Supporting Information

A Self-Supported Graphene/Carbon Nanotube Hollow Fiber for Integrated Energy Conversion and Storage

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Fig. S1 Raman spectra of as-grown graphene (black line) and G/CNTs (red line) on

Ni wires.



Fig. S2 SEM image of graphene ribbon formed after shrinking of graphene tube.



Fig. S3 Digital photographs of an etched G/CNTs hollow fiber drawn out from water.



Fig. S4 EDX element mapping of G/CNTs/PANI hollow fiber.



Fig. S5 Raman spectra of G/CNTs/PANI hollow fibers synthesized by using precursor with different aniline contents.



Fig. S6 a,b I-V curves of graphene ribbon, G/CNTs fiber (a), and G/CNTs/PANI fibers with different mass loading of PANI (b).



Fig. S7 Tensile strength-strain curves of graphene ribbon, G/CNTs fiber and G/CNTs/PANI fiber.



Fig. S8 Photographs of water droplets on G/CNTs fiber (a) and G/CNTs/PANI electrodes (b).



Fig. S9 a CV curves of a fiber-shaped supercapacitor at scan rates range from 0.05 V s⁻¹ to 0.5 V s⁻¹. **b** GCD curves of the supercapacitor under different current density. **c** Nyquist plot of the supercapacitor within frequency from 10^{-2} to 10^5 Hz. **d** CV curves of a fiber-shaped supercapacitor at scan rates range from 0.01 V s⁻¹ to 0.05 V s⁻¹. **e** GCD curves of the supercapacitor under different current densities. **f** Nyquist plot of the supercapacitor within frequency from 10^{-2} to 10^5 Hz.



Fig. S10 Comparison of gravimetric capacitance of our supercapacitors with other reported supercapacitors based on CNT/PANI electrodes [1-7].



Fig. S11 CV curves and GCD curves of fiber supercapacitor based on G/CNTs/PANI hollow fiber with PANI mass loading of 84.5%.



Fig. S12 Cyclic performance of the fiber shaped supercapacitor.

Device shape	Configuration	Specific	Reference
(state of		capacitance	
electrolyte)		$(mF cm^{-2})$	
fiber (gel)	Graphene/CNTs/PANI	472	This work
fiber (gel)	CNT/PANI array	37	[8]

Table S1. Comparison of our fiber shaped supercapacitor with other reported results.

CNT/PPy//CNT/MnO ₂	60.435	[9]
CNT/graphene	4.97	[10]
rGO/PEDOT:PSS	304.5	[11]
rGO-Ni-polyester	72.1	[12]
PANI/ Stainless steel	41	[13]
ppy/CNT	69	[14]
PEDOT@MnO2//	127	[15]
C@Fe ₃ O ₄		
RGO /CNT@CMC	177	[16]
	CNT/PPy//CNT/MnO ₂ CNT/graphene rGO/PEDOT:PSS rGO-Ni-polyester PANI/ Stainless steel ppy/CNT PEDOT@MnO ₂ // C@Fe ₃ O ₄ RGO /CNT@CMC	CNT/PPy//CNT/MnO2 60.435 CNT/graphene 4.97 rGO/PEDOT:PSS 304.5 rGO-Ni-polyester 72.1 PANI/ Stainless steel 41 ppy/CNT 69 PEDOT@MnO2// 127 C@Fe3O4 177



Fig. S13 Digital photograph of five fiber supercapacitors connected in series to power a LED. The insert shows an LED without being powered.



Fig. S14 a CV curves (10 mV s⁻¹), **b** GCD curves (1 mA cm⁻²) and **c** Nyquist curves $(10^{-2}-10^5 \text{ Hz})$ of a fiber-shaped supercapacitor under different bending angles. **d** Digital photographs of a fiber-shaped supercapacitor under different bending states $(0^\circ, 30^\circ, 90^\circ \text{ and } 150^\circ)$.



Fig. S15 *J-V* curve of a DSSC by using Pt wire as the counter electrode.



Fig. S16 *J-V* curves and digital photographs of a fiber-shaped DSSC on an elastic substrate under different bending states.



Fig. S17 Digital photograph of an integrated energy conversion and storage device.

