Supplementary Information

Boosting the Ultra-Stable Unencapsulated Perovskite Solar Cells by Using Montmorillonite/$CH_3NH_3PbI_3$ Nanocomposite as Photoactive Layer

Hsin-Hsiang Huang[a,b], Yen-Chen Shih[a,b], Leeyih Wang[*b], King-Fu Lin[*a]

Affiliations:

[a] Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan.

[b] Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.

∗The corresponding authors. E-mail: kflin@ntu.edu.tw; leewang@ntu.edu.tw

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Supplementary Tables:

Table S1 The parameters of equation (2) used to calculate the interaction energy between two adjacent nanoplatelets of MMT swelling in water.

d (nm)	n_0 (m^{-3})	ψ (V)	Υ_0	κ (m^{-1})	κ^{-1} (nm)	A (J)	ϕ_{net} (J/m^2)
0.2	6.65×10^{27}	0.03	0.289	7.72×10^{9}	1.29×10^{-10}	8.20×10^{-21}	-0.00139
0.3	4.43×10^{27}	0.05	0.419	6.30×10^{9}	1.58×10^{-10}	8.20×10^{-21}	0.0025
0.4	3.32×10^{27}	0.06	0.533	5.46×10^{9}	1.83×10^{-10}	8.20×10^{-21}	0.00379
0.5	2.66×10^{27}	0.07	0.631	4.88×10^{9}	2.04×10^{-10}	8.20×10^{-21}	0.00412
0.6	2.21×10^{27}	0.09	0.713	4.46×10^{9}	2.24×10^{-10}	8.20×10^{-21}	0.00399
0.7	1.90×10^{27}	0.11	0.778	4.13×10^{9}	2.42×10^{-10}	8.20×10^{-21}	0.00365
0.8	1.66×10^{27}	0.12	0.830	3.86×10^{9}	2.59×10^{-10}	8.20×10^{-21}	0.00323
0.9	1.47×10^{27}	0.13	0.871	3.64×10^{9}	2.74×10^{-10}	8.20×10^{-21}	0.00281
1.1	1.20×10^{27}	0.16	0.927	3.29×10^{9}	3.03×10^{-10}	8.20×10^{-21}	0.00205
2	6.65×10^{26}	0.30	0.994	2.44×10^{9}	4.09×10^{-10}	8.20×10^{-21}	4.84×10^{-4}
3	4.43×10^{26}	0.45	0.999	1.99×10^{9}	5.01×10^{-10}	8.20×10^{-21}	1.24×10^{-4}
4	3.32×10^{26}	0.61	0.999	1.73×10^{9}	5.79×10^{-10}	8.20×10^{-21}	3.74×10^{-5}
6	2.21×10^{26}	0.91	0.999	1.41×10^{9}	7.09×10^{-10}	8.20×10^{-21}	2.78×10^{-6}

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Table S2 Assignment of IR absorption peaks for the FTIR spectra of MMT and exMMT.[1,2]

Wave number (cm^{-1})	Assignment
467	τ (Si-O-Si)
523	τ (Si-O-Al)
623	Si-O、Al-O
800	τ (Si-O, amorphous)
1044	υ (Si-O, tetrahedral)
1120	υ (Si-O, amorphous)
1480	Mg-O
1643	υ (H-O-H)
3425	υ (-OH)
3636	υ (-OH)

Table S3 The crystal size of perovskite films incorporating various amounts of exMMTs estimated from the (110) peaks at 2θ = 14.1° in Fig. S7 by Scherrer's equation.

Sample	Crystal size (Å)
Pristine	680
0.0001 wt% - exMMT	695
0.001 wt% - exMMT	703
0.01 wt% - exMMT	730
0.1 wt% - exMMT	744

Table S4 The photovoltaic parameters of PSCs with and without incorporating 0.01 wt% exMMT.

	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	η (%)	R_S (Ω cm^2)	R_{sh} (KΩ cm^2)
$MAPbI_3$	**1.03 ± 0.01**	**20.37 ± 0.25**	**0.79 ± 0.01**	**16.65 ± 0.16**	**3.71 ± 0.23**	**2.60 ± 2.74**
exMMT/$MAPbI_3$	**1.05 ± 0.01**	**20.51 ± 0.14**	**0.80 ± 0.01**	**17.29 ± 0.15**	**2.95 ± 0.22**	**3.30 ± 1.63**

Table S5 The photovoltaic parameters of PSCs with $MAPbI_3$ and exMMT (0.01 wt%) / $MAPbI_3$ after storage in the environmental conditions shown in Fig. S17c.

Time (hour)					
Sample	**Fresh**	**25**	**75**	**125**	**175**
$MAPbI_3$ @ 50°C, RH 50%	**16.65 ± 0.33**	**12.18 ± 0.26**	**6.82 ± 0.56**	**4.03 ± 0.12**	**0.85 ± 0.17**
exMMT/$MAPbI_3$ @ 50°C, RH 50%	**17.28 ± 0.13**	**16.67 ± 0.19**	**16.59 ± 0.22**	**16.49 ± 0.14**	**16.40 ± 0.17**
exMMT/$MAPbI_3$ @ 55°C, RH 50%	**17.28 ± 0.13**	**16.42 ± 0.27**	**15.92 ± 0.15**	**15.23 ± 0.07**	**12.97 ± 0.11**
exMMT/$MAPbI_3$ @ 60°C, RH 50%	**17.28 ± 0.13**	**16.24 ± 0.19**	**15.29 ± 0.22**	**10.51 ± 0.14**	**5.61 ± 0.17**

Sample	**200**	**250**	**300**
$MAPbI_3$ @ 50°C, RH 50%			
exMMT/$MAPbI_3$ @ 50°C, RH 50%	**16.05 ± 0.22**	**14.79 ± 0.18**	**12.68 ± 0.15**
exMMT/$MAPbI_3$ @ 55°C, RH 50%	**10.98 ± 0.22**		
exMMT/$MAPbI_3$ @ 60°C, RH 50%			

Supplementary Figures:

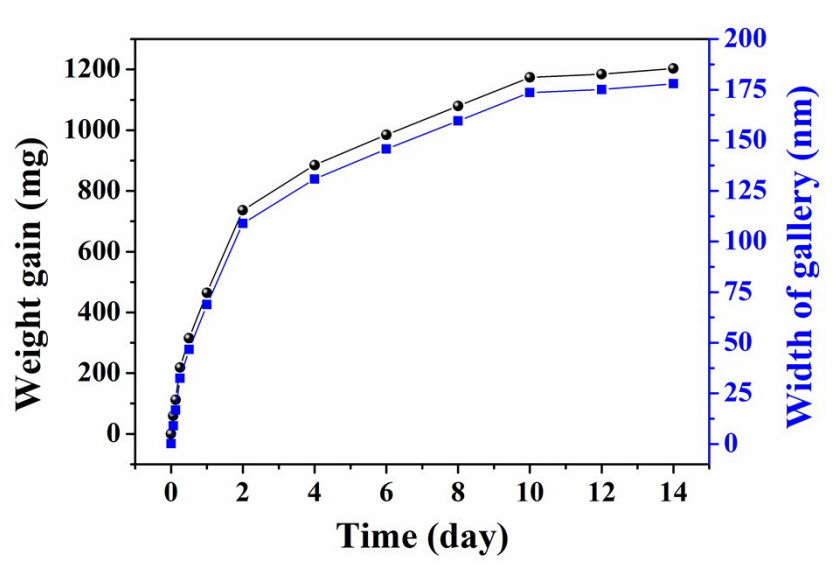

Fig. S1 Swelling of MMT in water. The weight gain and corresponding enlarged width of gallery between two adjacent nanoplatelets in MMT versus swelling time in water.

