Electronic Supplementary Information (ESI)

High-performance wearable supercapacitor based on PANI/N-CNT@CNT fiber with designed hierarchical core-sheath structure

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Experimental Section

1. Preparation of N-CNTs on CNT fiber:

Catalyst of Fe (1.2 nm)/Al_2O_3 (3 nm) on silicon wafer for spinnable CNT array was purchased from Tianjin Lattice Photoelectric Material Co. Ltd. Spinnable CNT array was synthesized by a typical CVD method with Fe (1.2 nm)/Al_2O_3 (3 nm) on a silicon wafer as catalyst, ethylene as carbon source, and a mixture of Ar and H_2 gases as carrying gas. The CVD growth process was carried out in a quartz tube furnace. The growth temperature and growth time of CNT array were controlled as 740 ^oC and 10 min, respectively. After spinnable CNT arrays were synthesized, CNT fiber was spun from the as-synthesized CNT array. In more details, adhering a blade to the edge of a CNT array, CNT sheet was continuously pulled out of the array and subsequently spun

into fiber.

2. The calculation of fiber's electrical conductivity:

The conductivity (σ) of the fiber electrode was calculated according to the definition[S1-S3]

$$\sigma = 1/\rho \quad (1)$$

where ρ is resistivity. Also according to the definition

$$\rho = R * S_s / L \quad (2)$$

where R, S_s and L stand for the resistance, cross-section area and length of the fiber electrode tested, respectively. In the formula, R was tested by a ELIKE JC-890D+ digital multimeter, S_s was calculated by

$$S_s = \pi (D/2)^2 \quad (3)$$

where D is the diameter of the fiber.

3. Calculation of fiber electrode surface area:

The surface area of the fiber electrode was calculated by

$$S = \pi \times D \times L \quad (4)$$

where D and L are the diameter and length of the fiber electrode covered by the electrolyte.

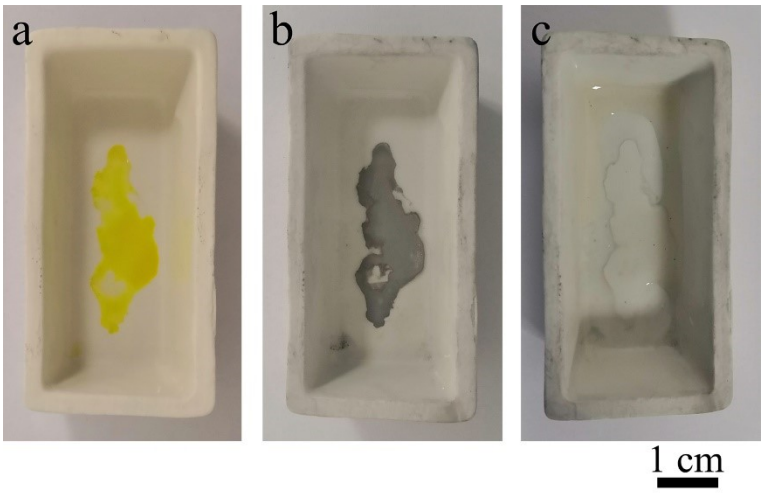

Figure S1. Ferric chloride (a) catalyst precursor solution, (b) reduced into iron during CVD process and (c) then dissolved in acid solution.

