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Supporting Information

Ultra-thin, Flexible and High-strength Polypyrrole/$Ti_3C_2T_x$ Film for Wide-band Gigahertz and Terahertz Electromagnetic Interference Shielding

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The EMI shielding property was obtained using an Agilent N5232 vector network analyzer based on the waveguide method in 8.2-12.4 GHz (X-Band), 12.5-18 GHz (Ku-Band), 18-26.3 GHz (K-Band) and 26.4-40 GHz (Ka-Band) with sample sizes of 22.58×10.16, 15.79×7.89, 10.67×4.32, 7.12×3.55 mm^2, respectively.

The total EMI SE (SE_T) values were the sum of the multiple internal reflections of microwaves (SE_M), the absorption of electromagnetic energy (SE_A), and the reflection (SE_R). Reflectivity (R), absorptivity (A), and transmissivity (T) were determined based on the measured parameters (S_{11} and S_{12}):

$$EMI\ SE_T = SE_R + SE_A + SE_M \quad (1)$$

$$R = \left|S_{11}^2\right| = \left|S_{22}^2\right| \quad (2)$$

$$T = \left|S_{12}^2\right| = \left|S_{21}^2\right| \quad (3)$$

$$A = 1 - R - T \quad (4)$$

$$SE_T = -10\ logT = -20\ logS_{12} \quad (5)$$

$$SE_R = -10\ log(1 - R) \quad (6)$$

The terahertz EMI shielding property was obtained using a fiber-coupled terahertz time domain spectroscopy (THz-TDS) system in 0.2-1.6 THz with sample sizes of 10×10 mm^2 by a THz-TDS in transmission mode. The terahertz EMI SE (SE_T) and transmissivity (T) were determined based on the measured E parameters (E_s and E_i):

$$SE_T = -10\ logT = -20\ \log\frac{E_s}{E_i} \quad (7)$$

Where E_s and E_i are the amplitudes (intensities) of transmission signals for the samples and the air cavity, respectively.

Supplementary Tables and Figures

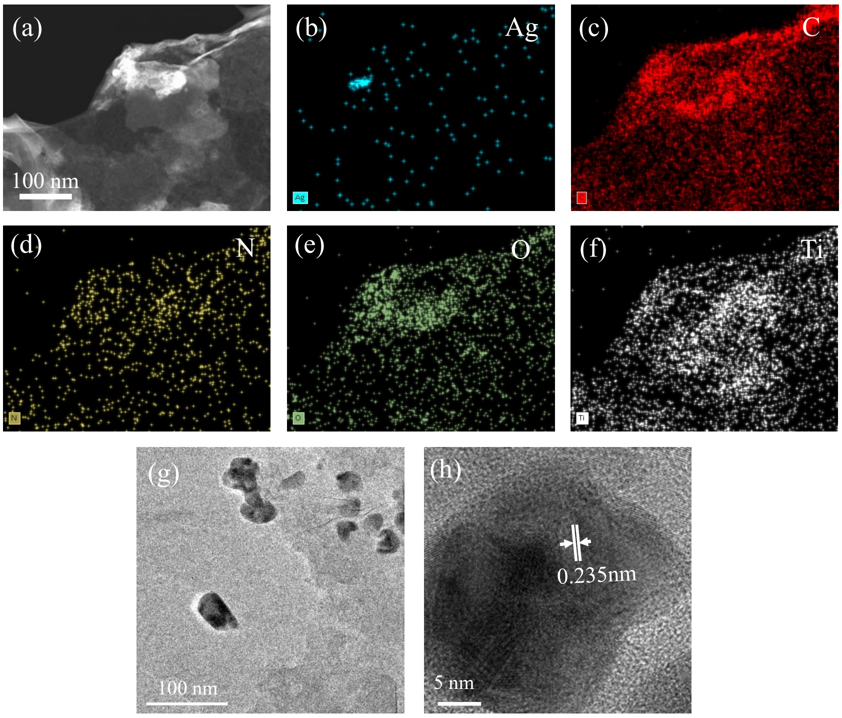

Figure S1. (a) TEM image of PPy/$Ti_3C_2T_x$ nanosheet. (b-f) Corresponding EDS mapping results. TEM (g-h) image of the nano Ag particles on the nanosheets.

