

Supporting Information

Bioinspired ultra-thin polyurethane/MXene nacre-like nanocomposite films with synergistic mechanical properties for electromagnetic interference shielding

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Calculation of electromagnetic interference shielding test results.

Scattering parameters what contained S_{11} , S_{12} , S_{22} , and S_{21} were output by vector network analyzer directly. Reflection (R), transmission (T) and absorption(A) coefficients could be calculated by following formulations:^{1,2}

$$R = |S_{11}|^2 = |S_{22}|^2$$

$$T = |S_{12}|^2 = |S_{21}|^2$$

$$R + T + A = 1$$

At the meanwhile, the effective absorbance (A_{eff}) could be indicated as:

$$A_{eff} = \frac{1 - R - T}{1 - R}$$

The electromagnetic interference shielding effectiveness (EMI SE) consists of reflection (SE_R), absorption (SE_A) and multiple internal reflections shielding effectiveness (SE_M), which could be expressed as:^{3,4}

$$SE_R = 10 \log \left(\frac{1}{1 - R} \right) = 10 \log \left(\frac{1}{1 - |S_{11}|^2} \right)$$

$$SE_A = 10 \log \left(\frac{1}{1 - A_{eff}} \right) = 10 \log \left(\frac{1 - R}{T} \right) = 10 \log \left(\frac{1 - |S_{11}|^2}{|S_{21}|^2} \right)$$

$$SE_T = SE_R + SE_A + SE_M$$

Where SE_T is the total shielding effectiveness. SE_M is usually merged in SE_A for multilayer electromagnetic interference shielding materials due to multiple internal reflections is usually absorbed or dissipated in internal of materials.⁵ Hence, SE_T can be written as:

$$SE_T = SE_R + SE_A$$

In order to objectively evaluate the EMI SE of the material. Specific shielding effectiveness (SSE) and thickness specific shielding effectiveness (SSE_t) were used for eliminating the contributions of density and thickness of material to shielding effectiveness.

$$SSE = \frac{EMI \ SE}{\rho} = dB \ cm^3 \ g^{-1}$$

$$SSE_t = \frac{SSE}{t} = dB \ cm^2 \ g^{-1}$$

Where ρ and t are density in $g \ cm^{-3}$ and thickness in cm of testing sample, respectively.

EMI shielding efficiency is calculated according to below equation:⁶

$$\text{Shielding efficiency (\%)} = 100 - \left(\frac{1}{\frac{SSE}{10^{10}}} \right) \times 100$$

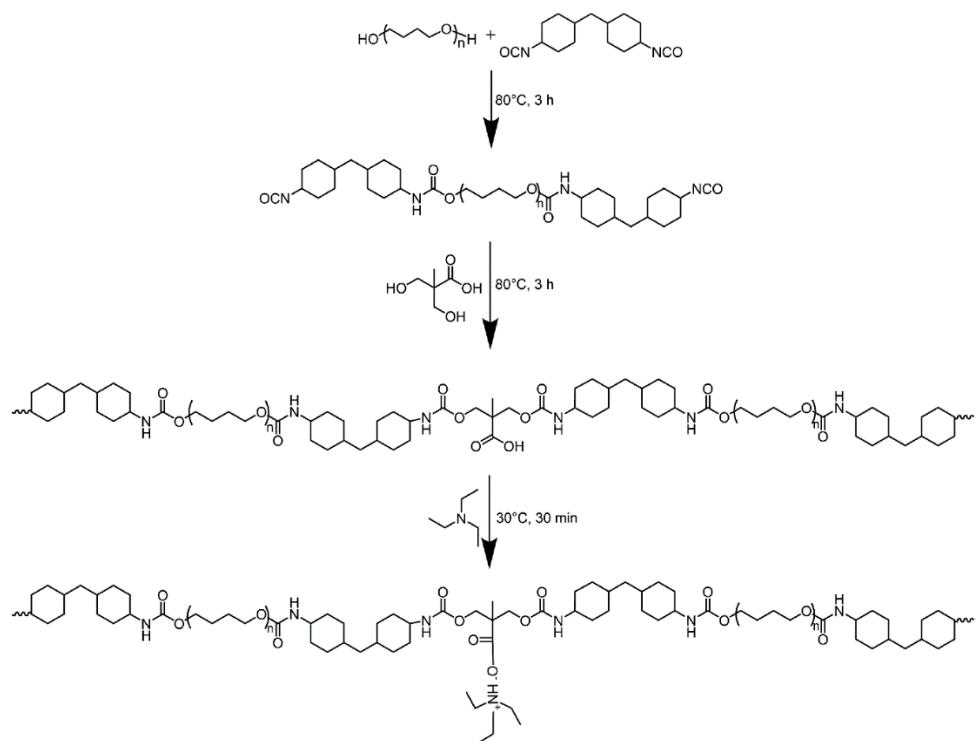


Figure S1. The synthetic route of waterborne polyurethane.

