T}_x$ in the wavelength region.^[50] The slightly lower transmittance of MG-PEDOT film compared to M-PEDOT film also implies a better dispersion of MXene in PEDOT:PSS with the addition of glucose, which is in accordance with the previous results. Nevertheless, MG-PEDOT films show a high transmittance over 92% in all the UV-VIS wavelength region, which indicates that MG-PEDOT films offer good optical properties for serving as effective HTL in PSCs.

To investigate the electrical property of the MG-PEDOT film, we firstly measure the conductivity of the film with the I - V plots of the hole-only devices, which indicates the more desirable conductivity of MG-PEDOT ($2.90 \times 10^{-5} \text{ S cm}^{-1}$) compared to PEDOT:PSS ($1.41 \times 10^{-5} \text{ S cm}^{-1}$) through the slope of curves, as shown in Figure S5 (Supporting Information). We further study the sheet resistance of PEDOT:PSS, M-PEDOT, G-PEDOT, and MG-PEDOT films on bare glass are measured by four-point probe for understanding the improved J_{SC} . As summarized in Table 1, the PEDOT:PSS film shows a quite high resistance of $471 \pm 5.0 \text{ M}\Omega \text{ sq}^{-1}$ and the addition of insulated glucose raises it to higher resistance of $11.2 \pm 2.0 \text{ G}\Omega \text{ sq}^{-1}$. The incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets significantly reduces the sheet resistance of M-PEDOT and MG-PEDOT to $1.2 \pm 0.2 \text{ M}\Omega \text{ sq}^{-1}$ and $0.7 \pm 0.02 \text{ M}\Omega \text{ sq}^{-1}$, respectively. The introduction of glucose slightly decreases the resistance and enables lower fluctuation due to its promotion of MXene dispersion. The reduction of sheet resistance mainly comes

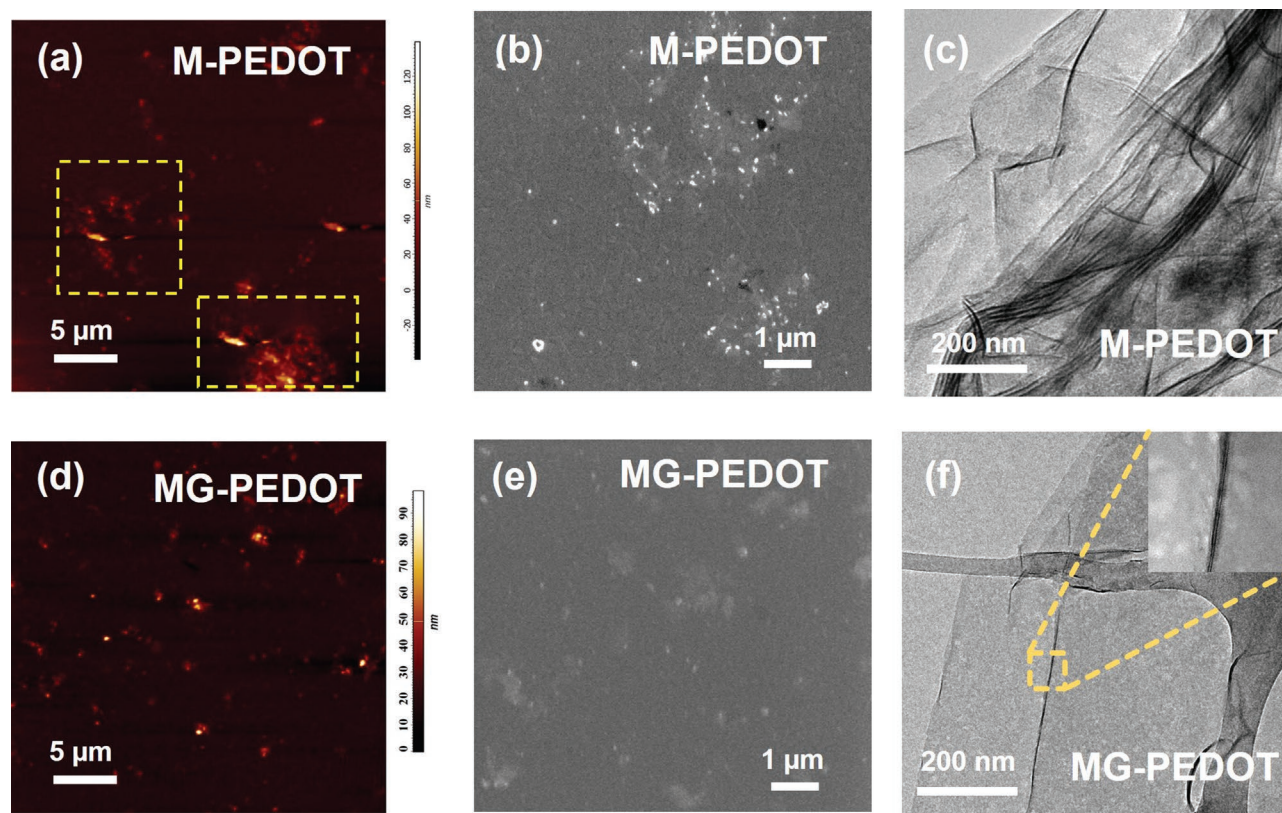


Figure 2. Morphology of MXene-modified PEDOT films. a–c) AFM, SEM and TEM images of M-PEDOT, respectively. d–f) AFM, SEM and TEM of MG-PEDOT, respectively. The aggregated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets are identified by dashed lines in a). The inserted TEM image in f) shows the edge of oligo layers MXene with higher resolution.

from the high conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets.^[51] The insulating PSS chains within the PEDOT:PSS films are reported to be wrapped around the PEDOT chains, while this core-shell structure sets barriers to the hole transfer among the conductive PEDOT domains, which results in the relatively low conductivity of PEDOT:PSS film.^[52] $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets with high conductivity were doped to eliminate shortages of PSS and improve electrical performance. Sheet resistances of the large-area (15 cm^2) were further measured, as shown in Figure S6 (Supporting Information) which shows the scalability of this enhancement. Consequently, the obtained MG-PEDOT film has superior electrical properties and equivalent optical properties comparing with the pure PEDOT:PSS film, which provides a good basis for it to be used as HTL in PSCs.

