Supporting Information for

Mixed Cations Enabled Combined Bulk and Interfacial Passivation for Efficient and Stable Perovskite Solar Cells

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Supplementary Figures and Tables

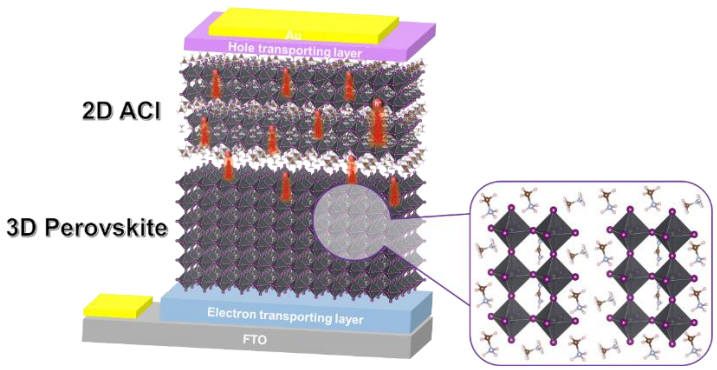


Fig. S1 Schematic depiction of the proposed 2D ACI/3D hybrid perovskite structure

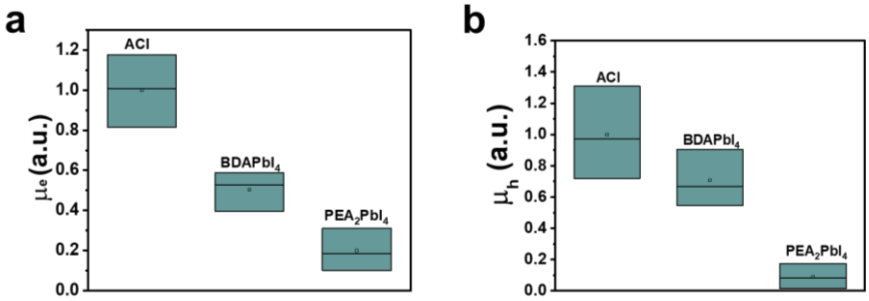


Fig. S2 Statistical comparison of the normalized out-of-plane hole **a** and electron **b** mobilities by SCLC (3 devices in each condition)

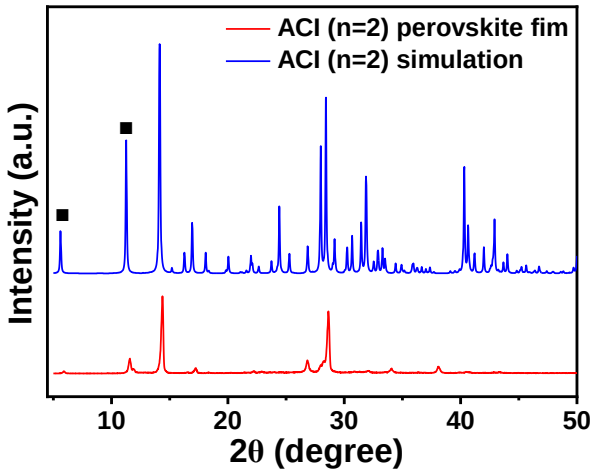


Fig. S3 XRD patterns of experimental and simulated 2D ACI (n=2)

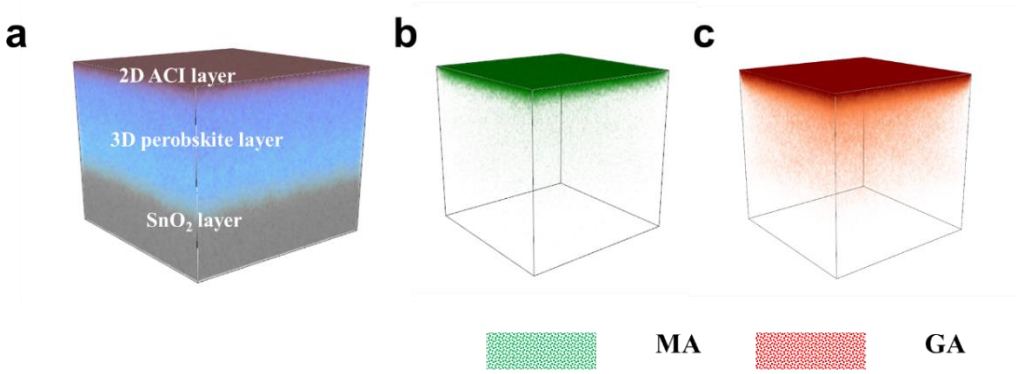


Fig. S4 a ToF-SIMS 3D images of the MGM-treated 3D film deposited on the FTO/SnO_2 substrate. **b** Side-view 3D images of MA distribution. **c** Side-view 3D images of GA distribution