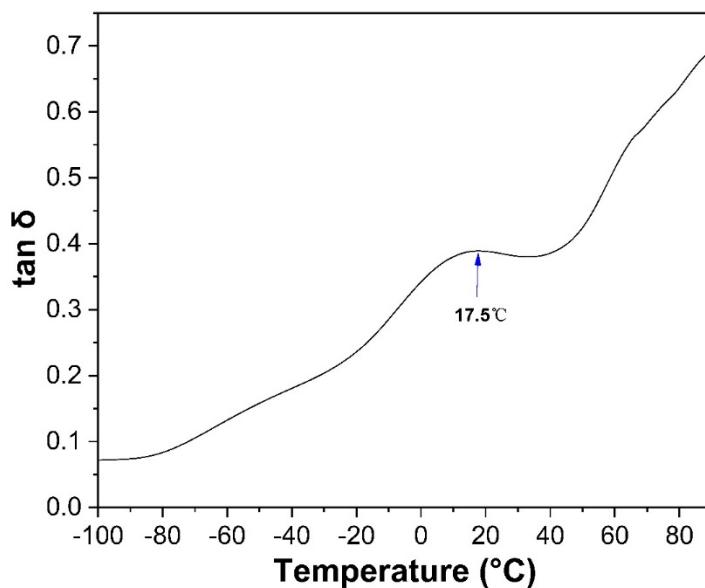


Figure S2. Temperature dependence of the tan δ of waterborne polyurethane tested by DMA.

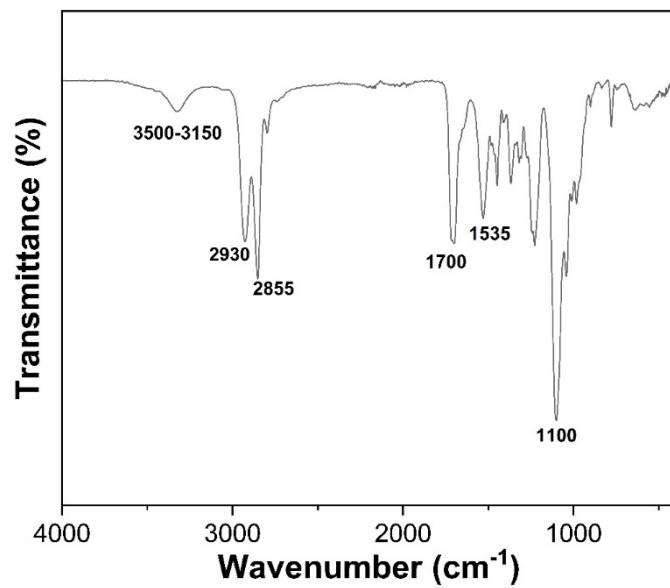


Figure S3. ATR-FTIR spectra of waterborne polyurethane.

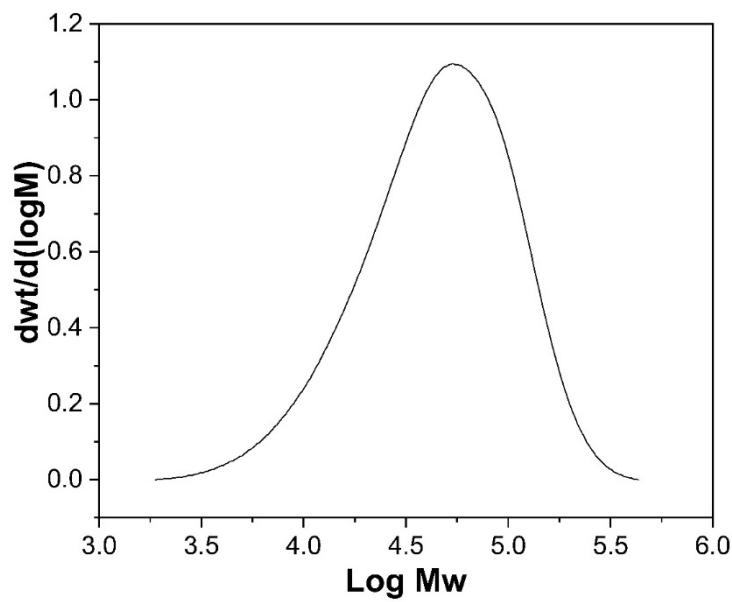


Figure S4. SEC testing curve of waterborne polyurethane with tetrahydrofuran as the eluent.