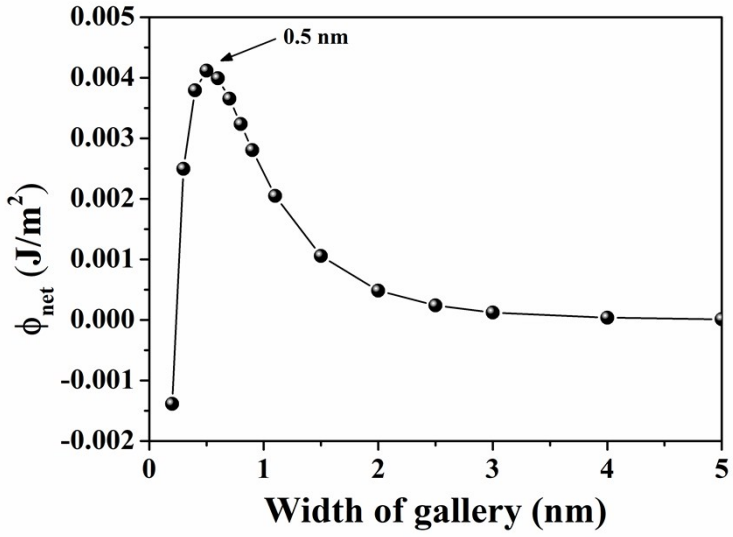

Fig. S2 Interaction energy between two adjacent nanoplatelets of swelling MMT. Interaction energy versus the width of gallery between two adjacent nanoplatelets of MMT swelling in water as estimated by equation (2).

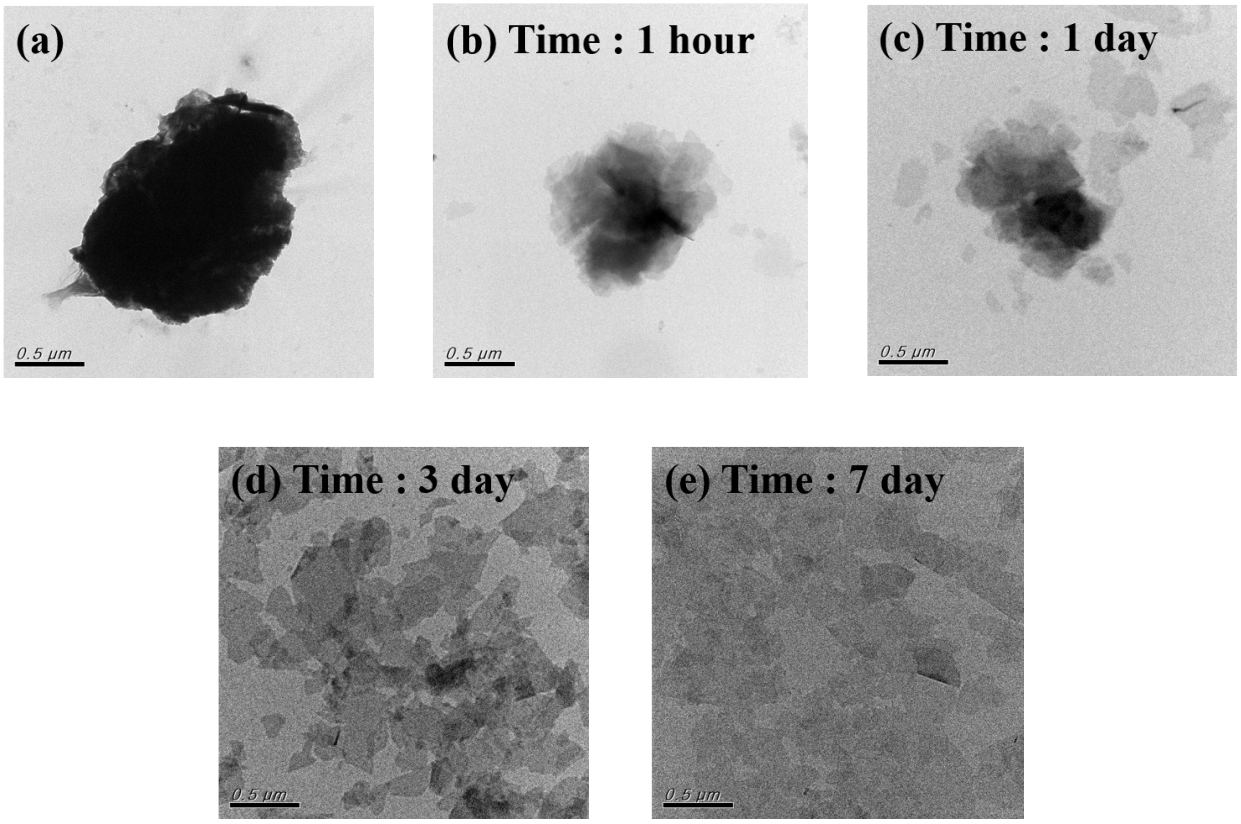

Fig. S3 Images of exfoliating MMT. TEM images of (a) pristine and (b-e) exfoliating MMTs prepared by sonication for the different indicated time after swelling in water.

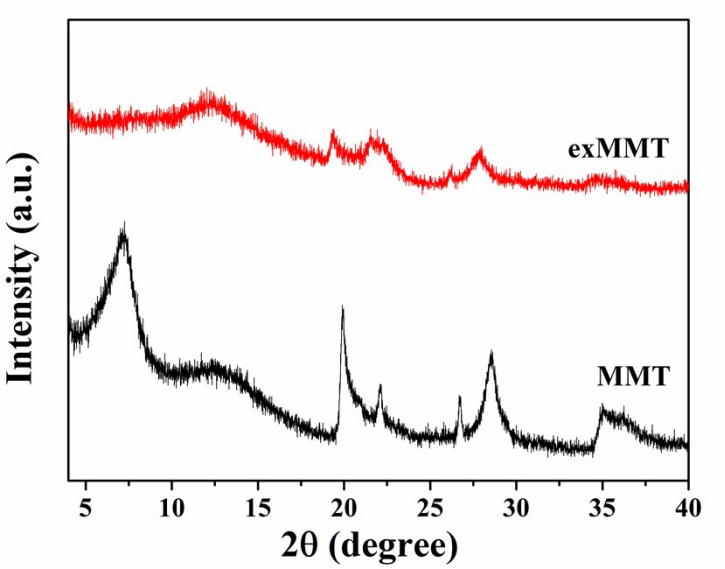

Fig. S4 XRD evidence of MMT exfoliation. XRD patterns of pristine MMT and exMMT prepared by sonication for 7 days after swelling in water.