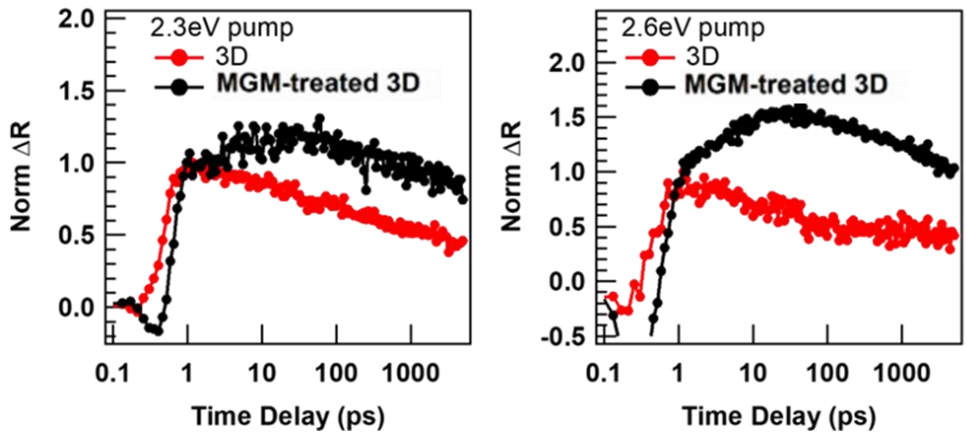


Fig. S5 Transient reflection (TR) comparison of the control and MCP-treated perovskite thin films. For control films, the TR kinetics rises within 1ps, and the decay starts, indicating a normal carrier diffusion/recombination process. For MGM-treated films, the TR kinetics exhibit additional rise kinetics from 1 to 30 ps, which is a characteristic of the charge transfer process

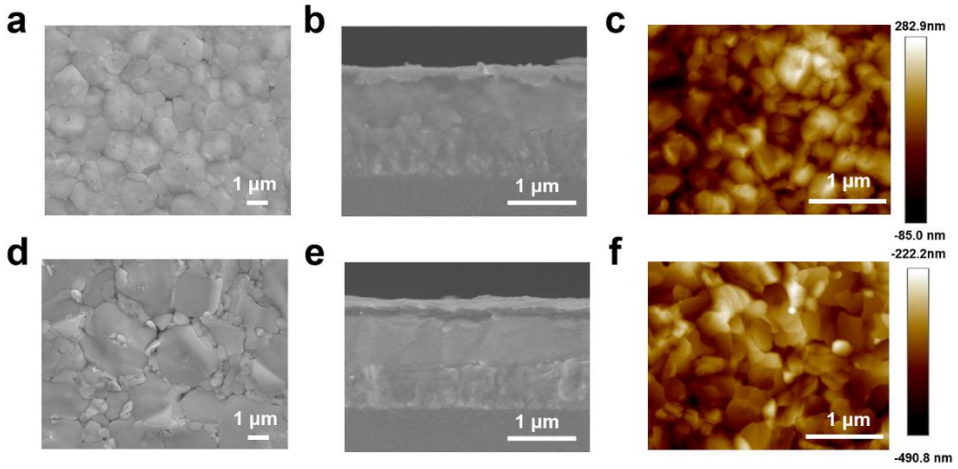


Fig. S6 a Top-view SEM images of 3D film. **d** Top-view SEM images of MGM-treated 3D film. The scale bar is 1μm. **b** Cross-sectional SEM image of 3D film. **e** Cross-sectional SEM image of MGM-treated 3D film. The scale bar is 1 μm. **c** Surface AFM images of 3D film. **f** Surface AFM images of MGM-treated 3D film. The scale bar is 1 μm