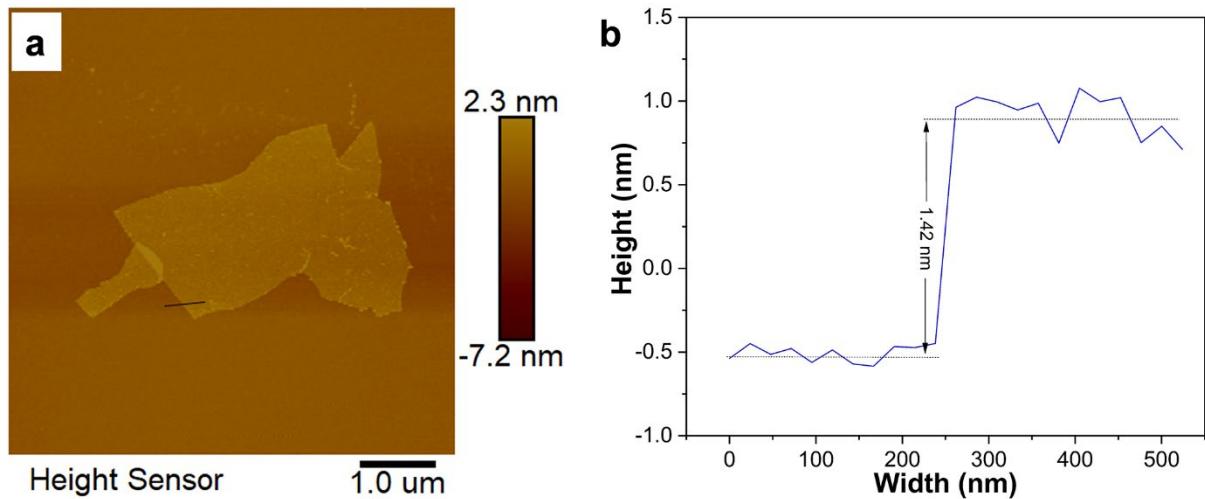


Figure S5. (a) AFM photograph and (b) the relevant height profile of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheet.

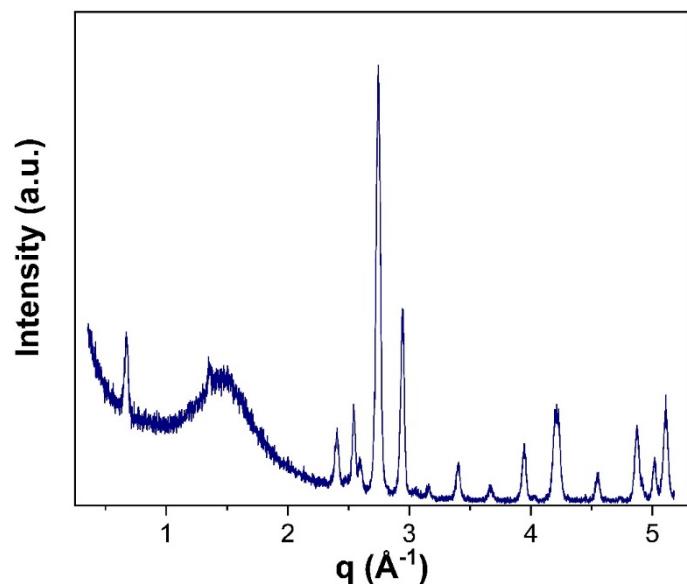


Figure S6. 1D-XRD pattern of Ti_3AlC_2 MAX phase powder.

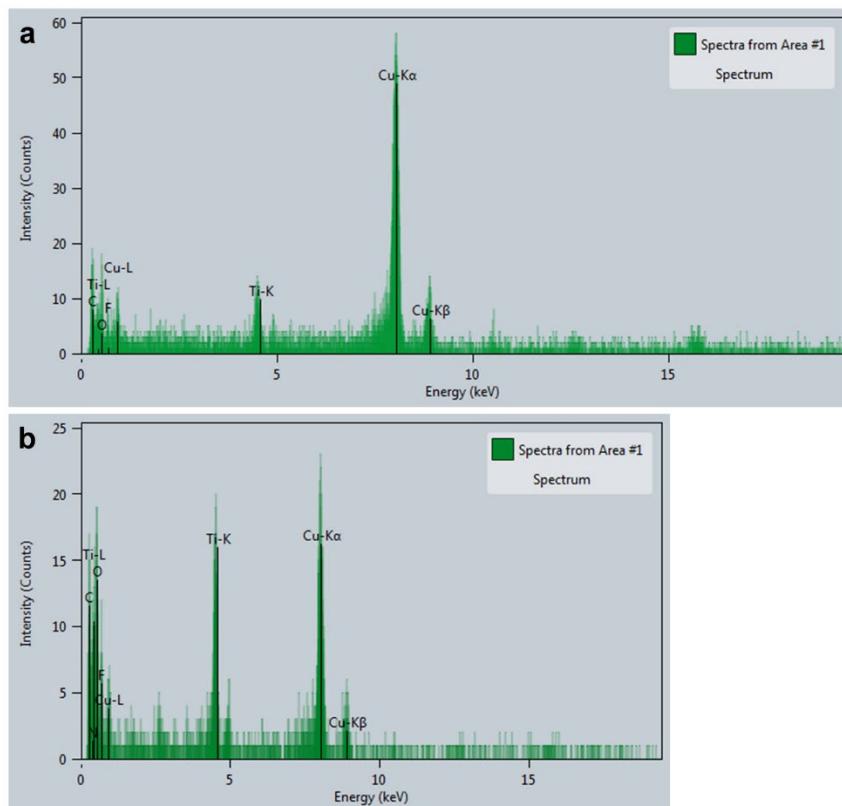


Figure S7. (a) and (b) are EDS full scale counts charts for elements of pure $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and PU/MX-20 core-shell nanosheets, respectively.