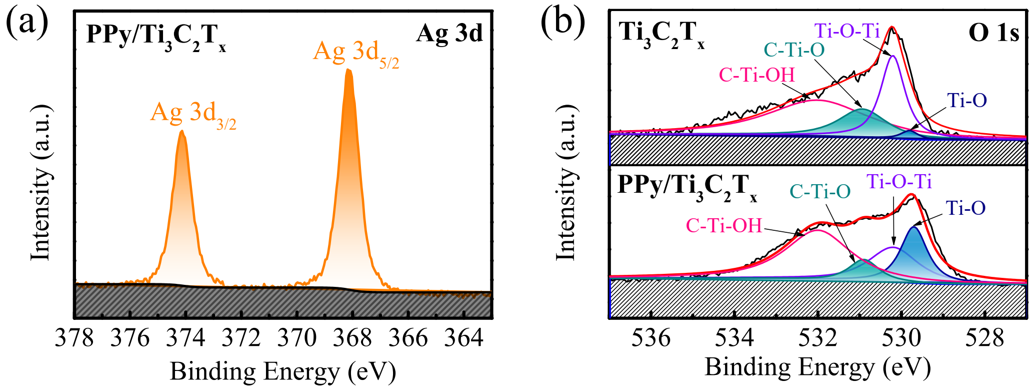

Figure S2. High-resolution XPS spectra of (a) Ag 3d and (b) O 1s for pristine $Ti_3C_2T_x$ film and PPy/$Ti_3C_2T_x$ film.

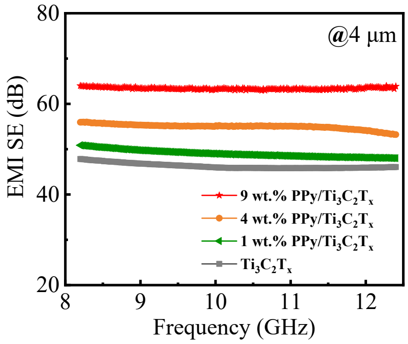

Figure S3. Total EMI SE of PPy/$Ti_3C_2T_x$ films with different PPy content in the frequency range of 8.2–12.4 GHz.

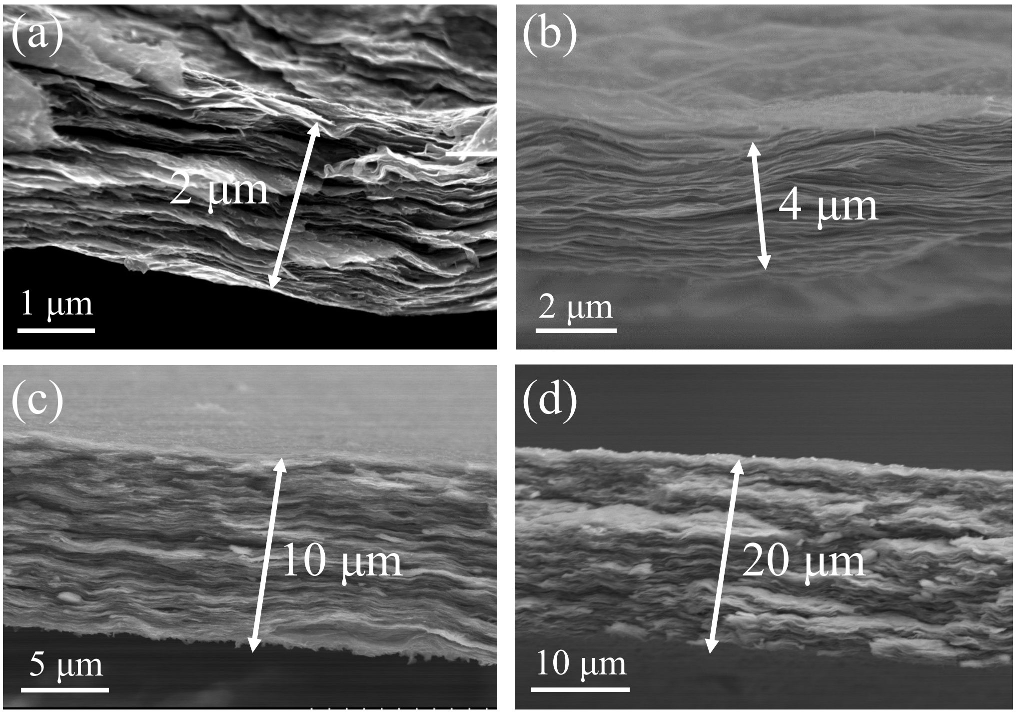

Figure S4. Cross-sectional SEM images of PPy/$Ti_3C_2T_x$ films (with 9 wt.% PPy) in different thickness.