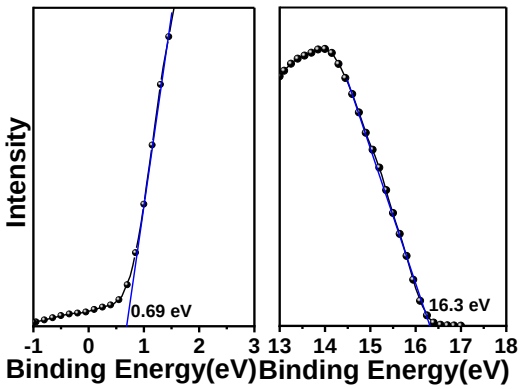


Fig. S7 UPS energy spectrum of the 3D film in cutoff region (right) and onset region (left)

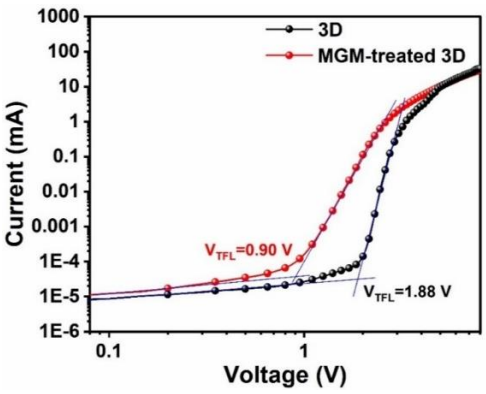


Fig. S8 Comparison of the control and MGM-treated perovskite thin films by space-charge-limited current measurement based on "electron-only" geometry (ITO/ SnO_2/perovskite/PCBM/Au)

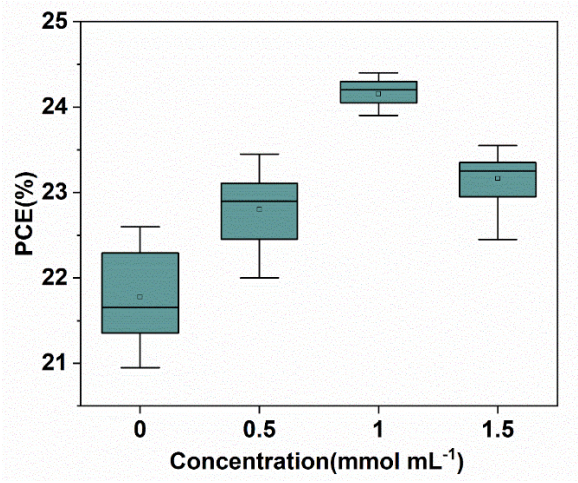


Fig. S9 The statistical distribution of the PCE of the devices with different MGM concentrations. Each condition has 20 devices

