Supporting Information for

MXene/Graphene Hybrid Fibers for High Performance Flexible Supercapacitors

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Calculation of the electrochemical capacitance for symmetric two-electrode supercapacitors: For ideal two-electrode symmetric system (as shown in Scheme S1), $C_1 = C_2 = C$, then the capacitance measured for the whole system is $C_{2E} = 1/2 C$. Accordingly, the capacitance for a single electrode is $C_1 = C_2 = C = 2C_{2E}$.



Scheme S1. Scheme of the composition of two-electrode system for supercapacitors

Thus the areal capacitance (C_A) (F cm⁻²) based on GCP derived from the equation is $C_A = C \times S^{-1} = 2C_{2E} \times S^{-1} = 2I \times \Delta t \times \Delta U \times S^{-1}$, where I stands for charge–discharge current, Δt is the discharge time (s), ΔU represents the potential window (V) and S is the surface area of a single fiber electrode (cm⁻²), equal to the circumference of the cross-section multiplied by the overlapped length (L) of fiber electrodes. Circumference is measured from cross profile of the SEM images of the fibers. Similarly, the volumetric capacitance C_V (F cm⁻³) can be calculated by $C_V = 2I \times \Delta t \times \Delta U^{-1} \times V^{-1}$, where V refers to the volume of a single fiber electrode (cm⁻³), which is equal to the cross-sectional area multiplied by the length of overlapped portion of fiber electrodes. Cross-sectional areas are measured through Photoshop (image processing software) by comparing the pixel with that of an internal reference.

The capacitances calculated from CV curves are also widely used for symmetric twoelectrode systems. In this case, C_A can be calculated based on the following equation:

$$C_A = 2C \times S^{-1} = 2 \times \frac{1}{2} \times S^{-1} \times v^{-1} \times \Delta U^{-1} \int_{U_0}^{U_0 + \Delta U} I \times U dU$$
$$= A \times S^{-1} \times v^{-1} \times \Delta U^{-1}$$

where *v* is the scan rate (V/s) and the integral term is equal to the area under the CV curve A. Similarly the volumetric capacitance can be calculated by $C_V = A \times V^{-1} \times v^{-1} \times \Delta U^{-1}$.

The practical energy (E) and power (P) of an entire supercapacitor could be obtained from E = $0.5 \times C \times U^2$ and P = E/t, respectively. I The areal energy density (EA) may be calculated by $E_V = E/(2 \times V) = 0.5 \times C_{2E} \times U^2/(2 \times V) = 0.125 \times (2 \times C_1/V) \times U^2 = 0.125 \times C_V \times U^2$. The specific capacitance in this work was calculated on the basis of two fiber electrodes in the symmetric supercapacitor. In terms of specific power (or power density, P_V), they could be obtained from P_V = E_V/t.



Figure S1. SEM images of Ti₃AlC₂ (a), LiF and HCl etched accordion-like Ti₃C₂ (b, c).



Figure S2. Photographic images of neat MXene fiber (a MXene content of 100%).



Figure S3. Zeta potential of MXene, GO, and MXene/GO-90 mixtrue.



Figure S4. Photographic image for Ti_3C_2 sheet in various solvents (0.14 mg mL⁻¹), including ethanol (EtOH), methanol (MeOH), isopropanol (IPA), tetrahydrofuran (THF), and ethyl acetate (EtOAc).



Figure S5. Photographic image for Ti_3C_2 sheet in IPA and water mixture with various ratio of IPA: water = 1:0, 3:1, 2:1, 1:1, 1:2, 1:3, and 0:1.



Figure S6. Photographic images of MXene/GO fiber with a MXene content of 95%.



Figure S7. SEM images and Ti-, C-, and O- element mappings for the MXene/rGO-50 fiber.



Figure S8. CV curves of MXene/rGO-90 fibers based FSSCs in 1M H₂SO₄ at different scan rate.



Figure S9. Volumetric capacitances at different current densities of the fabricated MXene/rGO FSCs with different MXene contents (0, 10, 50, 70, and 90%).

Table S1.	Comparison	of the	specific	areal	and	volumetric	capacitances	of	different	materials
used in FSS	SCs.									