2.2. High Quality Perovskite on Optimized MG-PEDOT

To optimize the concentration of MXene addition, we prepared perovskite layers on MG-PEDOT HTLs with different MXene concentrations. Interestingly, the crystallinity of perovskite increases with the addition of vertical-gradient and well-dispersed MXene in MG-PEDOT, according to the XRD results shown in Figure 4a (for MG-PEDOT series and its control sample) and Figure S7 (Supporting Information) (for M-PEDOT series and its control sample). The wettability of the PEDOT:PSS-based composites on ITO was investigated

as shown in Figure 4b and Figure S8 (Supporting Information). With the incorporation of both MXene and glucose into PEDOT:PSS, the contact angle of PEDOT:PSS-based films reduces from 38.7° to 24.3° , offering good coverage and homogeneous nucleation for perovskite crystallization, which is essential for forming high-quality perovskite film and subsequently improving device performances. The SEM results and corresponding grain size distribution (Figure 4c–h; Figures S9, S10, and S11, Supporting Information) are consistent with the XRD results (Figure 4a; Figure S7, Supporting Information). It can be observed that the perovskite film with compact grains are grown on MG-PEDOT when 0.1% MXene is added to the PEDOT:PSS. As a result, the perovskite film shows less grain boundary and cracks as compared to those perovskite films grown on pristine PEDOT or M-PEDOT with the addition of MXene at different concentrations. Figure S10 (Supporting Information) shows the SEM images of perovskite films prepared with 0.05% M-PEDOT, 0.1% M-PEDOT, 0.3% M-PEDOT, and 0.5% M-PEDOT, respectively. Results show that the crystallinity of perovskite film based on M-PEDOT is relatively poor, compared to those based on MG-PEDOT. We also studied cross-sectional SEM images of perovskite thin films deposited on top of PEDOT:PSS treated with glucose and MXene as shown in Figure S12 (Supporting Information). For the perovskite film deposited on the PEDOT:PSS HTL, we can clearly find both small-size grains (in top-view SEM images) and many obvious transversal grain boundaries. The severe transversal grain

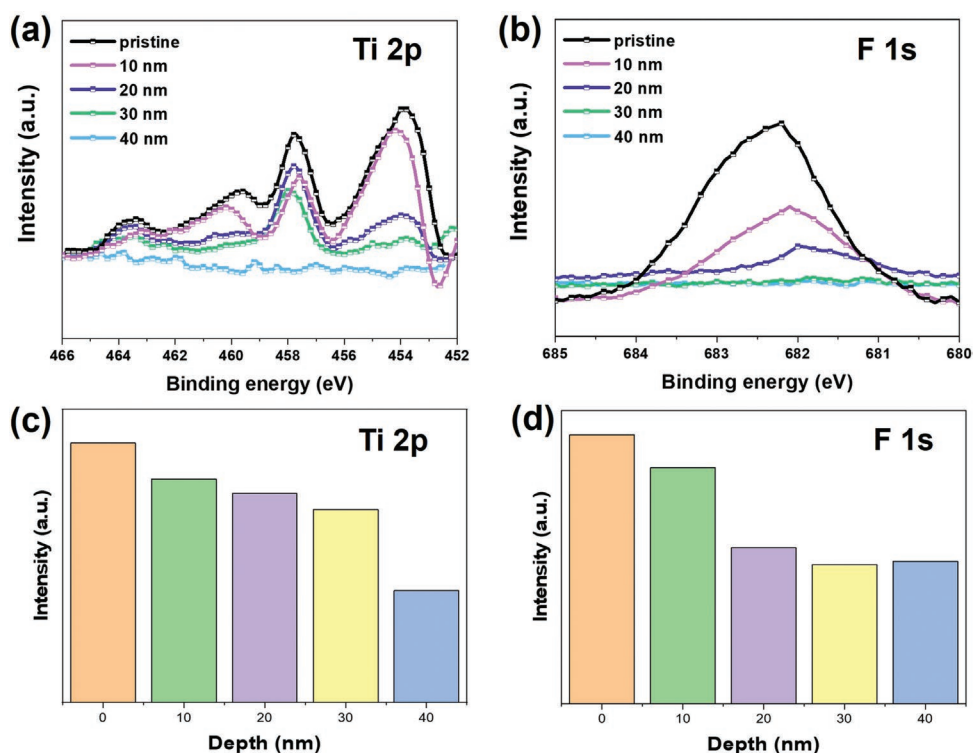


Figure 3. X-ray photoelectron spectroscopy (XPS) depth profile analysis in the a) Ti 2p region, b) F 1s region on the MG-PEDOT HTLs. c) Intensity versus depth of a) in the selected peak (457.7 eV). d) Intensity versus depth of b) in the selected peak (682.1 eV).

boundaries will cause defects and affect the transport of charge carriers. Consequently, perovskite films on MG-PEDOT show almost no transversal grain boundaries, and the grains grow oriented with larger grain size favoring device applications. It should be noted that all MG-PEDOT appearing later and not explicitly stated refers to 0.1% MG-PEDOT.