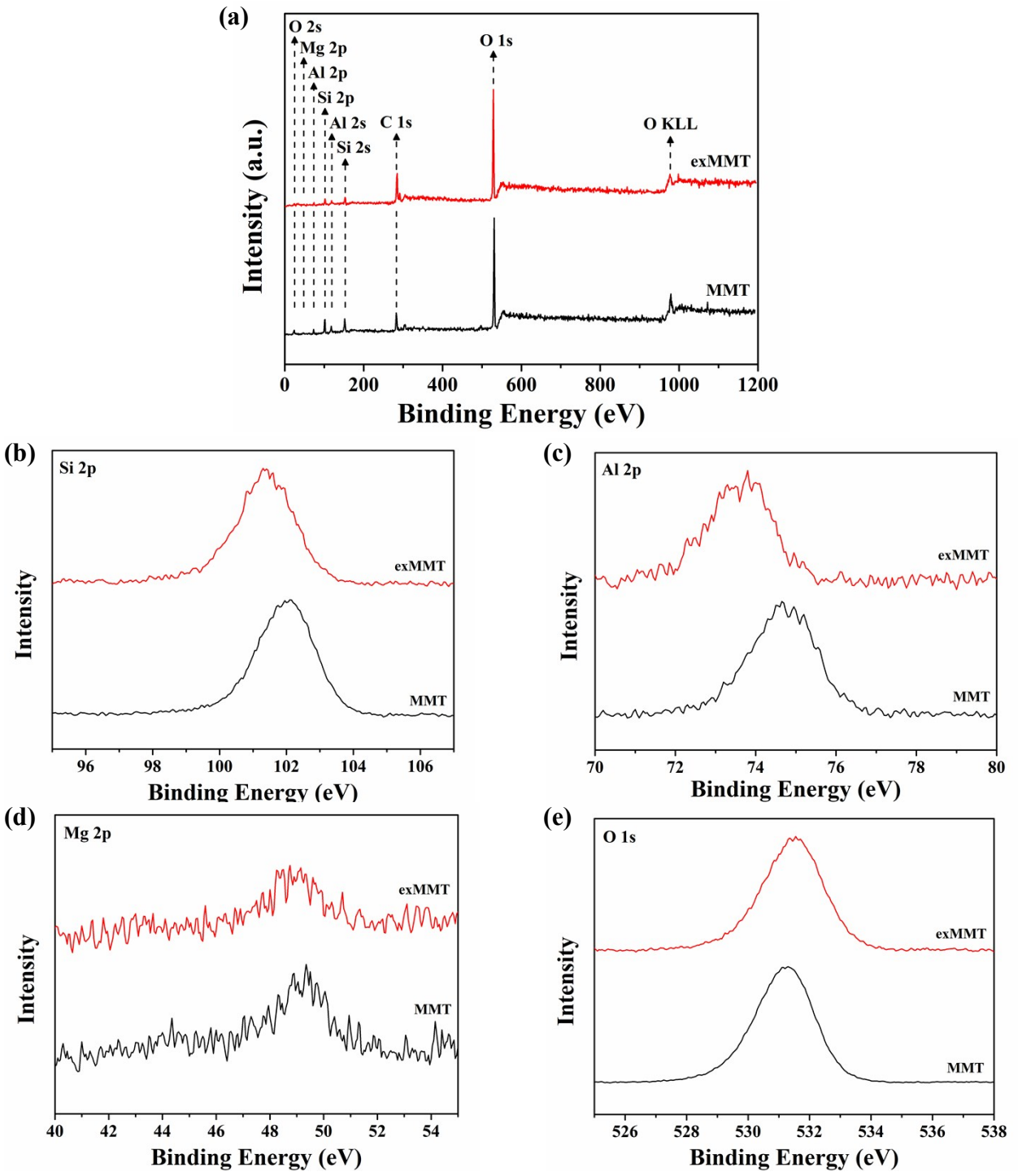

Fig. S5 XPS evidence of MMT exfoliation. (a) XPS spectra of MMT and exMMT, and their (b) Si 2p (c) Al 2p (d) Mg 2p (e) O 1s sectional spectra.

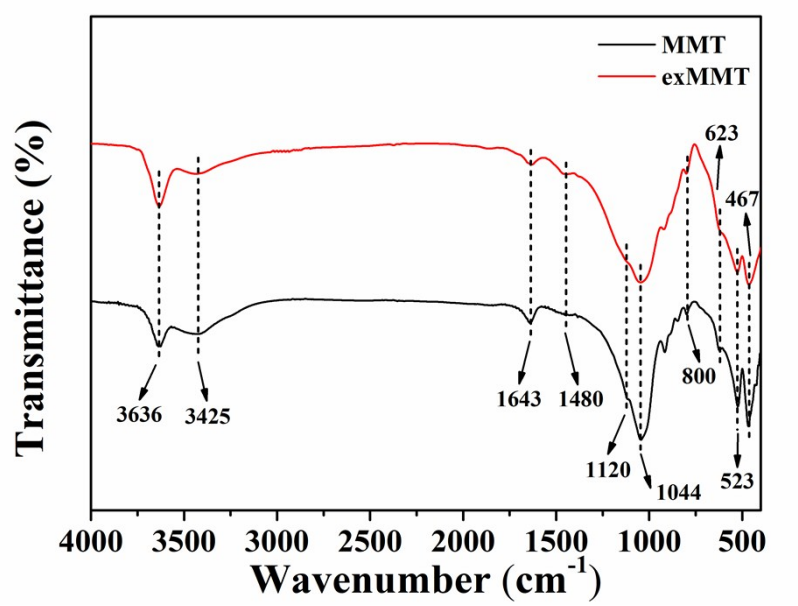

Fig. S6 IR spectroscopy evidence of MMT exfoliation. FTIR spectra of MMT and exMMT.

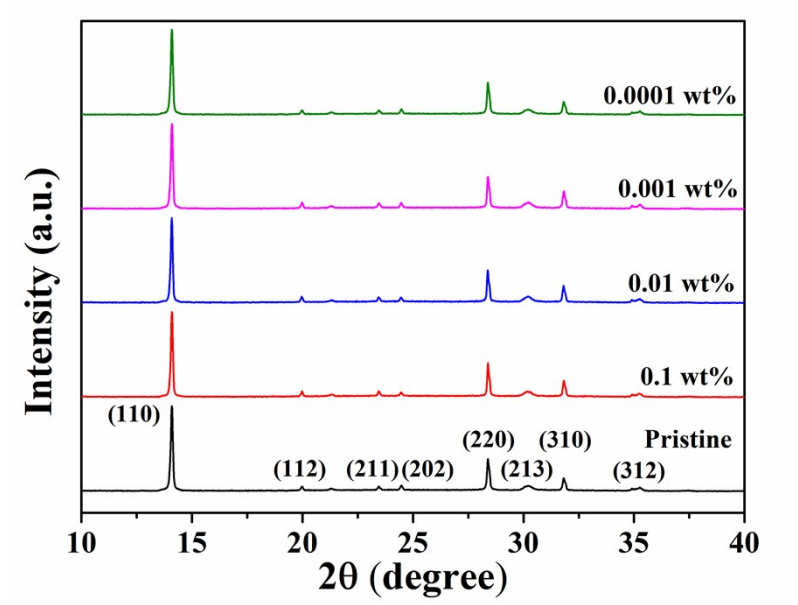

Fig. S7 Crystal structure of perovskites affected by exMMTs. XRD patterns of perovskite films incorporating various indicated amount of exMMTs.