		Diameter	Electrolyte	Working potential	Capacitance		Scan rate or	.
	Electrode Materials	(µm)		Window (V)	mF cm ⁻²	F cm ⁻³	current density	Ref.
1	MXene/rGO	25.8	PVA/H ₃ PO ₄	0 - 0.8	372.24	586.44	10 mV s ⁻¹	this work
2	GF/rGO fiber	30	PVA/H_2SO_4	0 - 0.8	1.7		30 mV s ⁻¹	[S1]
3	CNT fiber	15	PVA/H ₂ SO ₄	0 - 0.8	4.99	13.5	5 mV s ⁻¹	[S2]
4	coaxial fiber from CNT sheet	43	PVA/H ₃ PO ₄	0 – 1.0	8.66	32.09	1 μΑ	[S3]
5	rGO/CNT yarn	20	$1 \text{ M H}_2 \text{SO}_4$	0 - 1.0		68.4	31 mA cm ⁻³	[S4]
6	OMC/CNT yarn	150	PVA/H ₃ PO ₄	0 – 1.0	39.67		40 µA cm ⁻²	[S5]
7	SWCNT/activated carbon yarn	68	PVA/H ₂ SO ₄	0-0.8	37.1	48.5	2 mV s ⁻¹	[S6]
8	rGO/SWNT@CMC	~ 100	PVA/H ₃ PO ₄	0 - 0.8	177	158	0.1 mA cm ⁻²	[S7]
9	N-doped rGO/SWNT fiber	60	PVA/H ₃ PO ₄	0 – 1.0	116	300	26.7 mA cm^{-3}	[S8]
10	PANI nanowire array/CNT yarn	20	PVA/H ₃ PO ₄	0 - 0.8	38		20 mV s ⁻¹	[S9]
11	PPy/rGO fiber	35	PVA/H ₂ SO ₄	0 - 0.8	115		0.24 mA cm ⁻²	[S10]
12	GO/Fe ₃ O ₄ /CNT	100	$1 \text{ M Na}_2 \text{SO}_4$	0-0.6	0.98		20 µA cm ⁻²	[S11]
13	Spun MWCNTs/rGO yarn	24	PVA/H ₃ PO ₄	0 - 0.8		38.8	50 mA cm ⁻³	[S12]
14	Pt wire/CNTs/PANI	29.5	PVA/H ₃ PO ₄	0 – 1.0	52.5		5 mV s⁻¹	[S13]
15	Activated CF	5 ~ 10	PVA/H ₃ PO ₄	0 – 1.0		2.55	10 mVs ⁻¹	[S14]
16	CF/PANI//Functionalized CF	130	PVA/H ₃ PO ₄	-0.8 – 0 // 0 - 0.8		4.8	0.2 A cm ⁻³	[S15]

17	CF/MWCNT//electrospun CC	230	PVA/H ₃ PO ₄	0 – 1.0	86.8		2 mV s ⁻¹	[S16]
18	MoS ₂ /rGO	80	PVA/H ₃ PO ₄	0-0.8	598	368	5mV s ⁻¹	[S17]
19	CF/MnO ₂ /Ppy	9.5	PVA/H ₃ PO ₄	0-0.8		69.3	0.1 A cm ⁻³	[S18]
20	MnO ₂ /rGO fiber	40	PVA/H_2SO_4	0-0.8	9.6		10 mV s ⁻¹	[S19]
21	MnO ₂ /carbon fiber	68	PVA/H ₃ PO ₄	0-0.8		2.5	0.02 A cm ⁻³	[S20]
22	MnO ₂ /carbon fiber	31	PVA/KOH	0-0.5		90.4	100 mV s ⁻¹	[S21]
23	MnO₂/rGO/CNTs//N-doped RGO/CNTs asymmetric device	~ 50	PVA/Na ₂ SO ₄	0 – 1.8		11.1	25 mA cm ⁻³	[S22]
24	MnO ₂ /oxidized CNT fiber	13	PVA/H ₂ SO ₄	0-1.0	133	409.4	0.75 A cm ⁻³	[S23]
25	MnO₂/ZnO nanowires/Au–PMMA wire	220	PVA/H ₃ PO ₄	0 – 0.5	2.4		100 mV s ⁻¹	[S24]
26	Pt/MWCNTs/PEDOT	20	PVA/H ₂ SO ₄	0-0.8		180	10 mV s ⁻¹	[S25]
27	VN@C NWAs/CNT fiber//MnO₂/PEDOT:PSS/CNT	~ 70	PVA/Na ₂ SO ₄	0 – 1.8	213.5		0.3 mA cm ⁻²	[S26]
28	MoO ₃ /rGO	25	$1M H_2SO_4$	-0.8 - 0		321.8	2 mV s ⁻¹	[S27]
29	CNTs/Co ₃ O ₄	70 ~ 80	PVA/ H ₂ SO ₄	0-0.8	52.6		0.053 mA cm^{-2}	[S28]
30	Co ₃ O ₄ and carbon fiber–graphene	100	PVA/KOH	0 – 1.5		2.1	20 mA cm ⁻³	[S29]
31	Cotton/Ni/rGO	500	$1 \text{ M Na}_2 \text{SO}_4$	0-0.8		292.3	87.9 mA cm ⁻³	[S30]
32	Ni−Co DHs/Ni wire/graphitic/pen ink	300	6 M KOH	0 – 1.5	28.67		0.5 A g ⁻¹	[S31]
33	Ni wire/Ni(OH) ₂ // OMCg)/Ni wire	300	6 M KOH	0 – 1.5	35.67		0.1 mA	[S32]
34	Ni wire/NiCo ₂ O ₄		PVA/KOH	0 – 1.0		17.5	10 mV s ⁻¹	[S33]
35	hollow RGO/PEDOT:PSS/VC composite fibers	112	PVA/H ₃ PO ₄	0-0.8	304.5	143.3	0.08 mA cm ⁻²	[S34]