2.3. Flexible Large-Area Perovskite Solar Cells

To start with, we fabricate MAPbI₃ PSCs on regular rigid glass substrates to confirm that the new HTL can offer performance improvement by using MG-PEDOT, as shown in Figure S13a (Supporting Information). The J_{SC} values are in line with the integrated currents obtained from the external quantum efficiency (EQE) spectra, as shown in Figure S13b (Supporting Information). The MG-PEDOT incorporated PSCs exhibit negligible hysteresis and a very good reproducibility with a narrow PCE distribution from 18.5% to 20%, as shown in Figure S11 (Supporting Information). With the encouraging evidence of performance improvement in regular rigid PSCs, we then investigate flexible PSCs. The champion flexible PSCs employing the MG-PEDOT based MAPbI₃ perovskite yielded stable and hys-

teresis-free devices with PCE reaching 18.76% at the effective area of 0.04 cm², an enhancement by 36% compared to that of pristine PEDOT:PSS HTL, as shown in Figure S15 (Supporting Information). The operational and thermal stability of MAPbI₃ PSCs based on MG-PEDOT HTL were also improved, as shown in Figure S16 (Supporting Information).

To explore the improvement of the V_{OC} , the work function of the composite films with the incorporation of MXene are investigated through ultraviolet photoelectron spectroscopy (UPS). With the gradient and well-dispersed MXene structure in MG-PEDOT above (Figure 3a,b), we realize the tuning ability of HTL work function for improving the V_{OC} . The results of UPS and the corresponding energy level diagram of PSCs are shown in Figure 5a,b, respectively. The work function of MG-PEDOT is −5.3 eV, which is lower than that of PEDOT:PSS (−4.9 eV), and closer to the valence band of perovskite due to the incorporation of MXene and glucose in PEDOT:PSS. Figure S17 (Supporting Information) shows the UPS spectra for mixed MXene and glucose (MXene:G) and MXene. From the results, we can find that the promoted V_{OC} is attributed to the formation of a thin caramelized glucose layer atop PEDOT:PSS, which can modify the work function in MG-PEDOT. The glucose in the nanocomposite HTL could have the passivation effect on the halide vacancies at the grain boundary,^[34] which acts as the charge trapping state, and leads to a more efficient holes extraction from perovskite films to the anode and improved open-circuit voltage (V_{OC}) of PSCs. The Mott–Schottky plots in Figure 5c shows that the built-in potential can be obtained from the intersection with the voltage axis in the C^{-2} versus V curves. The fitting results show that the built-in potential of the device

Table 1. Sheet resistances of the films after annealing.

HTL	PEDOT:PSS	M-PEDOT	G-PEDOT	MG-PEDOT
Sheet resistance	47.1 ± 5.0	1.2 ± 0.2	11.2 ± 2.0	0.71 ± 0.02
	[MΩ sq ^{−1}]	[MΩ sq ^{−1}]	[GΩ sq ^{−1}]	[MΩ sq ^{−1}]