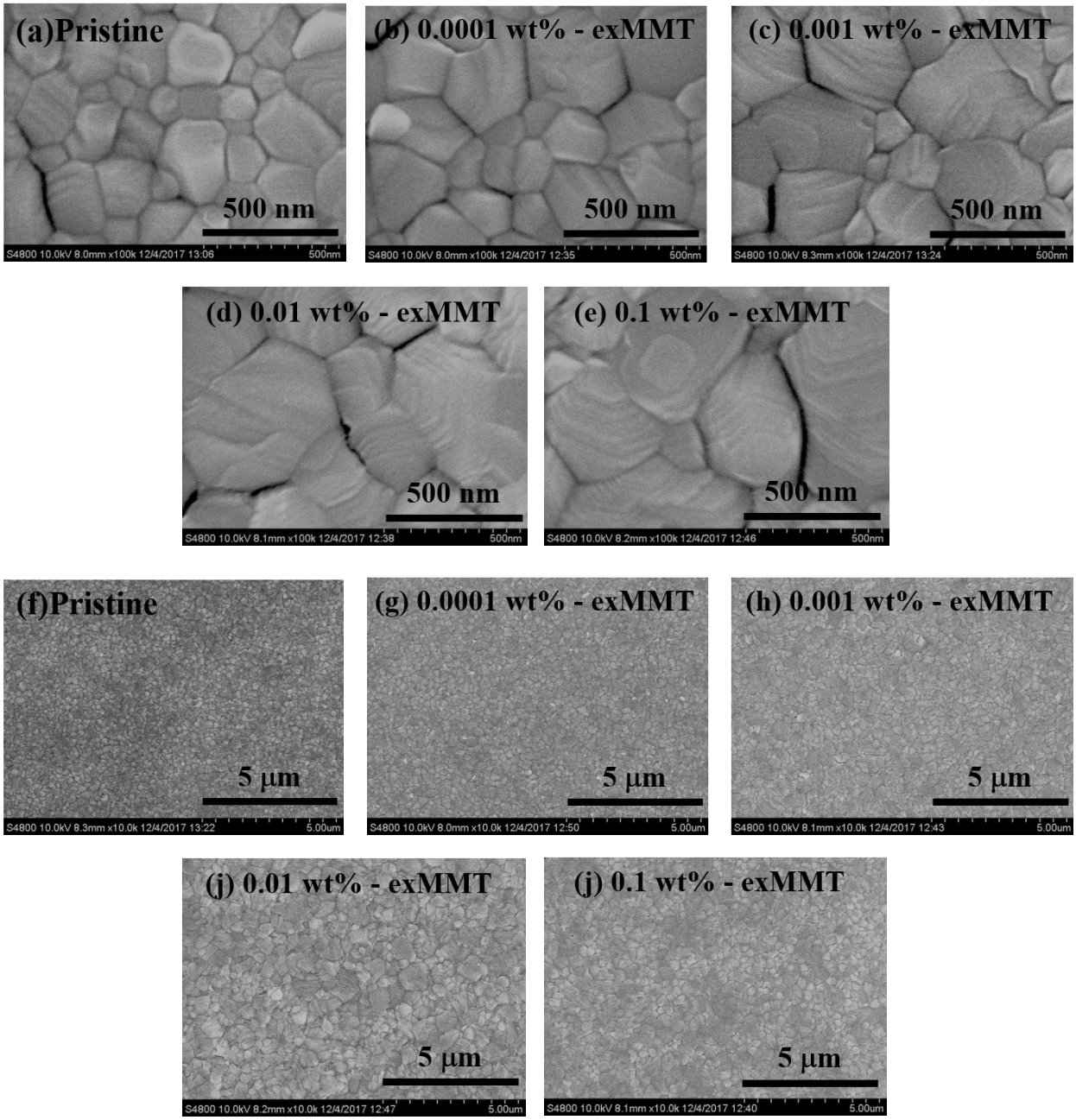

Fig. S8 Crystalline grain size of perovskite affected by exMMTs. SEM images [(a~e) ×100k, (f~j) ×10k] of perovskite films incorporating various indicated amount of exMMTs.

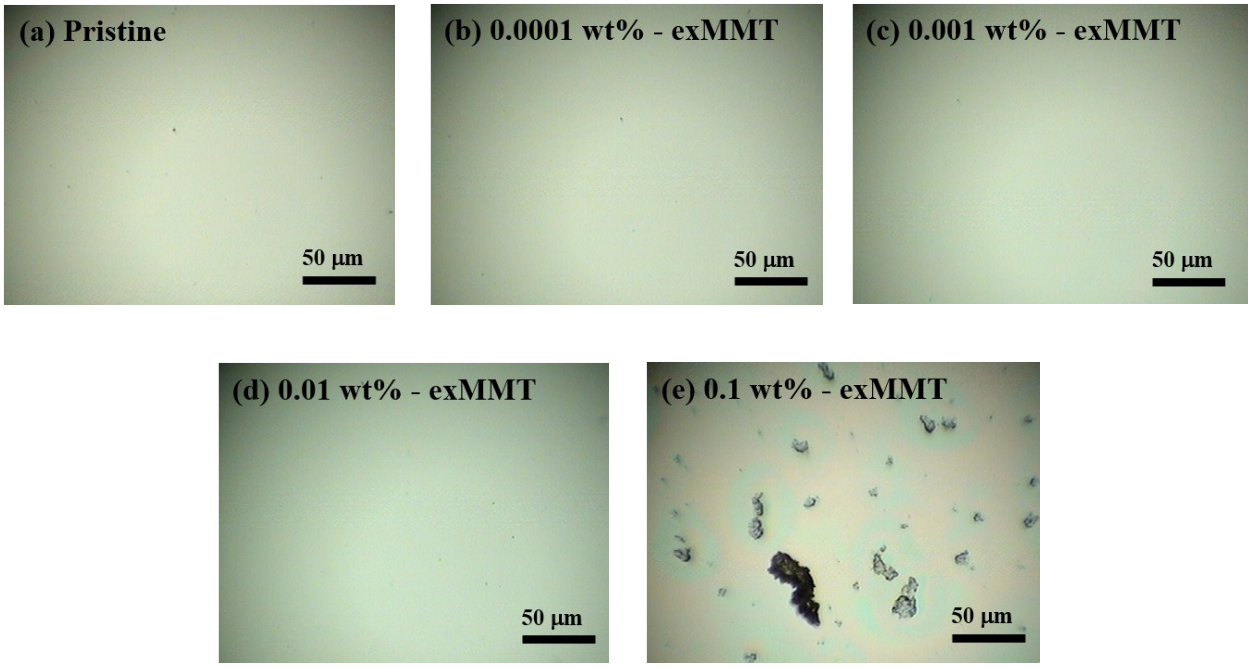

Fig. S9 Aggregation of exMMTs in perovskite. OM images of perovskite films incorporating various indicated amount of exMMTs.