Figure S10. Ragone plot of the MXene/rGO-90 based FSSCs in comparison with previously reported FSSCs with different fiber electrodes.



Figure S11. Digital images for the MXene/rGO-77 fiber based yarn supercapacitor, which evidenced the good mechanical flexibility of the yarn supercapacitors.



Figure S12. Capacitance ratio (C/C0, where C0 is the initial capacitance) versus bending times for MXene/rGO-77 FSSCs with bending angles of 180°.

References

[S1] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, Adv. Mater. 2013, 25,

2326.

[S2] P. Xu, T. Gu, Z. Cao, B. Wei, J. Yu, F. Li, J. H. Byun, W. Lu, Q. Li, T. W. Chou, Adv.

Energy Mater. 2014, 4, 1300759.

- [S3] X. Chen, L. Qiu, J. Ren, G. Guan, H. Lin, Z. Zhang, P. Chen, Y. Wang, H. Peng, *Adv. Mater.***2013**, 25, 6436.
- [S4] B. Wang, X. Fang, H. Sun, S. He, J. Ren, Y. Zhang, H. Peng, Adv. Mater. 2015, 27, 7854.
- [S5] J. Ren, W. Bai, G. Guan, Y. Zhang, H. Peng, Adv. Mater. 2013, 25, 5965.
- [S6] Q. Meng, H. Wu, Y. Meng, K. Xie, Z. Wei, Z. Guo, Adv. Mater. 2014, 26, 4100.
- [S7] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun and C. Gao, Nat. Commun. 2014, 5, 3754.
- [S8] D. S. Yu, K. Goh, H. Wang, L. Wei, Q. Zhang, L. Dai, Y. Chen, *Nat. Nanotechnol.* 2014, 9, 555.
- [S9] K. Wang, Q. Meng, Y. Zhang, Z. Wei and M. Miao, Adv. Mater. 2013, 25, 1494.
- [S10] X. Ding, Y. Zhao, C. Hu, Y. Hu, Z. Dong, N. Chen, Z. Zhang, L. Qu, J. Mater. Chem. A 2014, 2, 12355.
- [S11] H. Cheng, Z. Dong, C. Hu, Y. Zhao, Y. Hu, L. Qu, N. Chen and L. Dai, *Nanoscale* 2013, 5, 3428.
- [S12] Y. Ma, P. Li, J. W. Sedloff, X. Zhang, H. Zhang, J. Liu, ACS Nano 2015, 9, 1352.
- [S13] D. Zhang, M. Miao, H. Niu, Z. Wei, ACS Nano 2014, 8, 4571.
- [S14] D. Yu, S. Zhai, W. Jiang, K. Goh, L. Wei, X. Chen, R. Jiang, Y. Chen, Adv. Mater. 2015, 27, 4895.
- [S15] H. Jin, L. Zhou, C. L. Mak, H. Huang, W. M. Tang, H. L. W. Chan, *Nano Energy* 2015, 11, 662.
- [S16] L. Viet Thong, H. Kim, A. Ghosh, J. Kim, J. Chang, V. Quoc An, P. Duy Tho, J.-H. Lee, S.-W. Kim, Y. H. Lee, ACS Nano 2013, 7, 5940.