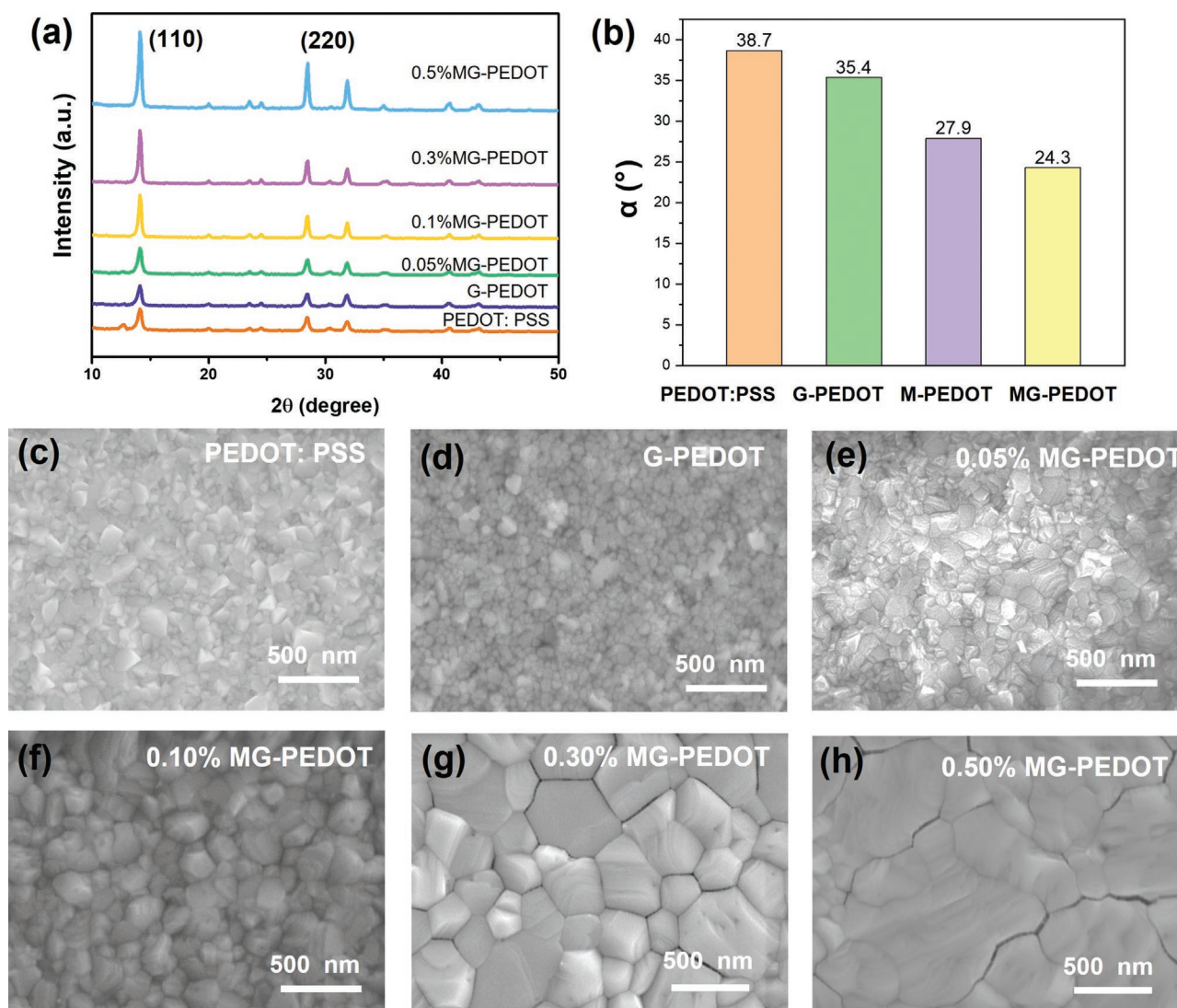


Figure 4. a) XRD patterns of perovskite films prepared with MG-PEDOT HTLs with Ti₃C₂T_x MXene concentration of 0.05%, 0.10%, 0.30%, and 0.50% (wt/vol). b) Measurement of the contact angles for the PEDOT:PSS, G-PEDOT, M-PEDOT and MG-PEDOT, respectively. c)–h) SEM images of perovskite films prepared with different HTLs.

based on MG-PEDOT is larger than that based on PEDOT, indicating a lower defect density in MG-PEDOT. The improved built-in potential of MG-PEDOT based device can offer a more favorable energy band structure, correlating with the improved V_{OC} of PSCs.

To investigate the charge transport/extraction properties of the MG-PEDOT composites, we also measured the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) to investigate the quality of perovskite films, as shown in Figures S18 and S19 (Supporting Information). The perovskite film on MG-PEDOT HTL shows a weaker peak intensity than that of the film upon the pristine PEDOT:PSS film, as shown in Figure S19 (Supporting Information). The low and similar PL intensity of the perovskite on MG-PEDOT layer reflects that the defects are effectively suppressed. Meanwhile, the MG-PEDOT film favors the hole extraction from the perovskite active layer to the anode as compared with the pure

PEDOT:PSS case. Furthermore, the perovskite films formed on MG-PEDOT layer offer a shorter carrier recombination lifetime than that based on pure PEDOT:PSS. To further probe the charge recombination, electrical impedance spectra (EIS) were measured for both MG-PEDOT:PSS and PEDOT:PSS in Figure S20 (Supporting Information). The EIS results were fitted with the inserted equivalent circuit. The equivalent circuit model is built based on reference.^[53] In the Nyquist plot, both the PSCs show a double circle shape wherein the low-frequency arc is associated with the dielectric relaxation, whereas the other one is related to the drift-diffusion and recombination process. MG-PEDOT:PSS based devices show a remarkable larger circle compared with that of the PEDOT:PSS based devices, due to a larger perovskite recombination resistance (R_{rec}) (with a fitted value for MG-PEDOT:PSS is 11 809 Ω and that of PEDOT:PSS is 6613 Ω), suggesting the non-radiative recombination suppression in perovskite/HTL interface,