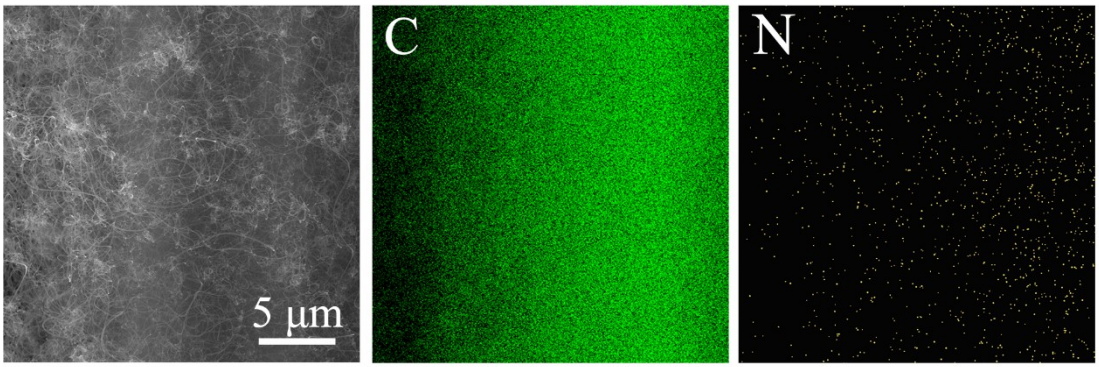

Figure S2. EDS mapping of N-CNT@CNT fiber composites.

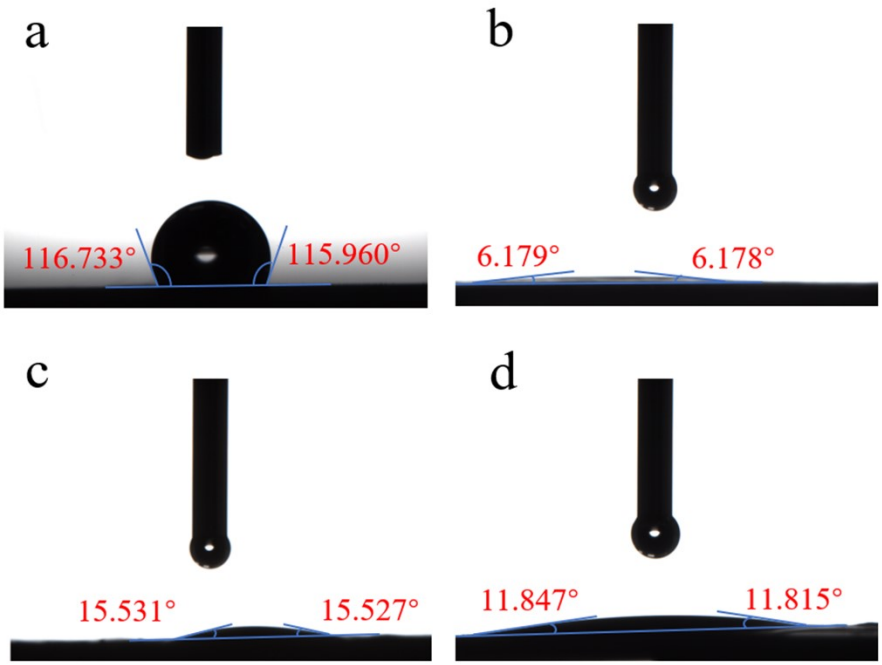

Figure S3. Static water contact angles on sheet electrodes with the same material structure of corresponding fiber electrodes. (a) CNT, (b) N-CNT@CNT, (c) PANI@CNT and (d) PANI/N-CNT@CNT.