Reference

- Y. Wu, Q. Wang, T. Li, D. Zhang, M. Miao, Fiber-shaped Supercapacitor and Electrocatalyst Containing of Multiple Carbon Nanotube Yarns and One Platinum Wire. Electrochim. Acta 245, 69-78 (2017). https://doi.org/10.1016/j.electacta.2017.05.117
- J. Li, W. Lu, Y. Yan, W. Chou, High performance solid-state flexible supercapacitor based on Fe₃O₄/carbon nanotube/polyaniline ternary films. J. Mater. Chem. A 5, 11271-11277 (2017). https://xs.scihub.ltd/10.1039/C7TA02008B
- J. Benson, I. Kovalenko, S. Boukhalfa, D. Lashmore, M. Sanghadasa, G. Yushin, Multifunctional CNT-Polymer Composites for Ultra-Tough Structural Supercapacitors and Desalination Devices. Adv. Mater. 25, 6625-6632 (2013). https://doi.org/10.1002/adma.201301317
- Q. Cheng, J. Tang, N. Shiny, Lu. Qin, Polyaniline modified graphene and carbon nanotube composite electrode for asymmetric supercapacitors of high energy density. J. Power Sources 241, 423-428 (2013). https://doi.org/10.1016/j.jpowsour.2013.04.105
- D. Potphode, P. Sivaraman, S. Mishra, M. Patri, Polyaniline/partially exfoliated multi-walled carbon nanotubes based nanocomposites for supercapacitors. Electrochim. Acta 155, 402-410 (2015). https://doi.org/10.1016/j.electacta.2014.12.126
- Z. Zhang, J. Deng, X. Li, Z. Yang, S. He, X. Chen, G. Guan, J. Ren, H. Peng, Superelastic Supercapacitors with High Performances during Stretching. Adv. Mater. 27, 356-362 (2015). https://doi.org/10.1002/adma.201404573
- S. He, L. Qiu, L. Wang, J. Cao, S. Xie, Q. Gao, Z. Zhang, J. Zhang, B. Wang, H. Peng, A three-dimensionally stretchable high performance supercapacitor. J. Mater. Chem. A 4, 14968-14973 (2016). https://doi.org/10.1039/C6TA05545A
- K. Wang, Q. Meng, Y. Zhang, Z. Wei, M. Miao, High-Performance Two-Ply Yarn Supercapacitors Based on Carbon Nanotubes and Polyaniline Nanowire Arrays. Adv. Mater. 25, 1494-1498 (2013). https://doi.org/10.1002/adma.201204598

- J. Yu, W. Lu, J.P. Smith, K.S. Booksh, L. Meng, Y. Huang, Q. Li, J.-H. Byun, Y. Oh, Y. Yan, T.-W. Chou, A High Performance Stretchable Asymmetric Fiber-Shaped Supercapacitor with a Core-Sheath Helical Structure. Adv. Energy Mater. 7, 1066976 (2017). https://doi.org/10.1002/aenm.201600976
- H. Sun, X. You, J. Deng, X. Chen, Z. Yang, J. Ren, H. Peng, Novel Graphene/Carbon Nanotube Composite Fibers for Efficient Wire-Shaped Miniature Energy Devices. Adv. Mater. 26, 2868-2873 (2014). https://doi.org/10.1002/adma.201305188
- G. Qu, J. Cheng, X. Li, D. Yuan, P. Chen, X. Chen, B. Wang, H. Peng, A Fiber Supercapacitor with High Energy Density Based on Hollow Graphene/Conducting Polymer Fiber Electrode. Adv. Mater. 28, 3646-3652 (2016). https://doi.org/10.1002/adma.201600689
- X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, Z.L. Wang, Wearable Self-Charging Power Textile Based on Flexible Yarn Supercapacitors and Fabric Nanogenerators. Adv. Mater. 28, 98-105 (2016). https://doi.org/10.1002/adma.201504403
- Y. Fu, H. Wu, S. Ye, X. Cai, X. Yu, S. Hou, H. Kafafy, D. Zou, Integrated power fiber for energy conversion and storage. Energy Environ. Sci. 6, 805-812 (2013). https://doi.org/10.1039/C3EE23970E
- 14. J. Sun, Y. Huang, C. Fu, Z. Wang, Y. Huang, M. Zhu, C. Zhi, H. Hu, High-performance stretchable yarn supercapacitor based on PPy@CNTs@urethane elastic fiber core spun yarn. Nano Energy 27, 230-237 (2016). https://doi.org/10.1016/j.nanoen.2016.07.008
- 15. J. Sun, Y. Huang, C. Fu, Y. Huang, M. Zhu, X. Tao, C. Zhi, H. Hu, A high performance fiber-shaped PEDOT@MnO₂//C@Fe₃O₄ asymmetric supercapacitor for wearable electronics. J. Mater. Chem. A 4, 14877-14883 (2016). https://doi.org/10.1039/C6TA05898A
- 16. L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, Coaxial wet-spun yarn supercapacitors for high-energy density and safe wearable electronics. Nat. Commun. 5, 3754 (2014). https://doi.org/10.1038/ncomms4754