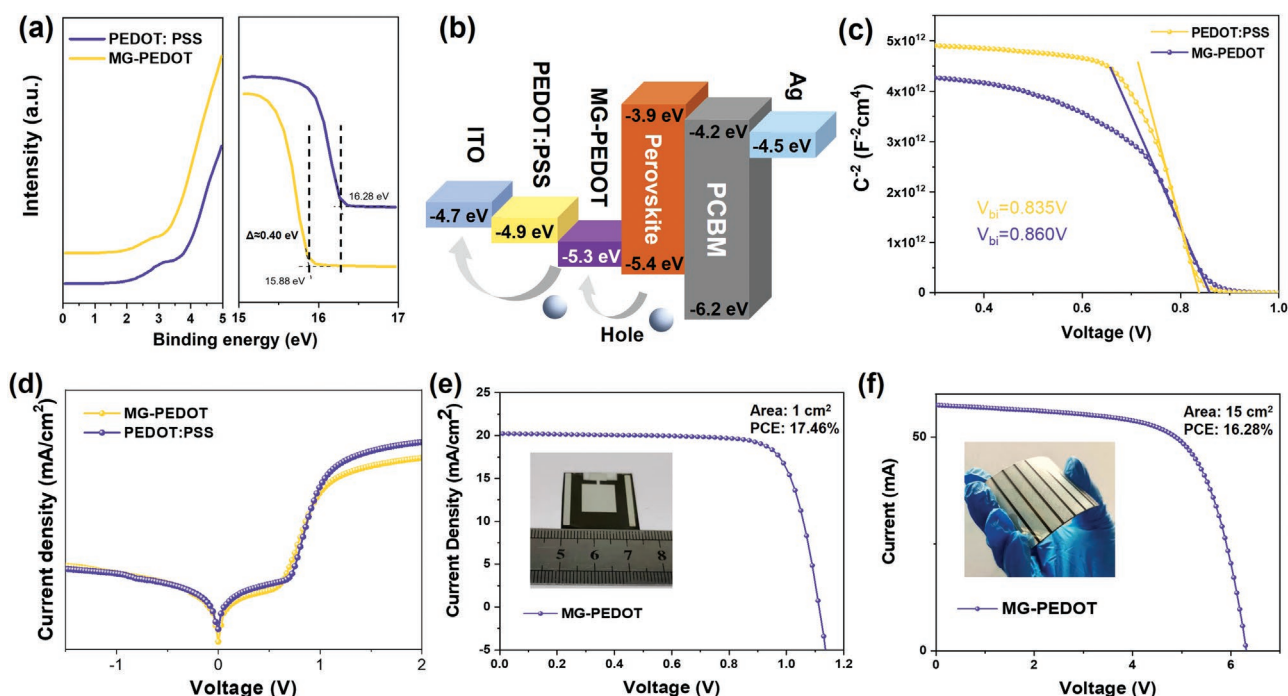


Figure 5. a) Ultraviolet photoelectron spectroscopy (UPS) spectra for the PEDOT:PSS and MG-PEDOT, b) Energy level diagram of the perovskite solar cells (data for the PEDOT:PSS, MG-PEDOT, and perovskite layers are provided by UPS measurement). For ITO, PEDOT:PSS, MG-PEDOT and Ag, their work functions are stated. c) Mott–Schottky plots of PSCs. d) Dark $J-V$ curves of the PSCs for PEDOT:PSS or MG-PEDOT HTLs. e) $J-V$ curves of the flexible PSCs based on MG-PEDOT (the device effective area is 1.00 cm²). f) $J-V$ curves of the flexible PSMs based on MG-PEDOT (the device effective area is 15.00 cm²).

which is consistent with TRPL measurement and Table S1 (Supporting Information) (with shorter lifetime as compared to the untreated one) the promotion in photovoltaic performance for MG-PEDOT based PSCs. In order to investigate the transport performance of photogenerated carriers, we measure the dark $J-V$ curves of the PSCs for PEDOT:PSS or MG-PEDOT HTLs. Figure 5d shows that the device with the MG-PEDOT HTL has the lower dark current density, indicating that more photogenerated carriers can efficiently pass through the PSCs instead of direct shunting, thereby reducing the carrier recombination and leakage current. Consequently, all the measured results show that MG-PEDOT HTL favors the carrier transportation and extraction from perovskite active layer to anode. Encouraged by the above satisfactory device performance and reproducibility, we further fabricate the large-area flexible devices. For the flexible PSCs, we first measure the $J-V$ characteristics of the PSCs based on MG-PEDOT HTLs. We achieve the PCE of 18.76% and 20.25%, for MAPbI₃ PSCs and Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})₃ mixed-cation PSCs respectively with an effective area of 0.04 cm², and the PCE of 18.34% for the mixed-cation PSCs with an effective area of 1 cm², as shown in Figure S14a,b (Supporting Information). For the flexible MG-PEDOT-based PSCs using MAPbI₃ and we achieve the J_{SC} of 21.67 mA cm⁻², V_{OC} of 1.11 V, FF of 0.78, and PCE of 18.76%, as shown in Figure S21 (Supporting Information) with the repeatability of distribution. To explore the scalable applications, we make the flexible MG-PEDOT-based PSCs with the device effective area of 15 cm². The PSCs show a high PCE of 17.46% (Figure 5e). Furthermore, we expand the effective area of the

flexible MG-PEDOT-based PSMs to 15 cm² and achieve a PCE of 16.28% (Figure 5f), showing a good potential for the application of scalability. Figure S22 (Supporting Information) shows the SEM images of perovskite films based on MG-PEDOT in the module. Each selection point is randomly chosen within nine regions, respectively. The SEM results show that the large-area perovskite films are uniform, which confirms the good scalability.

Alongside the MAPbI₃ perovskite, we further fabricate PSMs based on mixed-cation perovskite of Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})₃ to generalize the results. We achieve the PCE of 20.25% and 18.34% based on mixed-cation perovskite with an effective area of 0.04 cm² and 1 cm² respectively, as shown in Figure S23a,b (Supporting Information). The champion PCE is 17.06% based on the area of 15 cm² were achieved with the MG-PEDOT HTL as shown in Figure 6a. The statistics of flexible modules based on MG-PEDOT among 24 separate PSMs are shown in Figure 6b, which ensures the reproducibility of this optimization in different types of perovskite absorber layers. We achieve the highest efficiency with the MG-PEDOT HTL in the PSMs among the current work, as shown in Table 2. A summary of all fabricated PSCs studied in the work is shown in Table S2 (Supporting Information).