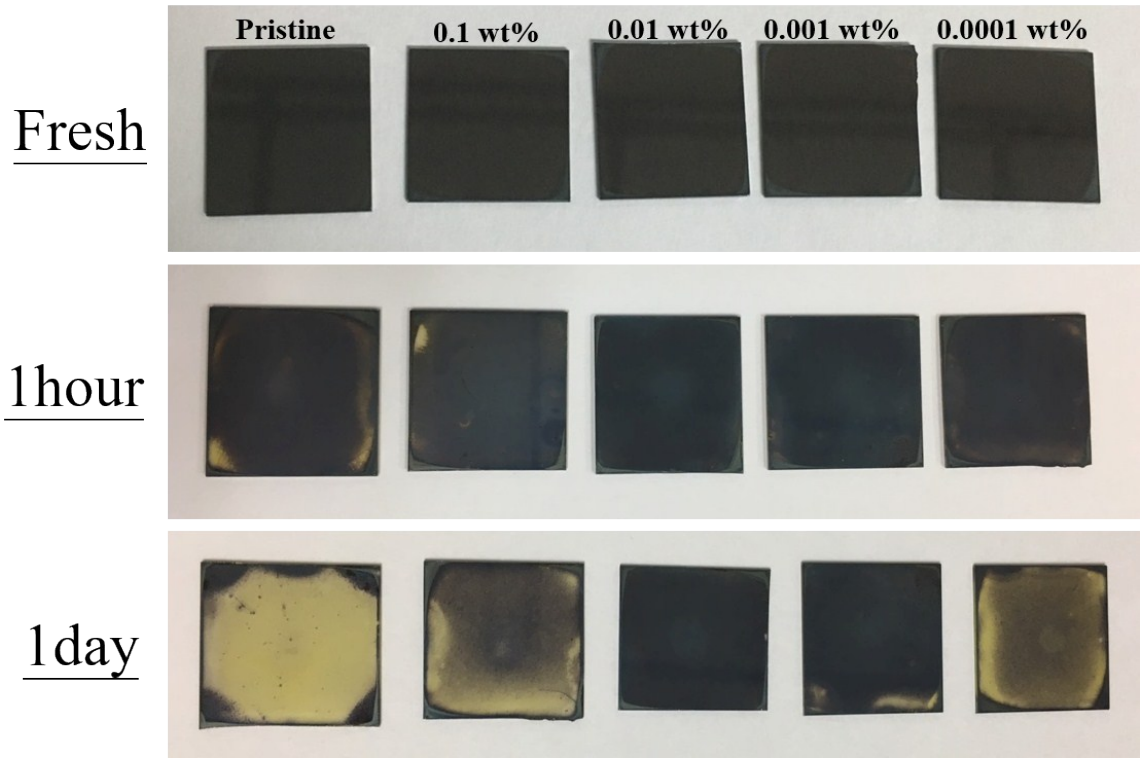

Fig. S10 Environmental stability of $MAPbI_3$ films with and without exMMT. Photos of $MAPbI_3$ films incorporating various indicated amount of exMMTs after storage in the environment of RH 70% and room temperature for 1 h and 1 day.

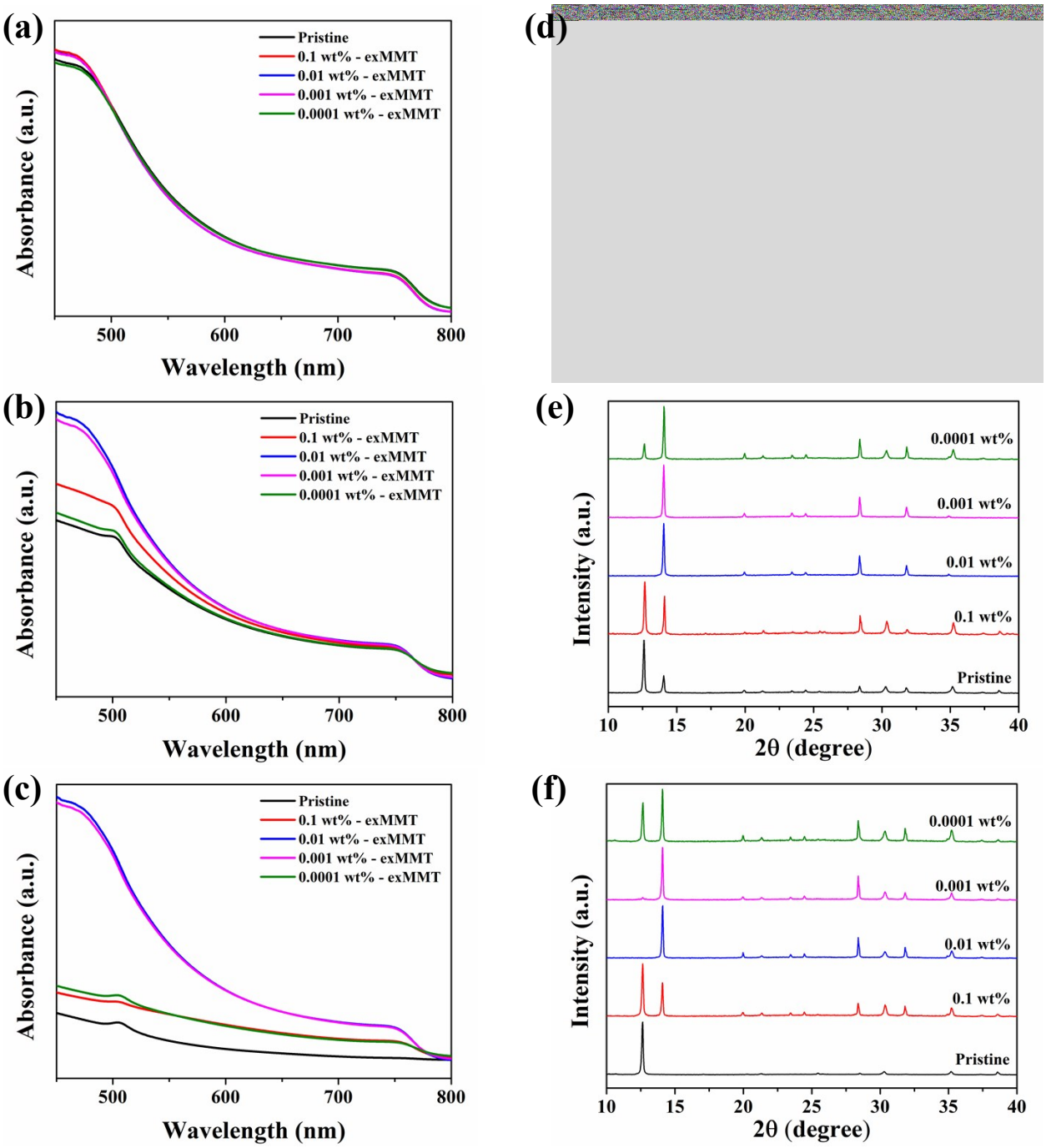

Fig. S11 Environmental stability of $MAPbI_3$ films with and without exMMT. UV−vis spectra and XRD patterns of $MAPbI_3$ films incorporating various indicated amount of exMMT after storage in the environment of RH 70% and room temperature for (a)(d) fresh, (b)(e) 1 h, and (c)(f) 1 day