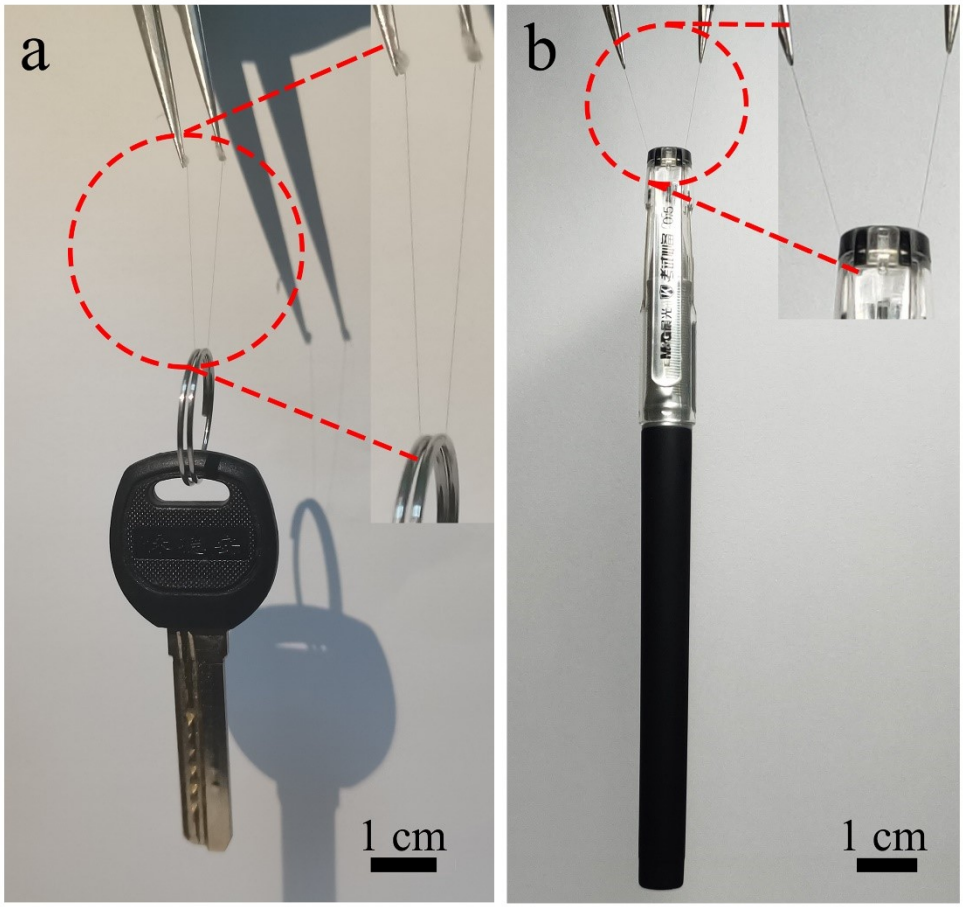

Figure S4. Optical images of N-CNT@CNT fiber lifting weights of a (a) key and (b) pen.

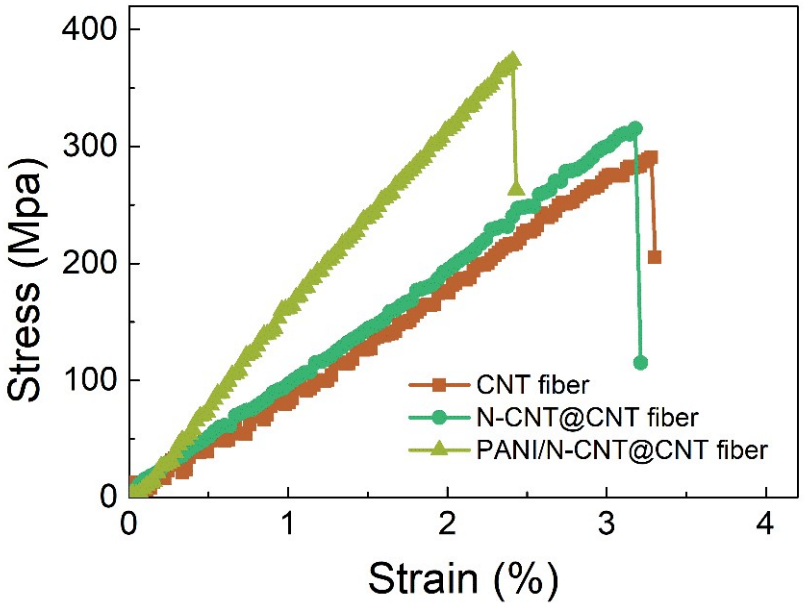

Figure S5. Typical tensile stress-strain curves for CNT fiber, N-CNT@CNT fiber and PANI/N-CNT@CNT fiber, respectively.