We also study the operational stability of encapsulated PSMs based on MG-PEDOT and PEDOT:PSS HTLs under 1.5 AM in ambient air as shown in Figure 6c. The PCE of the PSMs based on MG-PEDOT maintains at ≈83% of the original PCE for 1000 h. Figure 6d shows the thermal stability of the PSCs at 85 °C in ambient air. The PCE for the devices upon MG-PEDOT

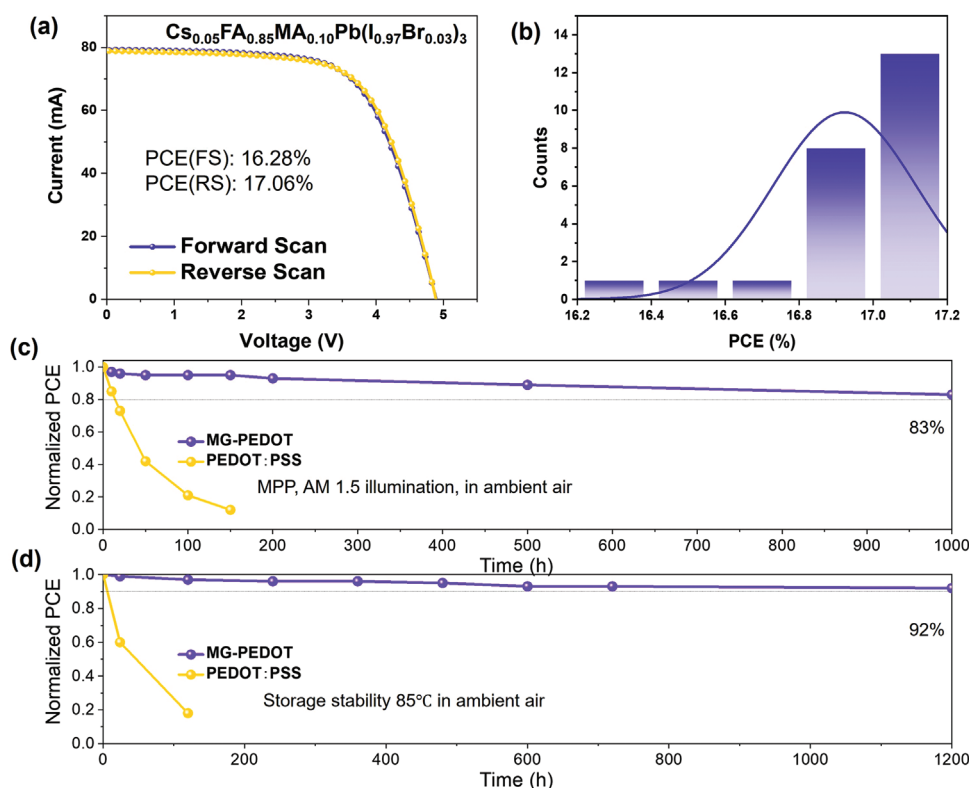


Figure 6. a) J - V curves of flexible modules with forward and reverse scan. b) The statistics of flexible modules based on MG-PEDOT among 24 separate PSMs. c) The stability of encapsulated flexible modules on the operational (under AM 1.5 illumination) in ambient air. d) The storage stability of encapsulated modules at 85 °C in ambient air.

is much more stable and can be retained for $\approx 92\%$ after 50 h. One of the main reasons for the instability of inverted structure PSCs with pristine PEDOT as HTL is the acidity of PEDOT:PSS leading to perovskite film degradation and indium tin oxide (ITO) corrosion.^[54] The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene are prepared via the MILD method, which are washed with deionized water during the synthesis process to obtain a small number of layers product with a pH of ≈ 7 . The added neutral MXene solution helps to neutralize the nanocomposite and thus alleviating the corrosion of PEDOT:PSS toward the photoactive layer and extending the operational lifetime of the PSMs.^[44] Consequently, by introducing MG-PEDOT as the HTL, the flexible PSMs show remarkable operational and storage (at high temperature) stability.

3. Conclusion

In summary, we reported a method of fabricating a unique MXene/Glucose/PEDOT:PSS nanocomposite HTL for flexible large-area perovskite solar module. The incorporation of glucose and its half-caramelization process can simultaneously enhance the dispersion of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in PEDOT:PSS and carry the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets float upwards, forming a composite HTL with a vertical-gradient distribution of MXene. This featured MG-PEDOT HTL offers the marvelous improvement of the conductivity, favorable energy level alignment, and benefits the crystallinity of the upper perovskite layer.

The flexible PSCs with MG-PEDOT show a remarkable PCE of 20.25%, which shows better performance than the flexible controlled devices (17.59%). Moreover, the flexible large-area (1.00 cm^2) PSCs achieve a PCE of 18.34%. Finally, we assemble the flexible perovskite modules into a 15 cm^2 sized module which PCE reaches 16.28%. Equally important, the encapsulated flexible module with MG-PEDOT HTL shows substantial improvement in the storage stability at 85 °C and operational stability under AM 1.5 illumination both in ambient air. This work shows that incorporation of the 2D materials into perovskite solar module is an effective strategy to further improve its photovoltaic performance and reliability.

4. Experimental Section

Materials: Titanium aluminum carbide (Ti_3AlC_2 , 400 mesh) powder was purchased from Jilin 11 Technology Co., Ltd. Lithium fluoride (98%) was purchased from Aladdin Reagent Company, Shanghai, China, and concentrated hydrochloric acid (12 m) was bought from Yuanli Chemical Corporation. Other chemical materials are bought and utilized without further optimization or purification, including D-(+)-Glucose (99.5%, Sigma-Aldrich), bathocuproine (BCP, Sigma-Aldrich), anhydrous N, N-dimethylformamide (DMF, Sigma-Aldrich), anhydrous dimethyl sulfoxide (DMSO, Sigma-Aldrich), anhydrous ethanol (99.5%, Sigma-Aldrich), anhydrous isopropyl alcohol (99.5%, Sigma-Aldrich), lead (II) iodide (PbI_2 , 99.999%, Afar Aesar), formamidine iodide (FAI, Dysol), methylammonium bromide (MABr, Dysol), methylammonium chloride (MACl, Xi'an Polymer Light Technology Corporation), cesium iodide (CsI, Dysol), polyurethane (Sigma-Aldrich), PEDOT:PSS solution (Clevios

Table 2. The summary of PCE of recent flexible perovskite solar modules.