Movie S1.mp4

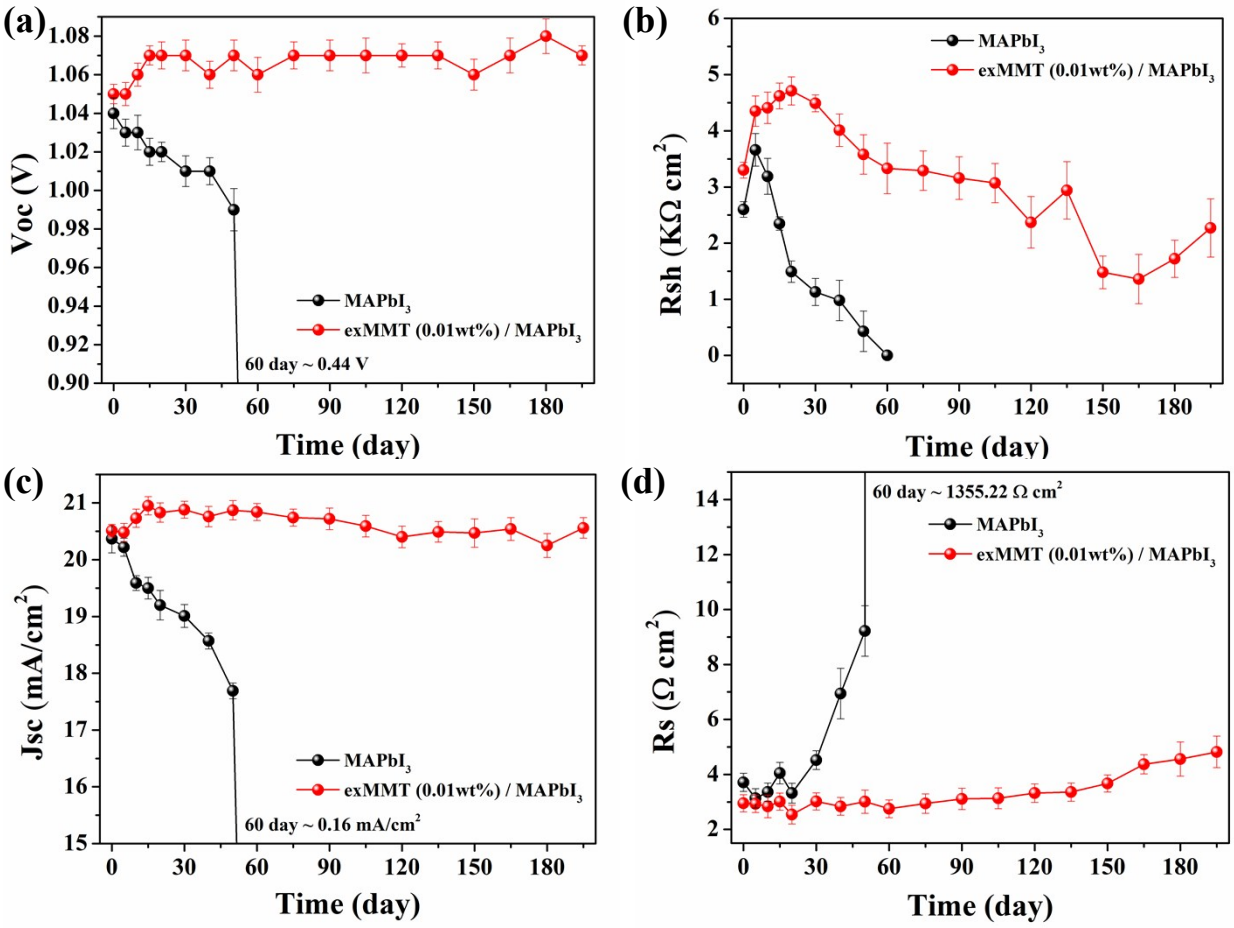

Fig. S12 Photovoltaic stability of PSCs with and without exMMT. (a) V_{OC}, (b) R_{sh}, (c) J_{SC}, and (d) R_S of the PSCs with and without incorporating 0.01 wt% exMMT as a function of storage time in the environmental condition of RH 25% for first 30 days and RH 50% for rest of the test at 25°C.

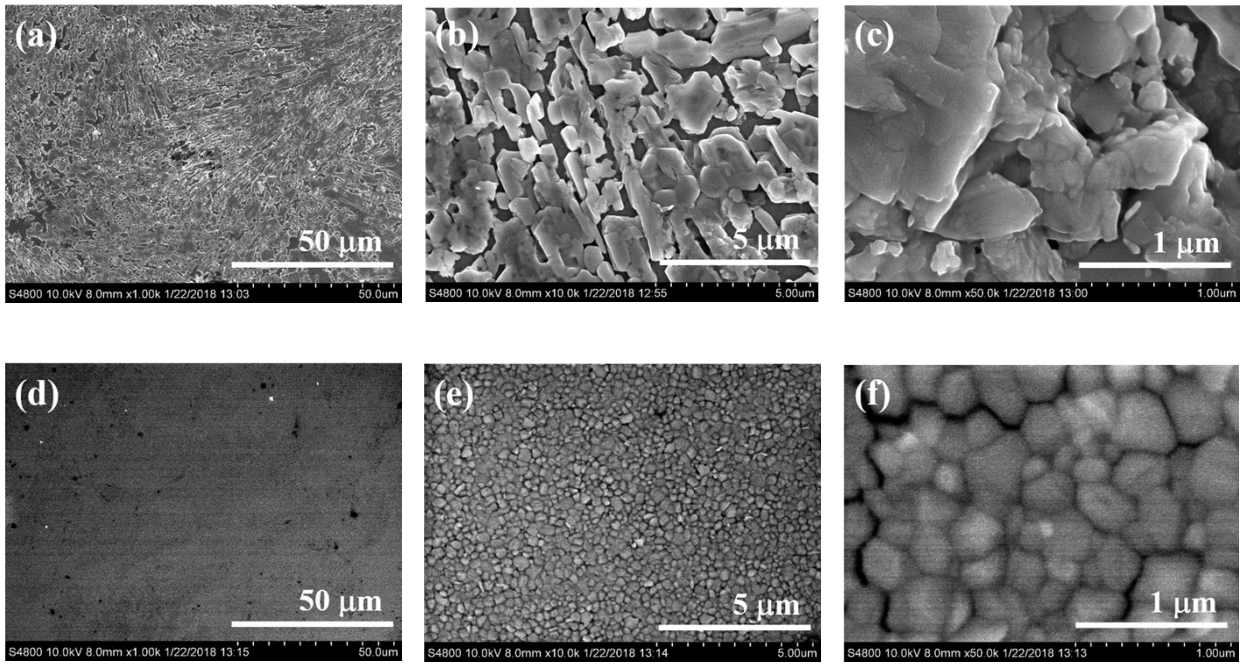

Fig. S13 Environmental stability of $MAPbI_3$ films with and without exMMT. SEM images of (a-c) $MAPbI_3$ and (d-f) exMMT (0.01 wt%) / $MAPbI_3$ films after storage for 60 days (0-30 day: 25°C, RH 25%; 30-60 day: 25°C, RH 50%).