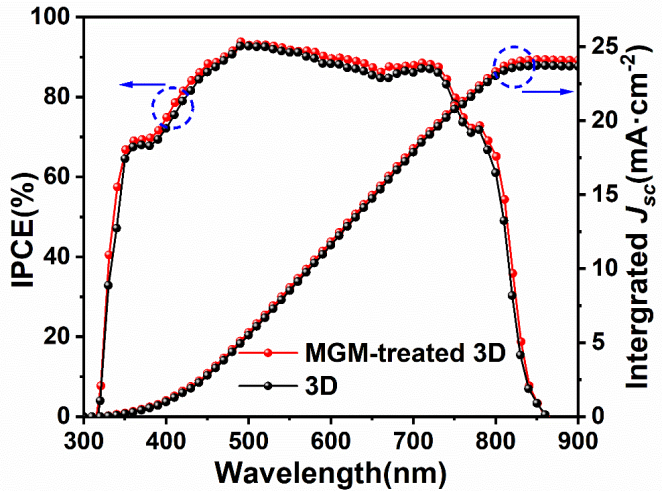


Fig. S10 IPCE of 3D film and MGM-treated 3D film-based devices

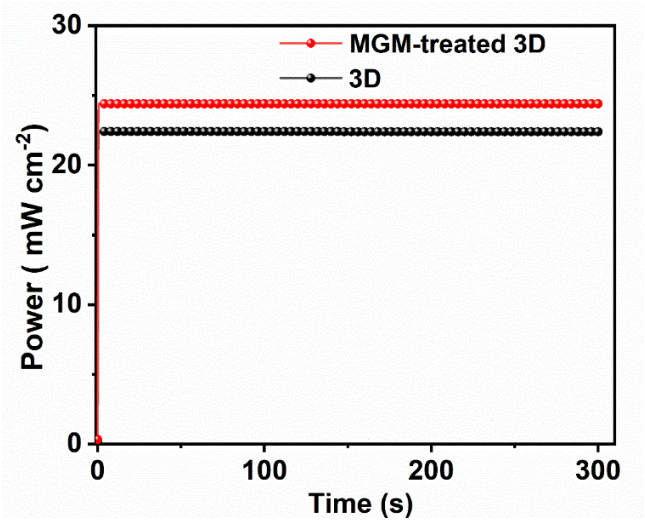


Fig. S11 SPO of 3D film and MGM-treated 3D film-based devices

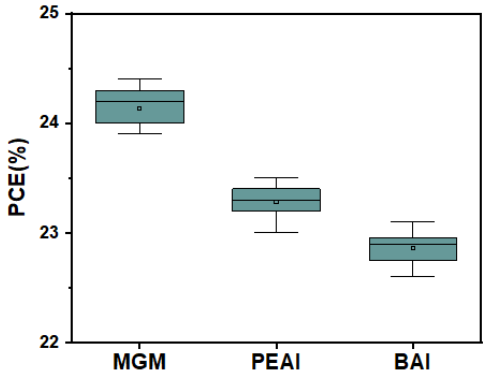


Fig. S12 The statistical PCE distribution of the devices with PEAI, BAI, and MGM treatment (15 devices in each condition)

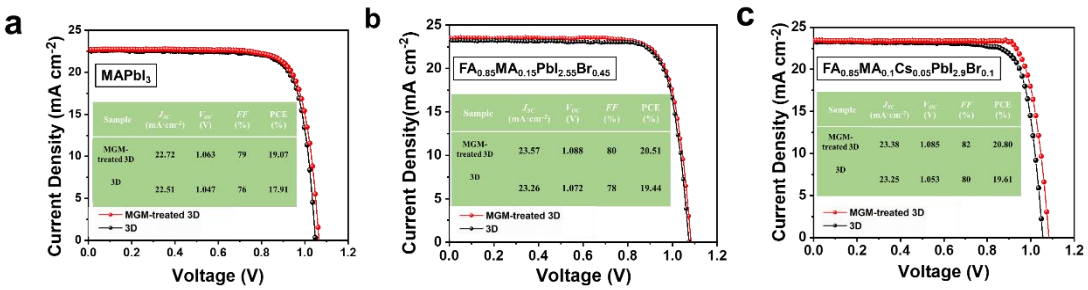


Fig. S13 a *J–V* curves of the n-i-p PSCs with $MAPbI_3$. **b** *J–V* curves of the n-i-p PSCs with $FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$. **c** *J–V* curves of the n-i-p PSCs with $FA_{0.85}MA_{0.1}Cs_{0.05}PbI_{2.9}Br_{0.1}$

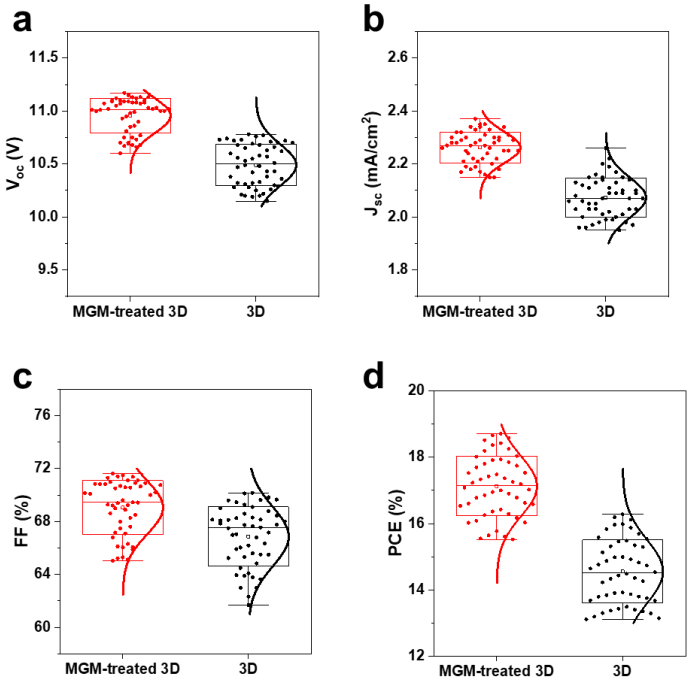


Fig. S14 The statistical box plots on (**a**) V_{OC}, (**b**) J_{SC}, (**c**) FF and (**d**) PCE of the MGM and control modules (50 devices in each condition)