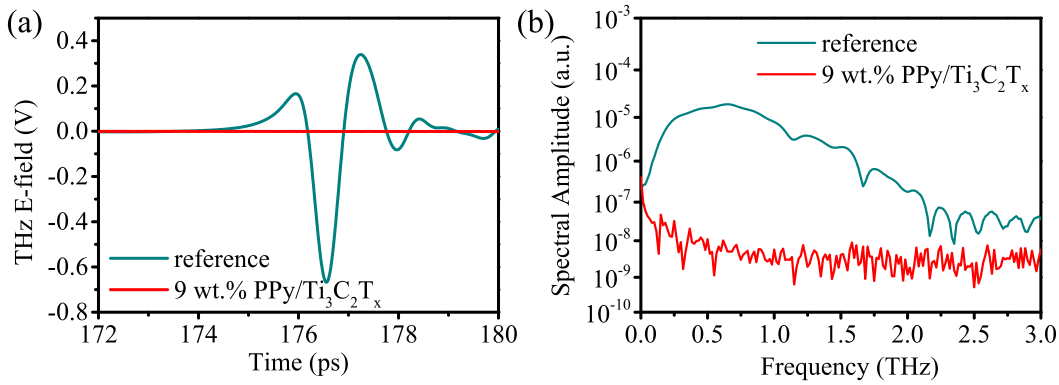

Figure S5. (a) Time-domain spectra and (b) measured transmitted THz signals of PPy/$Ti_3C_2T_x$ film and reference (air).

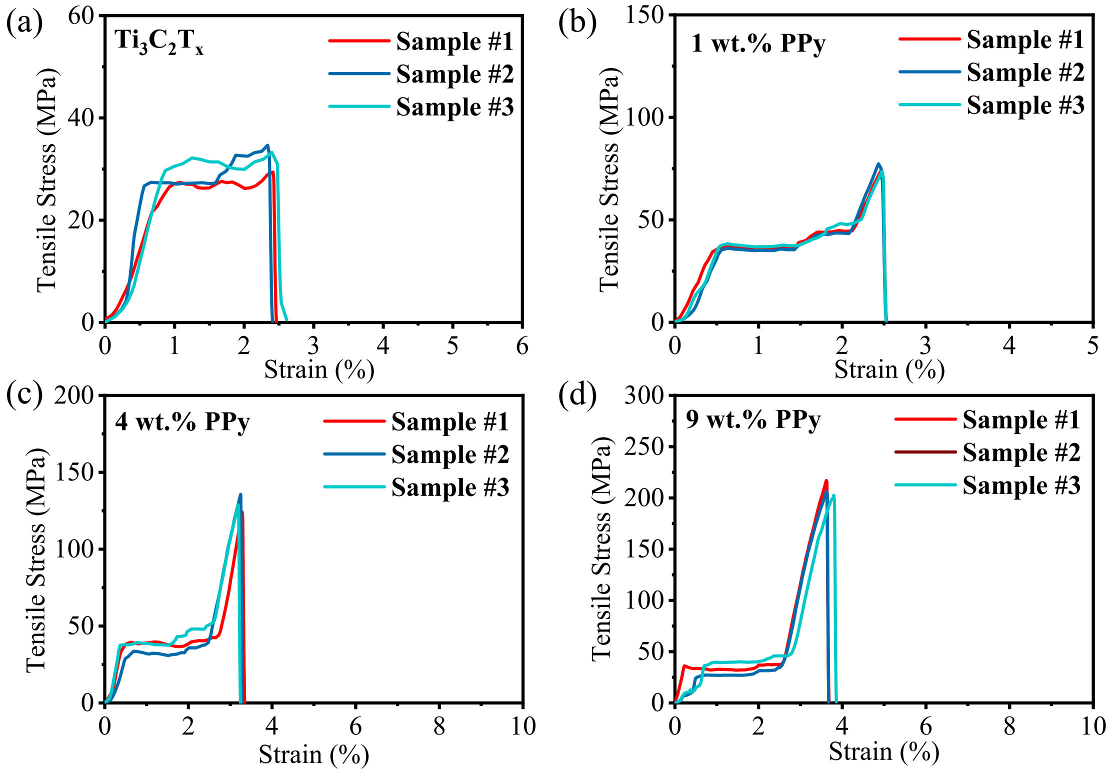

Figure S6. Tensile stress–strain curves of (a) pristine $Ti_3C_2T_x$ film and (b-d) PPy/$Ti_3C_2T_x$ films with different PPy content.