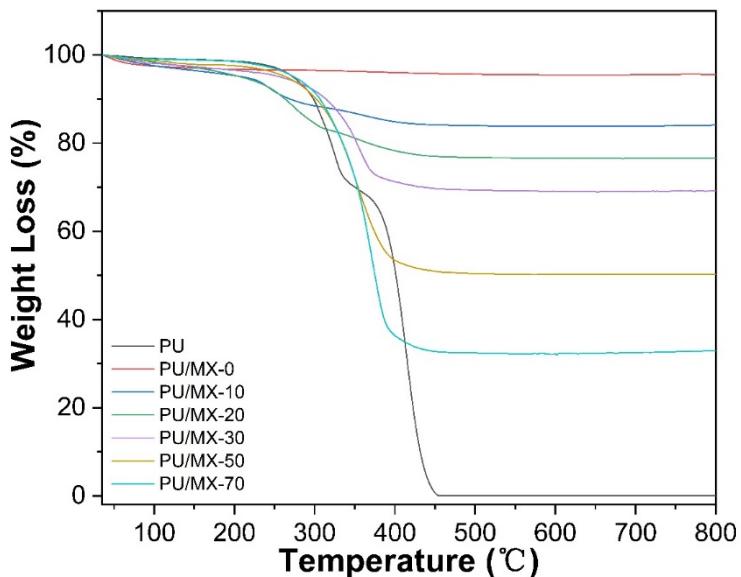


Figure S8. The TGA curves of PU and PU/MX nanocomposite films.

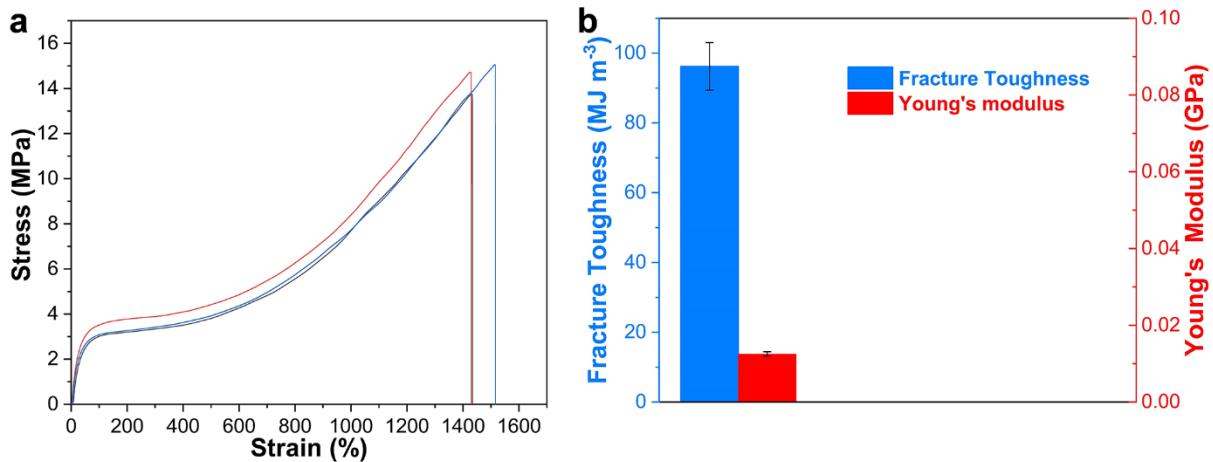


Figure S9. Mechanical properties of PU elastomer. (a) Strain-stress curves of PU elastomer, (b) the statistical results of fracture toughness and Young's modulus.