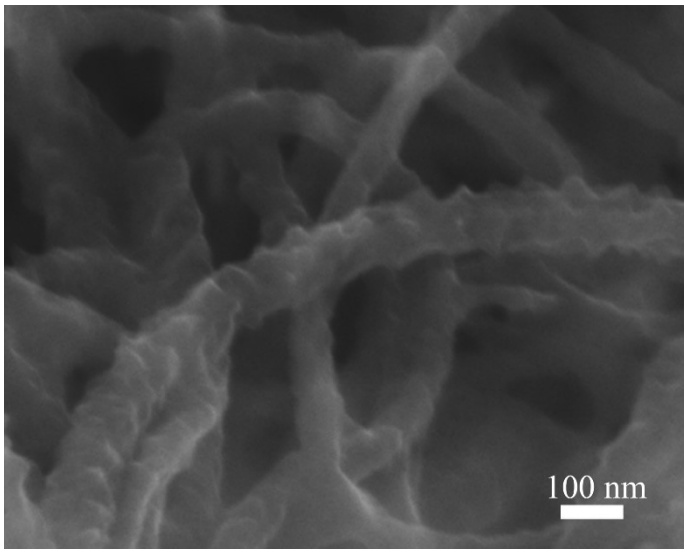

Figure S6. Magnified SEM image of PANI/N-CNT in PANI/N-CNT@CNT fiber.

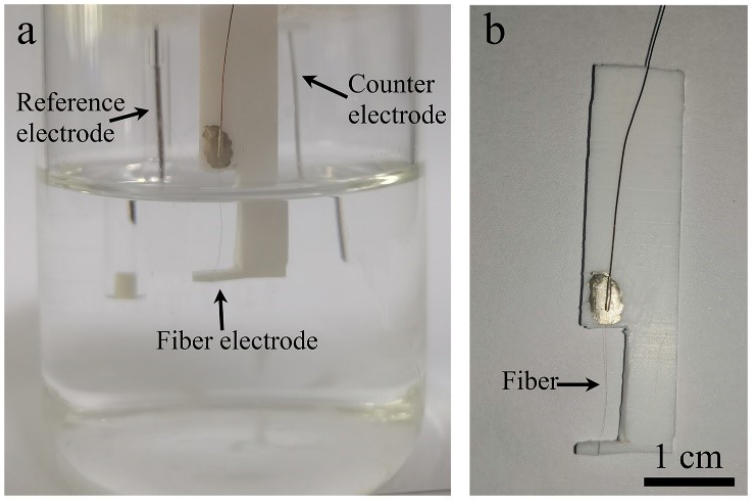

Figure S7. The optical photos of (a) fiber electrode in three-electrode system, (b) fiber electrode fixed on a plastic holder.

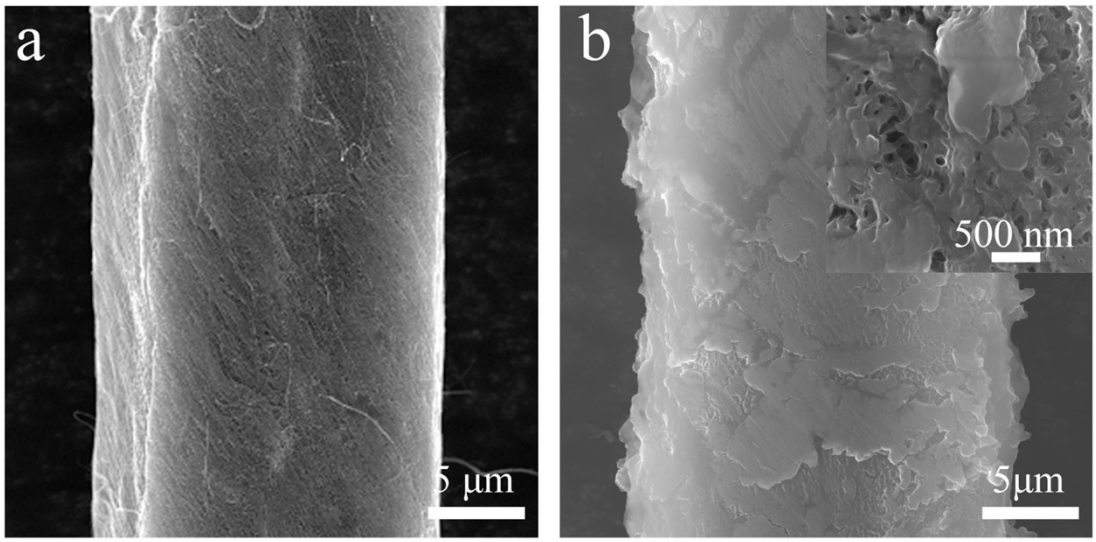

Figure S8. SEM images of (a) CNT fiber and (b) PANI@CNT fiber with 70% PANI, the inset in b is the magnified SEM image.