Table S1 Thickness, EMI shielding performance, thickness averaged specific EMI SE and frequency range of various shielding materials

Sample	Thickness (μm)	EMI (dB)	SSE/t (dB cm^2 g^{-1})	SE/t (dB μm^{-1})	Frequency range (Hz)	Ref.
PVDF-$Ti_3C_2T_x$	1000	48	-	0.05	8.2-12.4 G	[1]
PEDOT:PSS -$Ti_3C_2T_x$	11.1	42.1	19728	3.79	8.2-12.4 G	[2]
CNFs-$Ti_3C_2T_x$	35	39.6	7029	1.13	8.2-12.4 G	[3]
$Ti_3C_2T_x$-PS	2000	62	-	0.03	8.2-12.4 G	[4]
PANI-$Ti_3C_2T_x$	40	36	-	0.9	8.2-12.4 G	[5]
PVA-$Ti_3C_2T_x$	27	44.4	9343	1.65	8.2-12.4 G	[6]
$Ti_3C_2T_x$ foam	18	50	69444	2.78	8.2-12.4 G	[7]
$Ti_3C_2T_x$-SA	8	57	30830	7.13	8.2-12.4 G	[8]
$Ti_3C_2T_x$	11	68	25863	6.18	8.2-12.4 G	[8]
Aluminum	8	66	30555	8.25	8.2-12.4 G	[8]
Copper	10	70	7803	7	8.2-12.4 G	[8]
MGF	3000	61	366666	0.02	0.2-1.6 T	[9]
GFS	3000	74	70000	0.03	0.2-1.6 T	[9]
$Ti_3C_2T_x$ -PAA-ACC	130	45	-	0.34	0.2-2.0 T	[10]
rGO	375	65	-	0.17	0.1-1.0 T	[11]
MSF	10000	45	1956	0.005	0.3-1.6 T	[12]
SWCNT	200	15	-	0.08	0.2-2.5 T	[13]
PAL-$Ti_3C_2T_x$	38.3	50.5	-	1.32	0.2-1.6 T	[13]
NMP-$Ti_3C_2T_x$	12	17	-	1.41	0.2-1.6 T	[14]
	25	65	-	2.6	0.2-1.6 T	[14]
Zn^{2+}-$Ti_3C_2T_x$	85	51	451	0.6	0.2-2.0 T	[15]
9 wt.% PPy/$Ti_3C_2T_x$	4	64.5	33246	16.1	8.2-40.0 G	This work
	4	71.4	36983	17.8	0.2-1.6 T	This work

Table S2 Tensile stress, strain and various $Ti_3C_2T_X$ shielding materials

Sample	Tensile stress (MPa)	Strain (%)	Toughness (MJ m^{-3})	Ref.
$Ti_3C_2T_x$-PVDF-Ni	41.9	9	2.9	[16]
d- $Ti_3C_2T_x$-CNF	135.4	16.7	14.8	[17]
$Ti_3C_2T_x$-PVA	91	4.0	-	[18]
$Ti_3C_2T_x$-NC-Agnws	63.80	1.52	-	[19]
$Ti_3C_2T_x$-Go fiber	132.5	2.9	2.69	[20]
$Ti_3C_2T_x$-Kevlar	162	5.4	3.8	[21]
9 wt.% PPy/ $Ti_3C_2T_x$	200	3.8	2.3	This work

Table S3 EMI SE, Thickness, Frequency range, SSE/t and Tensile stress of various ultrathin EMI shielding films

Sample	EMI (dB)	Thickness (μm)	Frequency range (Hz)	SSE/t (dB cm^2 g^{-1})	Tensile stress (MPa)	Ref.
Graphene	48.3	43	8.2-12.4 G	6240	40.9	[22]
$Ti_3C_2T_X$	42.5	7.2	8.2-12.4 G	22529	5.62	[2]
$Ti_3C_2T_X$/CNFs	25	47	8.2-12.4 G	2647	44.2	[17]
$Ti_3C_2T_X$/polymer	42.1	11.1	8.2-12.4 G	19728	13.71	[2]
Cu foil	70	10	8.2-12.4 G	7803	250	[8]
9 wt.% PPy/$Ti_3C_2T_X$	64.5 71.4	4 4	8.2-40.0 G 0.2-1.6 T	33246 36983	200	This work

Supplementary References

1 K. Rajavel, S. Luo, Y. Wan, X. Yu, Y. Hu, P. Zhu, R. Sun and C. Wong, *Compos. Part A Appl. Sci. Manuf.*, 2020, **129**, 105693.