- [S17] B. J. Wang, Q. Q. Wu, H. Sun, J. Zhang, J. Ren, Y. F. Luo, M. Wang, H. S. Peng, J. Mater. Chem. A 2017, 5, 925.
- [S18] J. Tao, N. Liu, W. Ma, L. Ding, L. Li, J. Su, Y. Gao, Sci. Rep. 2013, 3. 2286.
- [S19] Q. Chen, Y. Meng, C. Hu, Y. Zhao, H. Shao, N. Chen, L. Qu, J. Power Sources 2014, 247, 32.
- [S20] X. Xiao, T. Li, P. Yang, Y. Gao, H. Jin, W. Ni, W. Zhan, X. Zhang, Y. Cao, J. Zhong, L. Gong, W.-C. Yen, W. Mai, J. Chen, K. Huo, Y. L. Chueh, Z. L. Wang, J. Zhou, ACS Nano 2012, 6, 9200.
- [S21] P. Xu, B. Wei, Z. Cao, J. Zheng, K. Gong, F. Li, J. Yu, Q. Li, W. Lu, J.-H. Byun, B.-S. Kim, Y. Yan, T.-W. Chou, ACS Nano 2015, 9, 6088.
- [S22] D. Yu, K. Goh, Q. Zhang, L. Wei, H. Wang, W. Jiang, Y. Chen, Adv. Mater. 2014, 26, 6790.
- [S23] M. Y. Li, M. Zu, J. S. Yu, H. F. Cheng, Q. W. Li, Small 2017, 13, 1602994
- [S24] J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. Liu, Z. L. Wang, Angew. Chem., Int. Ed. 2011, 50, 1683.
- [S25] J. A. Lee, M. K. Shin, S. H. Kim, H. U. Cho, G. M. Spinks, G. G. Wallace, M. D. Lima, X. Lepro, M. E. Kozlov, R. H. Baughman, S. J. Kim, *Nat. Commun.* 2013, 4, 1970.
- [S26] Q. Zhang, X. Wang, Z. Pan, J. Sun, J. Zhao, J. Zhang, C. Zhang, L. Tang, J. Luo, B. Song,
 Z. Zhang, W.Lu, Q. Li, Y. Zhang, Y. Yao, Nano Lett. 2017, 17, 2719.
- [S27] W. J. Ma, S. H. Chen, S. Y. Yang, W. P. Chen, W. Weng, Y. H. Cheng, M. F. Zhu, *Carbon* 2017, 113, 151.
- [S28] F. Su, X. Lv, M. Miao, Small 2015, 11, 854.

- [S29] X. Wang, B. Liu, R. Liu, Q. Wang, X. Hou, D. Chen, R. Wang and G. Shen, Angew. Chem., Int. Ed. 2014, 53, 1849.
- [S30] L. Liu, Y. Yu, C. Yan, K. Li, Z. Zheng, Nat. Commun. 2015, 6, 7260.
- [S31] L. B. Gao, J. U. Surjadi, K. Cao, H. T. Zhang, P. F. Li, S. Xu, C. C. Jiang, J. Song, D. Sun, Y. Lu, ACS Appl. Mater. Interfaces 2017, 9, 5409.
- [S32] X. L. Dong, Z. Y. Guo, Y. F. Song, M. Y. Hou, J. Q. Wang, Y. G. Wang, Y. Y. Xia, Adv. Funct. Mater. 2014, 24, 3405.
- [S33] Q. Wang, X. Wang, J. Xu, X. Ouyang, X. Hou, D. Chen, R. Wang, G. Shen, *Nano Energy* 2014, 8, 44.
- [S34] G. X. Qu, J. L. Cheng, X. D. Li, D. M. Yuan, P. N. Chen, X. L. Chen, B. Wang, H. S. Peng, Adv. Mater. 2016, 28, 3646.
- [S35] X. Cheng, X. Fang, P. Chen, S.-G. Doo, I. H. Son, X. Huang, Y. Zhang, W. Weng, Z. Zhang, J. Deng, X. Sun, H. Peng, J. Mater. Chem. A 2015, 3, 19304.
- [S36] X. Wang, B. Liu, R. Liu, Q. Wang, X. Hou, D. Chen, R. Wang, G. Shen, Angew. Chem. Int. Ed. 2014, 53, 1849.
- [S37] Z. Yu, J. Thomas, Adv. Mater. 2014, 26, 4279.