Device structure	PCE (%)	Area (cm ²)	Reference
PET/PEDOT:PSS:CFE/PEDOT:PSS/perovskite/PCBM/Ag	10.9	25	[55]
PET/ITO/F2HCNQ-NiO _x /CsFAMAPb(I _{0.93} Br _{0.07}) ₃ /PCBM/BCP/Ag	12.85	36.1	[56]
MgF ₂ /Willow glass/ITO/PTAA/MAPbI ₃ -NH ₄ Cl/C ₆₀ /BCP/Cu	15.86	42.9	[57]
PET/ITO/PEDOT:EVA/perovskite/PCBM/BCP/Ag	15.21	36	[6]
flexible substrate/ITO/2T-NATA/perovskite/C ₆₀ /BCP/Ag	13.15	16	[58]
PEN/ITO/SnO ₂ /perovskite/spiro-OMeTAD/Ag	15.8	49	[59]
PET/hc-PEDOT:PSS/NiO _x /perovskite/PC ₆₁ BM/BCP/Ag	16.15	15	[60]
PET/hc-PEDOT:PSS/oil-PEDOT:PSS/perovskite/PC ₆₁ BM/BCP/Ag	16.7	22.5	[61]
Flexible PET/ITO/PEDOT:GO/MAPbI ₃ /PC ₆₁ BM/Ag	10.26	25	[62]
Flexible PEN/ITO/PTAA/GBA-modified FA _{0.7} MA _{0.25} CS _{0.05} Pb(I _{0.93} Br _{0.07}) ₃ /PCBM/BCP/Ag	14.48	10.64	[63]
PEN/ITO/MG-PEDOT/Cs _{0.05} FA _{0.85} MA _{0.10} Pb(I _{0.97} Br _{0.03}) ₃	17.06	15	This work

Al 4083, Heraeus), methylamine iodide (MAI, 98% purity, Dyesol), and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, American Dye Source Inc), rigid indium tin oxide (ITO)/glass substrates (84% transmittance, 6 ohm sq⁻¹, Southern China Xiang's Science&Technology) and flexible ITO/Polyethylene naphthalate (PEN) substrates (80% transmittance, 6 ohm sq⁻¹, Southern China Xiang's Science&Technology).

Solution Preparation: Ti₃C₂T_x MXene powder was prepared by selective etching the Al layer from Ti₃AlC₂ MAX. At room temperature (RT), 2 g of LiF was added to 40 mL of 9 M HCl, and then the mixture was stirred magnetically for 30 min to obtain a uniform solution. Subsequently, 2 g of Ti₃AlC₂ MAX powder was added into the previously prepared solution. The mixed solution was then magnetically stirred at 35 °C for 24 h. After the complete reaction, the MXene product was washed with deionized water for five cycles, each of which is centrifuged at 3500 rpm for 5 min. It then yielded a dark green Ti₃C₂T_x MXene nanosheet supernatant with a pH of ≈7. After the final separation of MXene from the solution using a centrifuge, MXene was added to deionized water and sonicated in an ice bath for 1 h. After centrifugation at 3500 rpm for 1 h and concentrating, the stripped supernatant was yielded at a concentration of ≈10.0 mg mL⁻¹. PEDOT:PSS Al 4083 aqueous solution was used with a PEDOT:PSS weight concentration of 1.3% and has the ratio between PSS and PEDOT was 6:1. The dispersion of Ti₃C₂T_x MXene into PEDOT:PSS, was obtained by gently stirring for 90 min and 15 min of sonication at room temperature (RT). Ti₃C₂T_x MXene was incorporated to PEDOT:PSS solution with the concentration of 0.05%, 0.10%, 0.30%, and 0.50% (wt/vol), respectively. Then glucose power was added to the prepared MXene-PEDOT:PSS dispersion with the concentration of 1% wt mol⁻¹, stirring and sonicating for 15 min, respectively.

Fabrication of HTL on Rigid and Flexible Substrate: The scalable HTLs were fabricated by blade coating. First, ITO/Glass and ITO/PEN substrates were ultrasonically cleaned with acetone, abstergent aqueous, deionized water, and isopropyl alcohol for 45 min, respectively, and then blow-dried with nitrogen gas flow followed by plasma treatment for 20 min. For rigid PSCs, the MG-PEDOT solution was blade-coated onto ITO/Glass substrates at 25 °C. The space between the scraper and the substrate was set as 50 μm. The film with a thickness of ≈40 nm was blade-coated at the speed of 10 mm s⁻¹. The prepared film was annealed at 120 °C in the air for 15 min. As comparison, pure PEDOT:PSS solution was also blade-coated onto ITO/Glass substrates at a blading speed of 10 mm s⁻¹ and then annealed at 120 °C for 15 min. We used same processes as above for the flexible PSCs, while the condition of heat-annealing for blade-coated MG-PEDOT or PEDOT:PSS HTLs was switched to 100 °C for 15 min. Notably, the critical aspect of manufacturing high-performance and flexible devices is to secure the flatness of the substrates during the process. Hence, the ITO/PEN substrate is adhered to a glass/PDMS rigid platform for the device

fabrication. The prepared devices were peeled off from the platform for further characterization.