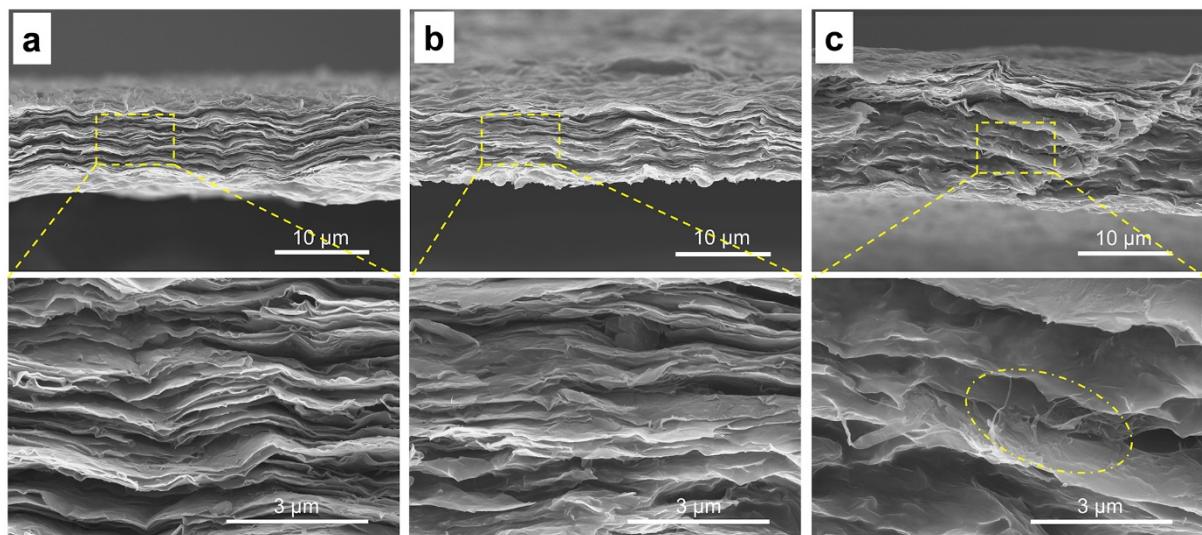


Figure S10. The SME photographs of cross-section morphology for (a) PU/MX-10, (b) PU/MX-30 and (c) PU/MX-50 films after tensile testing, respectively. The circled area in figure (c) shows polymer linkages among $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

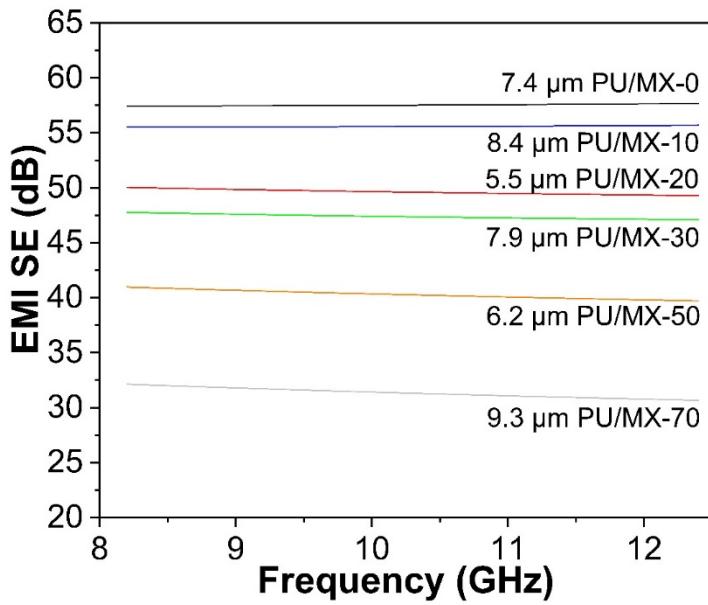


Figure S11. The theoretical total electromagnetic interference shielding effectiveness of PU/MX nanocomposite films calculated from Simon equation.