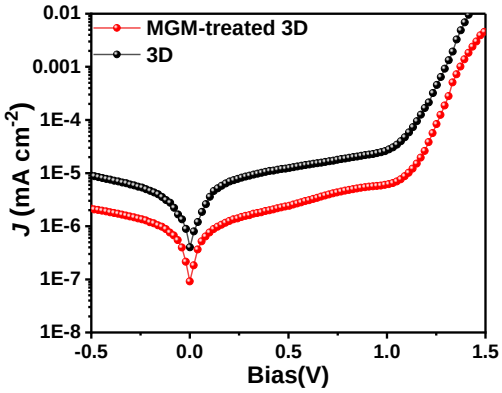


Fig. S15 The dark *J–V* of the MGM-treated 3D and 3D film-based devices

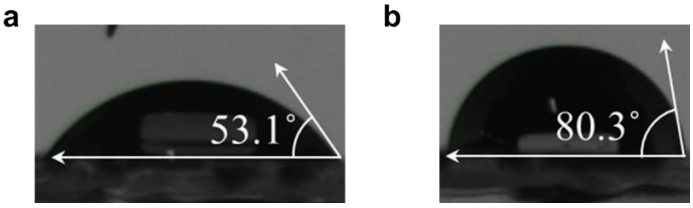
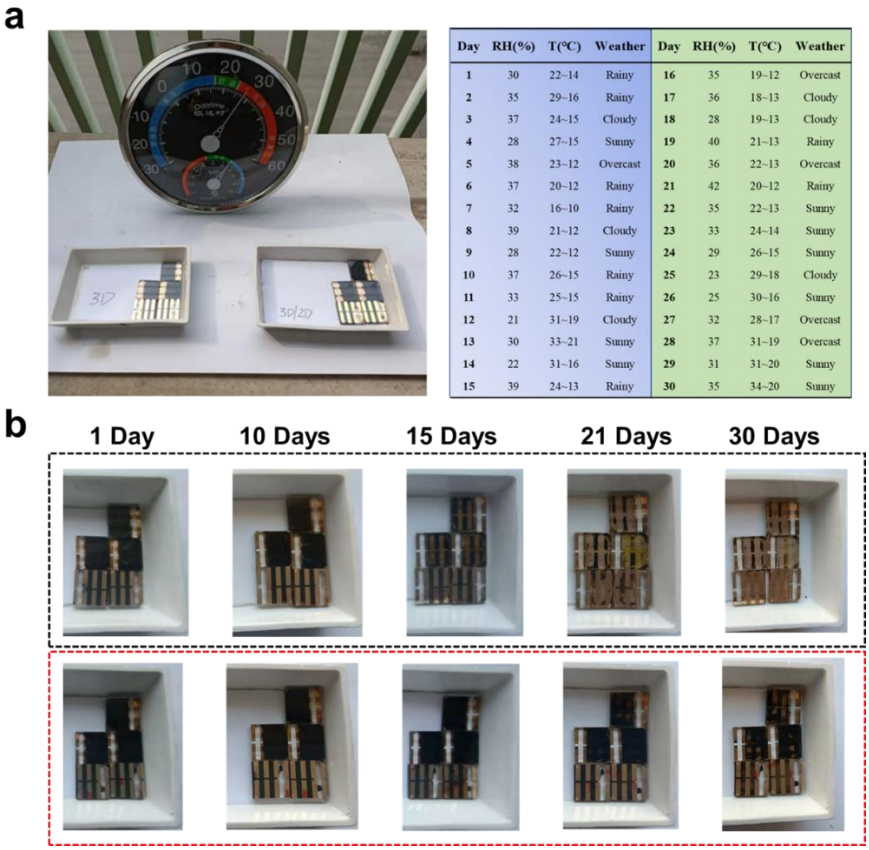


Fig. S16 The water contact angle of **a** the 3D film and **b** MGM-treated 3D film



Day	RH(%)	T(℃)	Weather	Day	RH(%)	T(℃)	Weather
1	30	22–14	Rainy	16	35	19–12	Overcast
2	35	29–16	Rainy	17	36	18–13	Cloudy
3	37	24–15	Cloudy	18	28	19–13	Cloudy
4	28	27–15	Sunny	19	40	21–13	Rainy
5	38	23–12	Overcast	20	36	22–13	Overcast
6	37	20–12	Rainy	21	42	20–12	Rainy
7	32	16–10	Rainy	22	35	22–13	Sunny
8	39	21–12	Cloudy	23	33	24–14	Sunny
9	28	22–12	Sunny	24	29	26–15	Sunny
10	37	26–15	Rainy	25	23	29–18	Cloudy
11	33	25–15	Rainy	26	25	30–16	Sunny
12	21	31–19	Cloudy	27	32	28–17	Overcast
13	30	33–21	Sunny	28	37	31–19	Overcast
14	22	31–16	Sunny	29	31	31–20	Sunny
15	39	24–13	Rainy	30	35	34–20	Sunny