Fabrication of Perovskite Solar Cells: The CH₃NH₃PbI₃ perovskite precursor solution is obtained by dissolving 1 μ PbI₂ and MAI (molar ratio of 1:1) in anhydrous Dimethylformamide (DMF). The polyurethane (PU) added into the precursor was dissolved in anhydrous Dimethylformamide (DMF) (5 mg mL⁻¹). The mixed-cation perovskite precursor solution was prepared by dissolving a mixture of PbI₂ (742.2 mg), FAI (224.4 mg), MABr (16.2 mg), MACl (20.3 mg), and CsI (19.8 mg) in 1 mL of mixed solvent of DMF/DMSO (volume ratio of 4:1) with a chemical formula of Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})₃. The amounts of PU were incorporated into the perovskite solution at the mass concentration of 0.02 wt%. Afterward, the perovskite precursor solution was blade-coated onto the rigid or flexible substrates at the speed of 10 mm s⁻¹ and the space between the scraper and the substrate is 50 μm. Then, the coated films were annealed at 100 °C for 15 min on a hot plate and resulted into the thickness of ≈400 nm. The 20 mg mL⁻¹ PC₆₁BM dissolved in chlorobenzene and 0.5 mg mL⁻¹ BCP dissolved in anhydrous ethanol were blade-coated to the perovskite layers to fabricate the ETL with the thickness of 50 nm. Finally, the silver electrode with the thickness of 90 nm for the small-area device and 120 nm for the perovskite module were deposited by vacuum evaporation with the vacuum of 6 × 10⁻⁴ Torr. The preparation condition of PSMs is the same as that of the small area photovoltaic device, while have different effective area. There are six sub cells on the 50 × 50 mm² ITO/PEN substrate, where each sub cell is 50 mm in length and 5 mm in width. The scribing techniques are applied via the rectification unit to ensure that the dislocation of each layer for the perovskite solar modules is ≈0.1 mm.

Film Characterizations: The morphology of perovskite films is measured by scanning electron microscope (SEM) at an accelerating voltage of 5.0 kV (JEOL, JSM-7500F, Japan). The UV-vis spectra are measured by Ultraviolet-visible Spectrophotometer (Shimadzu, UV-2501 PC). Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements at the peak emission of ≈770 nm (on the excitation at 480 nm) are carried out by the steady-state and lifetime spectrometer (FLS920, Edinburgh Instruments Ltd.). The TRPL excitation fluence is ≈4 nJ cm⁻² from a 405 pulsed laser which has a wavelength of 405 ± 8 nm and pulse width of 45 ps. The PL decay data is recorded using time-correlated single photon counting technique. X-ray diffraction (XRD) measurement is recorded with D8-Discover 25 diffractometer (Bruker). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was used for binding energy and element distribution analysis. All recorded peaks were adjusted for electrostatic effect via setting the C-C component of the C 1s peak to 284.8 eV. Sample etching was performed using an argon ion etcher with

a 600 V accelerated voltage. The etch area was $\approx 1.3 \text{ cm}^2$. The etching rate was approximately within 2 nm s^{-1} , which is estimated with the profilometer (Bruker). Electrical impedance spectroscopy (EIS) was performed by a Zahner electrochemical workstation. The contact angle with the droplet of deionized water is performed by the KRÜSS DSA100 contact angle meter.

Perovskite Solar Cell Characterization: The Keithley 2400 Sourcemeter was used to get the current density-voltage (J - V) curves and current-voltage (I - V) curves for the PSCs and PSMs. The reverse and forward scan range were from 1.3 to 0 V and from 0 to 1.3 V, with a 30 ms delay time and a scan rate of 0.2 V s^{-1} and 8.0 mV for each step. The incident photo-to-electron conversion efficiency spectra (IPCE) was recorded by the monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp) and the monocrystalline silicon diode realizes the calibration of the incident light. These measurements were conducted at nitrogen atmosphere and at room temperature. The size of PSCs was measured by calibrated apertures (1.00 and 15.00 cm^2).

Stability Measurement: Thermal stability was recorded by storing the encapsulated PSMs on a hot plate setting at 85°C in the ambient air. The J - V curves were measured after cooling the PSMs down to room temperature. For operational stability, the J - V curves were recorded first to verify the voltage at maximum power point (MPP). Then the operational stability tests were carried out at the MPP for the encapsulated PSMs under UV-filtered AM 1.5 illumination (100 mW cm^{-2} , with a UV filter with a 420-nm cut-off) in the ambient air. It should be noted that during the whole MPP tracking, the external bias and illumination were continuously applied on the PSMs except the calibration of the light source. The temperature of PSMs during MPP tracking was monitored with an IR thermal gun. The devices were encapsulated in a nitrogen glovebox. UV-curable epoxy was coated around the device area, and a glass cover slide was attached to enclose the area. The encapsulation was then finished off by exposing the construct to UV light off for 10 min. The bending tests were conducted with a customized stretching machine. The results of bending test were an average of more than 50 samples.

Supporting Information

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

Acknowledgements

R.Z. and Z.H. contributed equally to this work. This research was supported by the feed funds (Grant Nos. 202011159254 and 202111159113), from the University Grant Council of the University of Hong Kong, the General Research Fund (Grant Nos. 17201819, 17211220, and 17200021), Collaborative Research Fund (Grant No. C7035-20G and C5037-18G), the Innovation and Technology Fund (MRP/040/21X, ITS/277121FP) from the Innovation and Technology Commission from Hong Kong Special Administrative Region, China, and the National Natural Science Foundation of China (22005131, 52173169).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

flexible PSCs, gradient structures, MXenes, PEDOT: PSS, perovskites

Received: September 3, 2022

Revised: November 6, 2022

Published online:

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