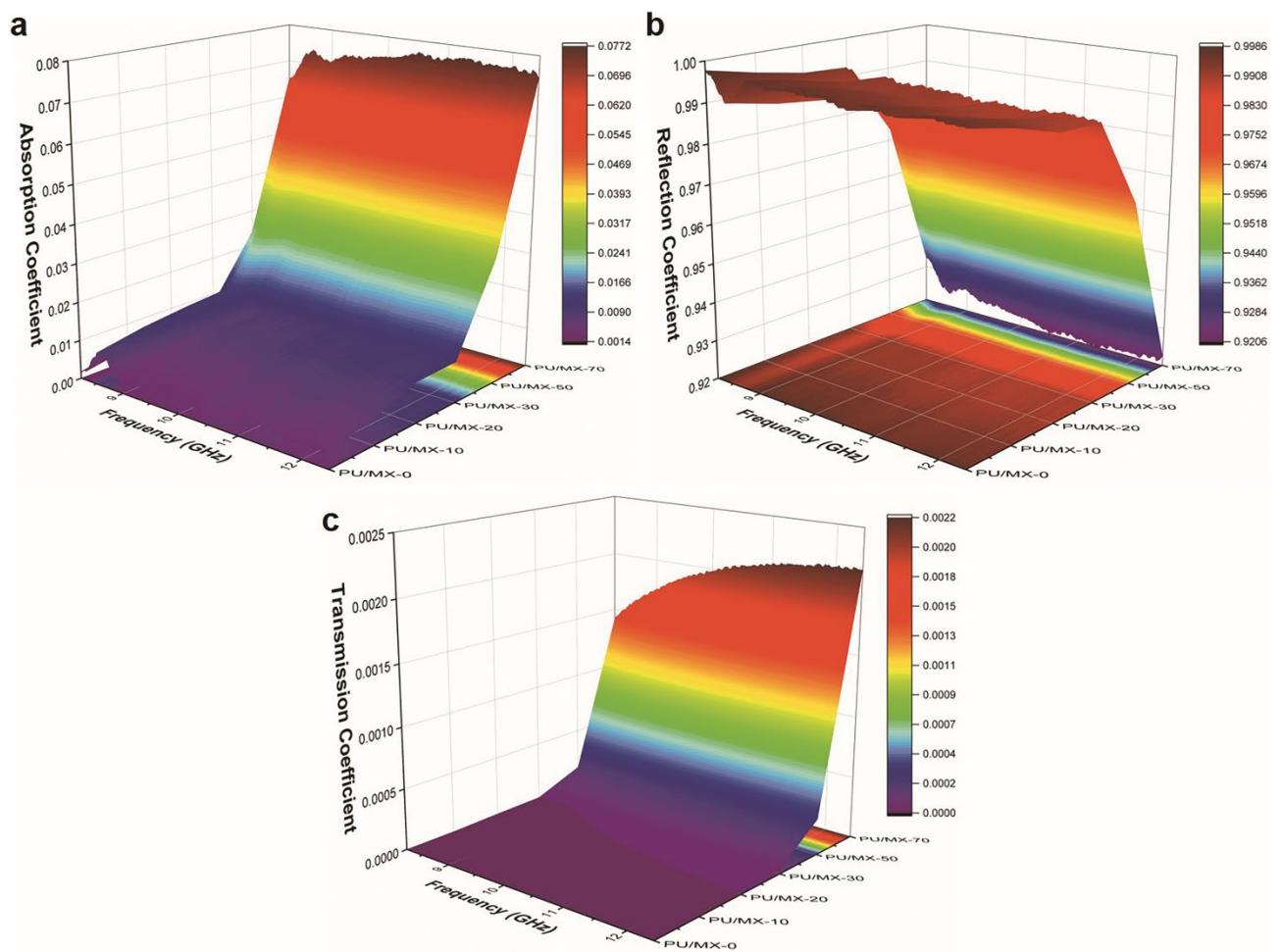


Figure S12. (a), (b) and (c) are the absorption, reflection and transmission coefficients of PU/MX nanocomposite films, respectively.

Table S1. The PU contents of PU/MX nanocomposite films determined by TGA.

Sample name	Weight loss from 100°C to 800°C (wt. %)	Theoretical content of PU (wt. %)	PU content measured by TGA (wt. %)
PU/MX-0	1.86	0	/
PU/MX-10	13.48	10	11.93
PU/MX-20	21.82	20	20.51
PU/MX-30	28.94	30	27.82
PU/MX-50	48.47	50	47.89
PU/MX-70	66.06	70	65.97
PU	99.19	100	/

The PU contents of PU/MX nanocomposites are calculated by following equation:

$$PU\ content = \frac{M_{PU|MX-X} - M_{Ti_3C_2T_x}}{M_{PU} - M_{Ti_3C_2T_x}} \times 100\%$$

Where $M_{PU/MX-X}$, M_{PU} and $M_{Ti_3C_2T_x}$ are the weight loss of polyurethane/Ti₃C₂T_x nanocomposites, PU and Ti₃C₂T_x MXene film, respectively.

Table S2. The detail information of interlayer diffraction spacing (d-spacing) and full width at half maximum (FWHM) for the 002 peak of Ti_3AlC_2 MAX phase and PU/MX nanocomposite films were determined by XRD.

Sample name	d-spacing (Å)	FWHM (°)
PU/MX-0	12.47	0.73
PU/MX-10	12.91	0.92
PU/MX-20	13.71	0.85
PU/MX-30	14.24	0.87
PU/MX-50	14.57	0.90
PU/MX-70	14.62	0.91
MAX Phase	9.38	0.44

Table S3. The detail mechanical results of PU/MX nanocomposite films and PU.

Sample name	Tensile Strength (MPa)	Strain-to-Failure (%)	Fracture Toughness (MJ m ⁻³)	Young's Modulus (GPa)
PU/MX-0	28.92 ± 4.24	3.46 ± 0.65	0.67 ± 0.20	2.53 ± 0.11
PU/MX-10	63.61 ± 1.51	4.05 ± 0.09	1.57 ± 0.04	5.73 ± 0.18
PU/MX-20	96.09 ± 7.69	4.4 ± 0.50	2.66 ± 0.39	7.87 ± 0.76
PU/MX-30	64.75 ± 1.59	4.25 ± 0.11	1.62 ± 0.06	4.42 ± 0.44
PU/MX-50	30.96 ± 1.14	3.8 ± 0.07	0.72 ± 0.04	2.13 ± 0.21
PU/MX-70	21.45 ± 0.55	6.84 ± 0.72	1.13 ± 0.17	1.45 ± 0.13
PU	14.51 ± 0.68	1457.04 ± 49.33	96.21 ± 6.81	0.0125 ± 0.0006

Table S4. The density and electrical conductivity of PU/MX nanocomposite films.

Sample	Density (g cm ⁻³)	Electrical Conductivity (S cm ⁻¹)
PU/MX-0	4.02	5983.5 ± 203.6
PU/MX-10	2.99	4236.7 ± 185.9
PU/MX-20	2.66	2897.4 ± 165.7
PU/MX-30	2.42	1599.6 ± 47.8
PU/MX-50	2.15	598.5 ± 15.0
PU/MX-70	1.63	96.8 ± 2.5

Table S5. The EMI shielding efficiency (%) of PU/MX nanocomposite films.

Sample	EMI Shielding Efficiency (%)
PU/MX-0	99.999 928
PU/MX-10	99.999 795
PU/MX-20	99.998 842
PU/MX-30	99.998 193
PU/MX-50	99.983 693
PU/MX-70	99.857 886

Table S6. The comparison of the thickness specific shielding effectiveness of PU/MX nanocomposite films and other previous EMI shielding composites.