Fig. S17 (**a**)The photograph of devices in the natural environment(left) and the real condition of the stability test in the past 30 days(right); (**b**)The photographs of the 3D film (up) and b MGM-treated (down) 3D film-based devices at different stages in the natural environment

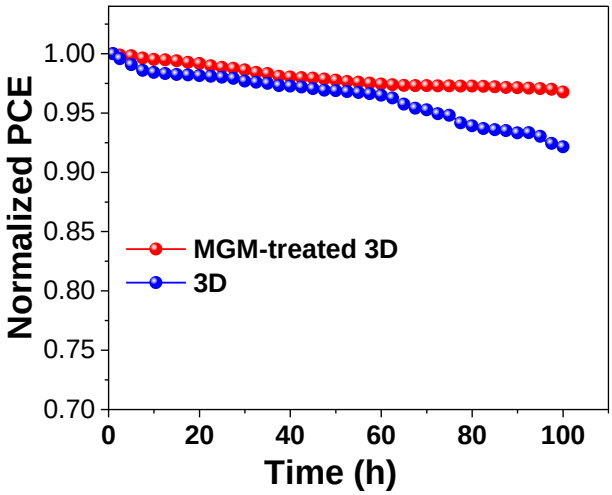


Fig. S18 Operation ISOS-L-1 stability (maximum power point tracking, in Ar, continuous one-sun illumination at ~30 °C) of unencapsulated PSCs based on 3D and MGM-treated 3D film

Table S1 Summarry of the ionic radii of some ammonium cations

Cations	MA^+	FA^+	Cs^+	GA^+	BA^+	PEA^+	BDA^{2+}
Radii(Å)	2.17	2.53	1.67	2.78	3.93	4.31	4.57

Note: MA^+: methanaminium; FA^+: formamidinium; Cs^+: cesium ;GA^+: guanidinium; BA^+: butylammonium; PEA^+: phenethylammonium; BDA^+: butane-1,4-diammonium;

Table S2 TRPL parameters of amplitudes (A1 and A2) and time constant (τ1 and τ2) for the MCP-treated 3D film and 3D film

Sample	τ_1 (μs)	A1 (%)	τ_2 (μs)	A2 (%)	τ_{av} (μs)
3D	0.88	42.8	1.8	57.2	1.55
MGM treatment	0.35	15.2	5.72	74.8	5.67
3D/Sprio	0.98	48.2	0.07	51.8	0.48
MGM treatment /Sprio	0.71	5.3	0.04	94.7	0.08

Supplementary Note S1

The curves are fitted using a bi-exponential decay model as Eq. S1:

$$I(\mathrm{t}) = I_0 + A_1 e^{-(t/\tau_1)} + A_2 e^{-(t/\tau_2)} \qquad \text{(S1)}$$

Average lifetime (τ_{av}) is calculated from Eq. S2:

$$\tau_{av} = \frac{A_1 \times {\tau_1}^2 + A_2 \times {\tau_2}^2}{A_1 \times \tau_1 + A_2 \times \tau_2} \qquad \text{(S2)}$$

Table S3 The champion photovoltaic parameters of the 3D film and MGM-treated 3D film-based small area devices (0.12cm^2) under different scan directions

Sample	Scan Direction	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE (%)*
3D	Forward	1.13	25.00	0.79	22.3
	Backward	1.13	25.02	0.80	22.6
MGM treatment	Forward	1.16	25.21	0.83	24.3
	Backward	1.16	25.23	0.84	24.5

Table S4 The champion photovoltaic parameters of the 3D film and MGM-treated 3D film-based mini-module devices(Aperture area 64 cm^2)

Sample	V_{oc}(V)	I_{sc}(mA)	J_{sc}(mA/cm^2)	FF (%)	PCE (%)
3D	10.76	140.03	2.19	69.09	16.3
MGM treatment	11.13	150.21	2.35	71.51	18.7