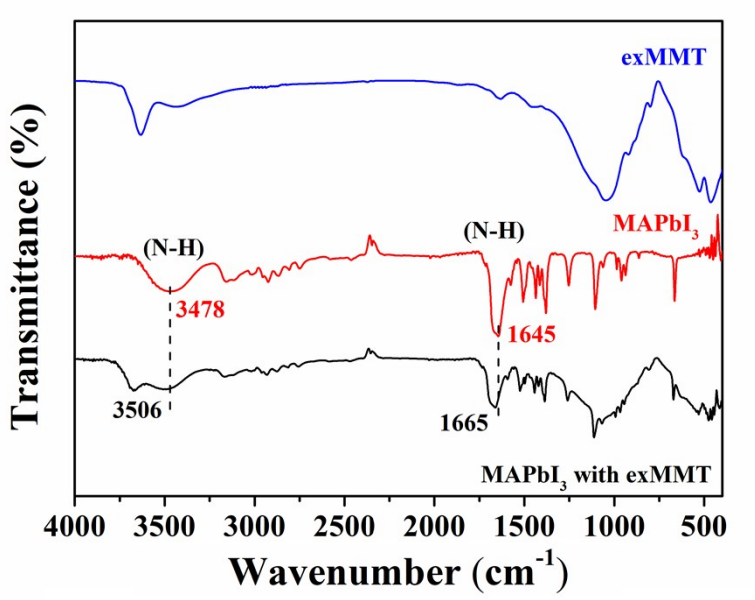

Fig. S14 IR spectroscopy evidence of $MAPbI_3$ bonding with exMMT. FTIR spectra of exMMT, $MAPbI_3$ and exMMT (1 wt%) / $MAPbI_3$ films on KBr substrate.

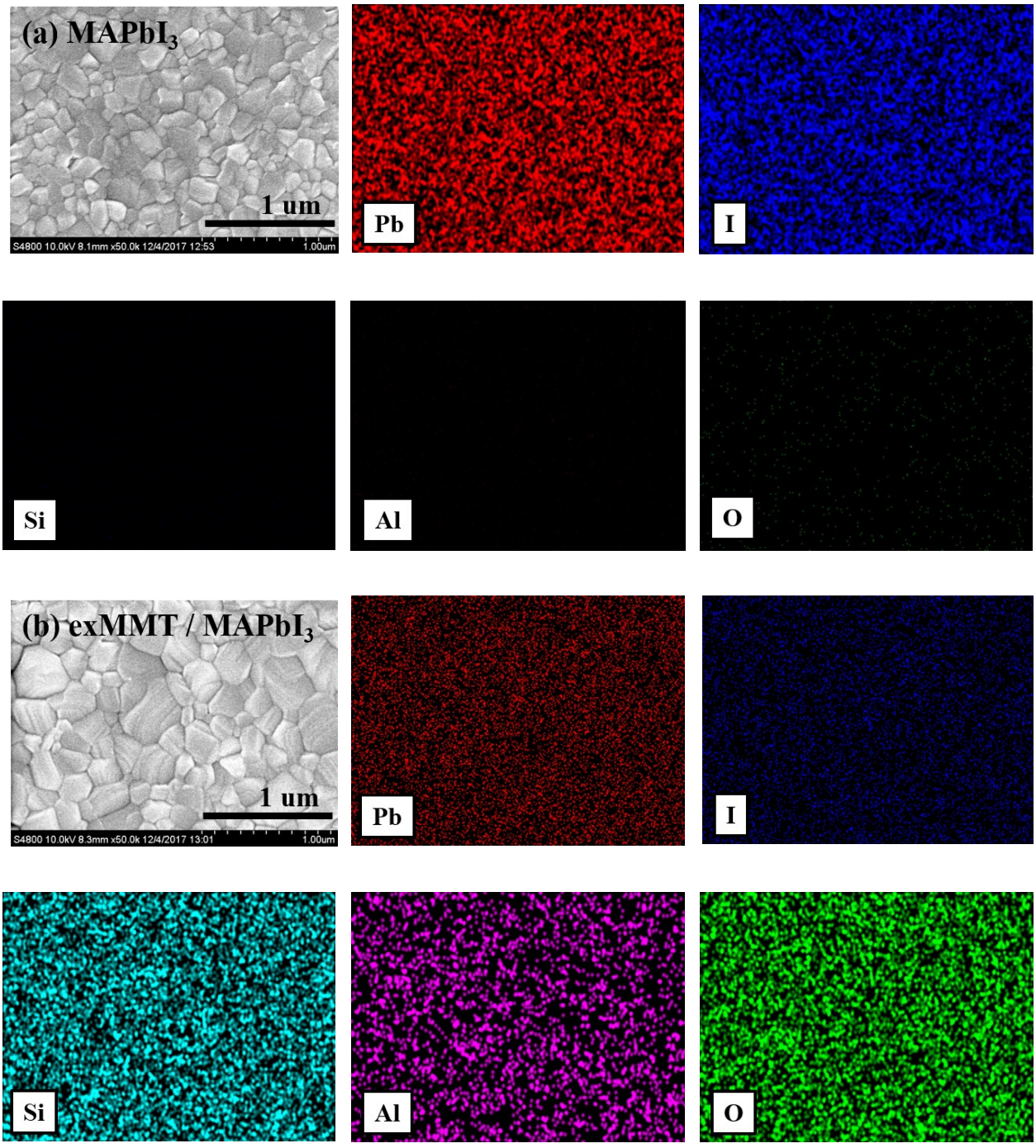

Fig. S15 Evidence of exMMTs on the surface of exMMT (0.01 wt%)/$MAPbI_3$. SEM images and EDX mappings of Pb, I, Si, Al and O atoms for (a) $MAPbI_3$ and (b) exMMT (0.01 wt%) / $MAPbI_3$ films.

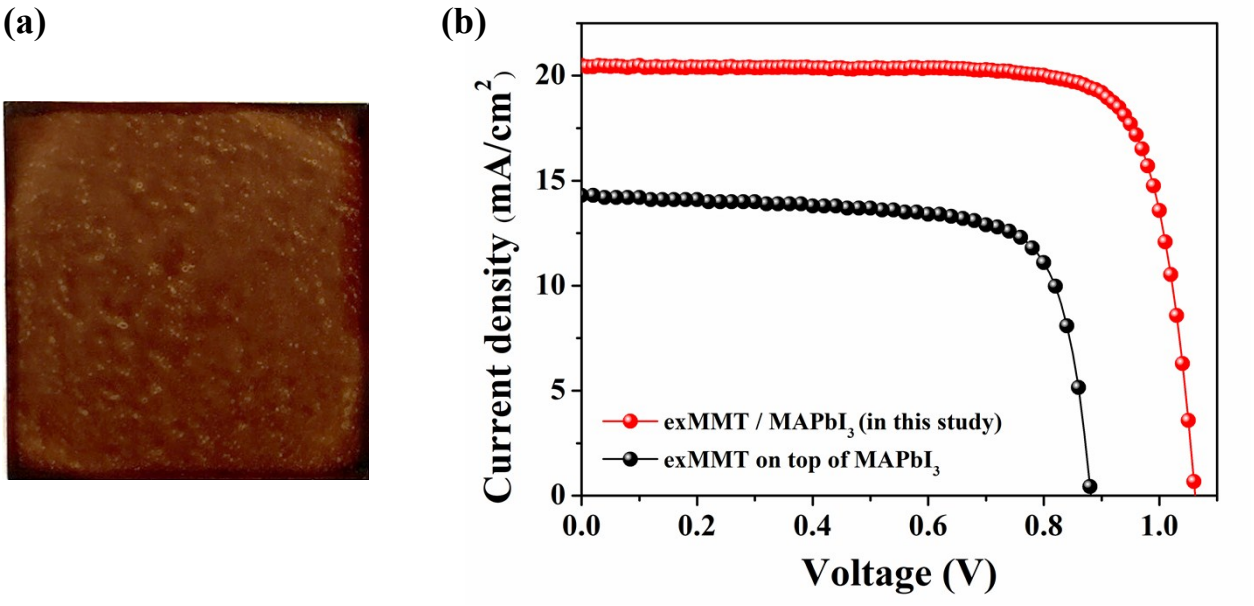

Fig. S16 Film image and photovoltaic performance of $MAPbI_3$ deposited with spin-coated exMMT. (a) Photo of the $MAPbI_3$ deposited with 0.01 wt% exMMT layer by spin coating and (b) *J-V* curve of PSC with 0.01 wt% exMMT layer spin-coated on top of $MAPbI_3$ compared to that with exMMT (0.01 wt%) / $MAPbI_3$ employed in this study.