No.	Sample	Filler	Filler	Thickness	SE	SSE _t	Ref.
			Content	(cm)	(dB)	(dB cm ² g ⁻¹)	
1	MXene-SA	Ti ₃ C ₂ T _x	90 wt %	0.0008	57	30830	5
2	Ti₃C₂T_x/CNF	Ti ₃ C ₂ T _x	90 wt %	0.0047	24	2647	7
	Ti₃C₂T_x/PEDOT:						
3		Ti ₃ C ₂ T _x	87.5 wt %	0.0011	42.1	19497.8	8
	PSS						
4	Ti₂CT_x/PVA	Ti ₂ CT _x	0.15 vol %	0.5	28	5136	9
	3D rGO-MXene		rGO/	60.4 wt %/			
5		Ti ₃ C ₂ T _x	39.6 wt %	0.32	/	~14299.2	10
	foam						
6	Ti₃C₂T_x/SA	Ti ₃ C ₂ T _x	90 wt %	0.0014	43.9	14830	11
7	Ti₃C₂T_x/CA	Ti ₃ C ₂ T _x	90 wt %	0.0026	54.3	17586	11
8	CNF5@MXene4	Ti ₃ C ₂ T _x	50 wt %	0.0035	39.6	7029	12
9	CSA-M0.6-T20mg	Ti ₃ C ₂ T _x	28.57 wt %	0.00384	50.01	11354.35	13
	MWCNT/WPU						
10		MWCNT	76.2 wt %	0.1	21.1	5410	14
	foam						
11	MWCNT/WPU	MWCNT	61.5 wt %	0.005	20.45	3408	15
			70 wt %/				
12	MWCNT/SWCNT	/	30 wt %	0.013	65	5910	16
13	P(St-BA)/S-GNS	Graphene	25 wt %	0.005	21.5	10652	17
	Graphene/						
14		Graphene	99 wt %	0.15	69.1	20827	18
	PEDOT: PSS						

15	rGO/PI	rGO	16 wt %	0.08	21	937.5	19
Cotton-derived carbon network							
16		/	/	0.03	46.9	26055	20
17	GF/CNT/PDMS	Graphene /CNT	2.7 wt %/2 wt %	0.16	75	5206	21
18	Graphene/PDMS	Graphene	0.8 wt %	0.1	30	5000	22
19	PU/MX-0	Ti ₃ C ₂ T _x	100 wt %	0.00074	61.4	20641.93	
20	PU/MX-10	Ti ₃ C ₂ T _x	90 wt %	0.00084	56.9	22610.65	
21	PU/MX-20	Ti ₃ C ₂ T _x	80 wt %	0.00055	49.4	33771.92	This work
22	PU/MX-30	Ti ₃ C ₂ T _x	70 wt %	0.00079	47.4	24781.33	
23	PU/MX-50	Ti ₃ C ₂ T _x	50 wt %	0.00062	37.9	28427.74	
24	PU/MX-70	Ti ₃ C ₂ T _x	30 wt %	0.00093	28.5	18756.17	

Table S7. The comparison of mechanical properties of PU/MX nanocomposite films and other reported EMI shielding materials.

No.	Sample Name	Tensile	Fracture Toughness	Ref.
		Strength (MPa)	(MJ m ⁻³)	
1	Ti₃C₂T_x/CNF	44.2	1.2	7
2	Ti₃C₂T_x/PEDOT: PSS	13.71	~0.021	8
3	CNF5@MXene4	112.5	2.7	12
4	CSA-M0.6-T20mg	84.4	~7.7	13
5	MXene foam	~4	~0.0105	23
6	MXene-CNT	25	~0.0625	6
7	MWCNT/WPU	2.6	~0.175	15
8	CNT-NR	16.2	0.068	24
9	MWCNT/SWCNT	17.4	~0.243	16
10	MWCNT/PC	15	~0.0018	25
11	RGO/PVA	62.4	~1.8	26
12	MG/PVA	55.2	~2.4	26
13	rGO coated Fe₃O₄@SiO₂@polypyrrole	1.22	~0.05	27
14	Ag-NW/PANI	44	~0.33	28
15	CF/PAM/wood fiber	39.52	~0.07	29
16	CNF-coated CF paper	13.4	~0.224	30
17	PU/MX-0	32.18	0.78	This work
18	PU/MX-10	65.18	1.64	