2 R. Liu, M. Miao, Y. Li, J. Zhang, S. Cao and X. Feng, *ACS Appl. Mater. Interfaces*, 2018, **10**, 44787–44795.

3 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.

4 R. Sun, H. Bin Zhang, J. Liu, X. Xie, R. Yang, Y. Li, S. Hong and Z. Z. Yu, *Adv. Funct. Mater.*, 2017, **27**, 1702807.

5 Y. Zhang, L. Wang, J. Zhang, P. Song, Z. Xiao, C. Liang, H. Qiu, J. Kong and J. Gu, *Compos. Sci. Technol.*, 2019, **183**, 107833.

6 X. Jin, J. Wang, L. Dai, X. Liu, L. Li, Y. Yang, Y. Cao, W. Wang, H. Wu and S. Guo, *Chem. Eng. J.*, 2020, **380**, 122475.

7 J. Liu, H. Bin Zhang, R. Sun, Y. Liu, Z. Liu, A. Zhou and Z. Z. Yu, *Adv. Mater.*, 2017, **29**, 1702367.

8 F. Shahzad, M. Alhabeb, C. B. Hatter, B. Anasori, S. M. Hong, C. M. Koo and Y. Gogotsi, *Science*, 2016, **353**, 1137–1140.

9 Z. Huang, H. Chen, S. Xu, L. Y. Chen, Y. Huang, Z. Ge, W. Ma, J. Liang, F. Fan, S. Chang and Y. Chen, *Adv. Opt. Mater.*, 2018, **6**, 1801165.

10 Y. Zhu, J. Liu, T. Guo, J. J. Wang, X. Tang and V. Nicolosi, *ACS Nano*, 2021, **15**, 1465–1474.

11 S. Dong, Q. Shi, W. Huang, L. Jiang and Y. Cai, *J. Mater. Sci. Mater. Electron.*, 2018, **29**, 17245–17253.

12 W. Shui, J. Li, H. Wang, Y. Xing, Y. Li, Q. Yang, X. Xiao, Q. Wen and H. Zhang, *Adv. Opt. Mater.*, 2020, **8**, 2001120.

13 J. T. Hong, D. J. Park, J. Y. Moon, S. B. Choi, J. K. Park, F. Rotermund, J.-Y. Park, S. Lee and Y. H. Ahn, *Appl. Phys. Express*, 2012, **5**, 015102.

14 Q. Zou, W. Guo, L. Zhang, L. Yang, Z. Zhao, F. Liu, X. Ye, Y. Zhang and W. Shi, *Nanotechnology*, 2020, **31**, 505710.

15 Z. Lin, J. Liu, W. Peng, Y. Zhu, Y. Zhao, K. Jiang, M. Peng and Y. Tan, *ACS Nano*, 2020, **14**, 2109–2117.

16 S. J. Wang, D. Sen Li and L. Jiang, *Adv. Mater. Interfaces*, 2019, **6**, 1–9.

17 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.

18 Z. Ling, C. E. Ren, M. Q. Zhao, J. Yang, J. M. Giammarco, J. Qiu, M. W. Barsoum and Y. Gogotsi, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 16676–16681.

19 M. Miao, R. Liu, S. Thaiboonrod, L. Shi, S. Cao, J. Zhang, J. Fang and X. Feng, *J. Mater. Chem. C*, 2020, **8**, 3120–3126.

20 S. Seyedin, E. R. S. Yanza and J. M. Razal, *J. Mater. Chem. A*, 2017, **5**, 24076–24082.

21 Z. Zhang, S. Yang, P. Zhang, J. Zhang, G. Chen and X. Feng, *Nat. Commun.*, 2019, **10**, 2920.

22 Y. Liu, J. Zeng, D. Han, K. Wu, B. Yu, S. Chai, F. Chen and Q. Fu, *Carbon*, 2018, **133**, 435–445.