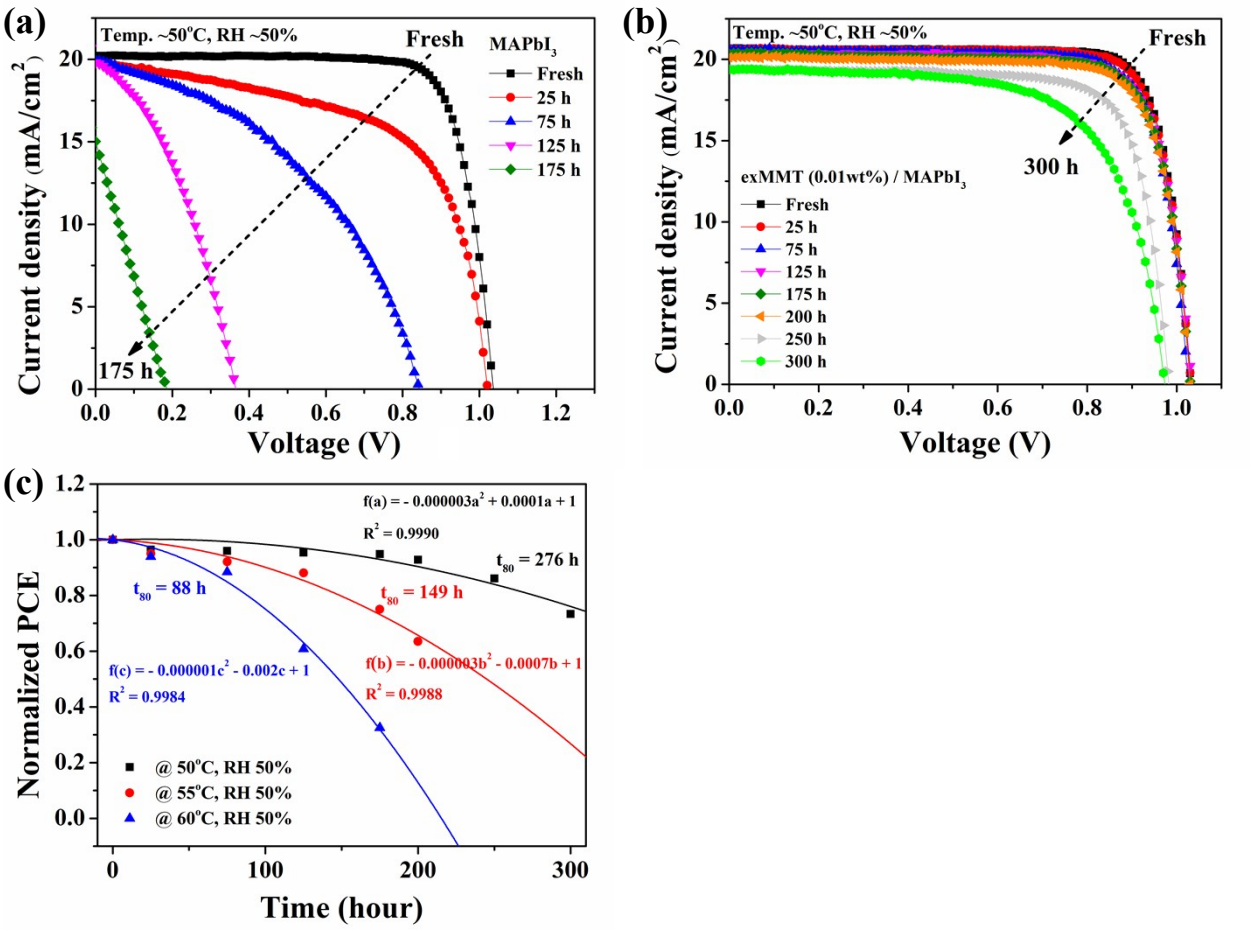

Fig. S17 Damp-heat tests of PSCs. *J-V* curves of PSCs with (a) $MAPbI_3$ and (b) exMMT (0.01 wt%) / $MAPbI_3$ after storage for different indicated time at 50°C and RH 50%. (c) Normalized PCEs of PSCs with exMMT (0.01 wt%) / $MAPbI_3$ versus storage time in the environmental conditions of RH 50% at different indicated temperature.

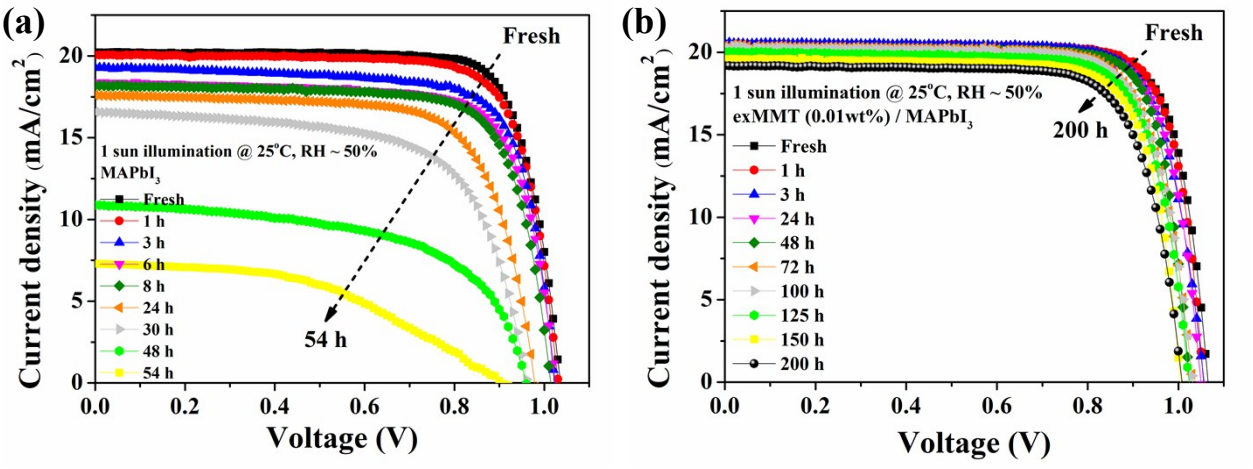

Fig. S18 Light-soaking aging tests of PSCs. *J-V* curves of PSCs with (a) $MAPbI_3$ and (b) exMMT (0.01 wt%) / $MAPbI_3$ under constant illumination of full sunlight for different indicated time at 25°C and RH ~50%.

Reference

1. P. Praus, M. Motakova and M. Ritz, *Acta Geodyn. Geomater.,* 2012, **9**, 63-70.

2. K. L. Lin, T. H. Weng, C. H. Lee and K. F. Lin, *J. Polym. Sci. A,* 2009, **47**, 5891-5897.