19	PU/MX-20	101.58	3.21	
20	PU/MX-30	66.94	1.69	This
21	PU/MX-50	32.15	0.78	work
22	PU/MX-70	22.05	1.32	

References

1. S. T. Hsiao, C. C. M. Ma, W. H. Liao, Y. S. Wang, S. M. Li, Y. C. Huang, R. B. Yang and W. F. Liang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10667-10678.
2. X. Li, X. Yin, S. Liang, M. Li, L. Cheng and L. Zhang, *Carbon*, 2019, **146**, 210-217.
3. Z. Li, Z. Wang, W. Lu and B. Hou, *Metals*, 2018, **8**, 652.
4. H. B. Zhang, Q. Yan, W. G. Zheng, Z. He and Z. Z. Yu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 918-924.
5. F. Shahzad, M. Alhabeb, C. B. Hatter, B. Anasori, S. Man Hong, C. M. Koo and Y. Gogotsi, *Science*, 2016, **353**, 1137-1140.
6. G. M. Weng, J. Li, M. Alhabeb, C. Karpovich, H. Wang, J. Lipton, K. Maleski, J. Kong, E. Shaulsky, M. Elimelech, Y. Gogotsi and A. D. Taylor, *Adv. Funct. Mater.*, 2018, **28**, 1803360.
7. W. T. Cao, F. F. Chen, Y. J. Zhu, Y. G. Zhang, Y. Y. Jiang, M. G. Ma and F. Chen, *ACS Nano*, 2018, **12**, 4583-4593.
8. R. Liu, M. Miao, Y. Li, J. Zhang, S. Cao and X. Feng, *ACS Appl. Mater. Interfaces*, 2018, **10**, 44787-44795.
9. H. Xu, X. Yin, X. Li, M. Li, S. Liang, L. Zhang and L. Cheng, *ACS Appl. Mater. Interfaces*, 2019, **11**, 10198-10207.
10. X. Li, X. Yin, C. Song, M. Han, H. Xu, W. Duan, L. Cheng and L. Zhang, *Adv. Funct. Mater.*, 2018, **28**, 1803938.
11. Z. Zhou, J. Liu, X. Zhang, D. Tian, Z. Zhan and C. Lu, *Adv. Mater. Interfaces* 2019, **6**, 1802040.
12. B. Zhou, Z. Zhang, Y. Li, G. Han, Y. Feng, B. Wang, D. Zhang, J. Ma and C. Liu, *ACS Appl. Mater. Interfaces*, 2020, **12**, 4895-4905.
13. Y. Zhang, W. Cheng, W. Tian, J. Lu, L. Song, K. M. Liew, B. Wang and Y. Hu, *ACS Appl. Mater. Interfaces*, 2020, **12**, 6371-6382.

14. Z. Zeng, H. Jin, M. Chen, W. Li, L. Zhou and Z. Zhang, *Adv. Funct. Mater.*, 2016, **26**, 303-310.
15. Z. Zeng, M. Chen, H. Jin, W. Li, X. Xue, L. Zhou, Y. Pei, H. Zhang and Z. Zhang, *Carbon*, 2016, **96**, 768-777.
16. S. Lu, J. Shao, K. Ma, D. Chen, X. Wang, L. Zhang, Q. Meng and J. Ma, *Carbon*, 2018, **136**, 387-394.
17. L. Wei, W. Zhang, J. Ma, S. L. Bai, Y. Ren, C. Liu, D. Simion and J. Qin, *Carbon*, 2019, **149**, 679-692.
18. Y. Wu, Z. Wang, X. Liu, X. Shen, Q. Zheng, Q. Xue and J. K. Kim, *ACS Appl. Mater. Interfaces*, 2017, **9**, 9059-9069.
19. Y. Li, X. Pei, B. Shen, W. Zhai, L. Zhang and W. Zheng, *RSC Advances*, 2015, **5**, 24342-24351.
20. X. Ma, Y. Li, B. Shen, L. Zhang, Z. Chen, Y. Liu, W. Zhai and W. Zheng, *ACS Appl. Mater. Interfaces*, 2018, **10**, 38255-38263.
21. X. Sun, X. Liu, X. Shen, Y. Wu, Z. Wang and J. K. Kim, *Composites Part A*, 2016, **85**, 199-206.
22. Z. Chen, C. Xu, C. Ma, W. Ren and H. M. Cheng, *Adv. Mater.*, 2013, **25**, 1296-1300.
23. J. Liu, H. B. Zhang, R. Sun, Y. Liu, Z. Liu, A. Zhou and Z. Z. Yu, *Adv. Mater.*, 2017, **29**, 1702367.
24. L. C. Jia, M. Z. Li, D. X. Yan, C. H. Cui, H. Y. Wu and Z. M. Li, *J. Mater. Chem. C* 2017, **5**, 8944-8951.
25. S. Pande, A. Chaudhary, D. Patel, B. P. Singh and R. B. Mathur, *RSC Advances*, 2014, **4**, 13839-13849.
26. B. Yuan, C. Bao, X. Qian, L. Song, Q. Tai, K. M. Liew and Y. Hu, *Carbon*, 2014, **75**, 178-189.
27. Y. Yuan, W. Yin, M. Yang, F. Xu, X. Zhao, J. Li, Q. Peng, X. He, S. Du and Y. Li, *Carbon*, 2018, **130**, 59-68.
28. F. Fang, Y. Q. Li, H. M. Xiao, N. Hu and S. Y. Fu, *J. Mater. Chem. C*, 2016, **4**, 4193-4203.
29. B. Dang, Y. Chen, N. Yang, B. Chen and Q. Sun, *Nanotechnology*, 2018, **29**, 195605.
30. S. Mondal, S. Ganguly, P. Das, P. Bhawal, T. K. Das, L. Nayak, D. Khastgir and N. C. Das, *Cellulose*, 2017, **24**, 5117-5131.