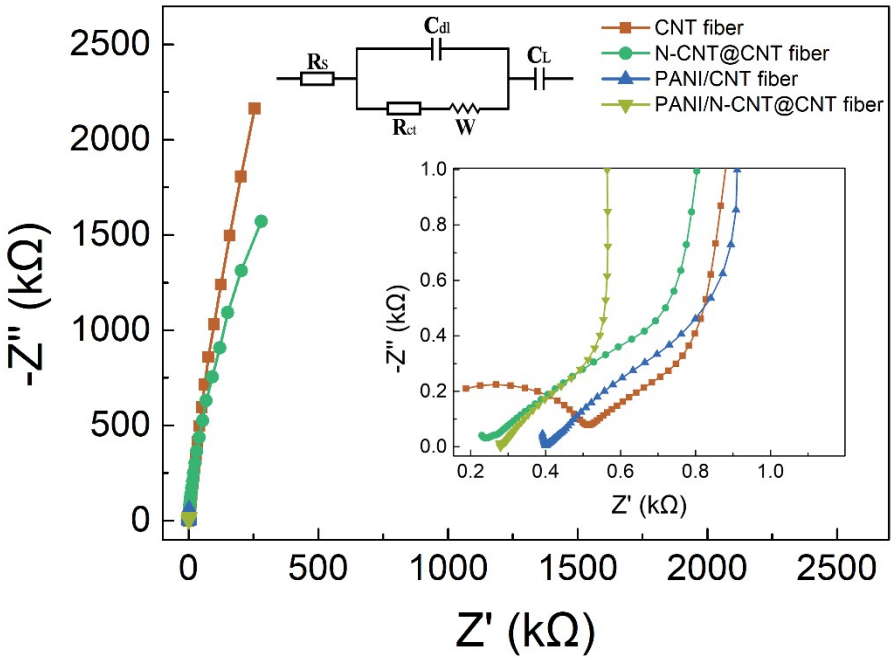

Figure S9. Nyquist plots of fiber electrodes with different structures. The insets are the Nyquist plots in the high-frequency region and the Equivalent circuit to fit the EIS data.[60, S4] The equivalent values of R_s and R_{ct} were summarized in Table S2. R_s, R_{ct}, W, C_{dl} and C_L stand for the series resistance, charge transfer resistance, Warburg element, double-layer capacitance and pseudocapacitance, respectively.

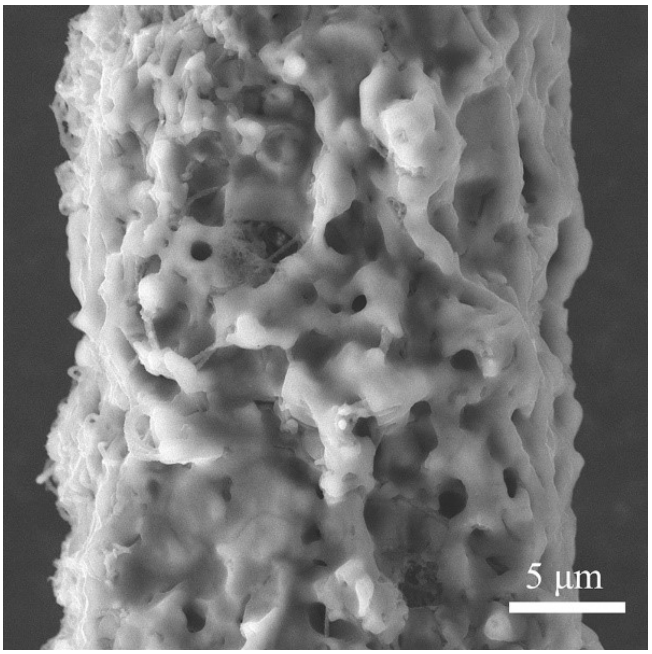

Figure S10. SEM images of PANI/N-CNT@CNT fiber with PANI weight percentage of 80%.

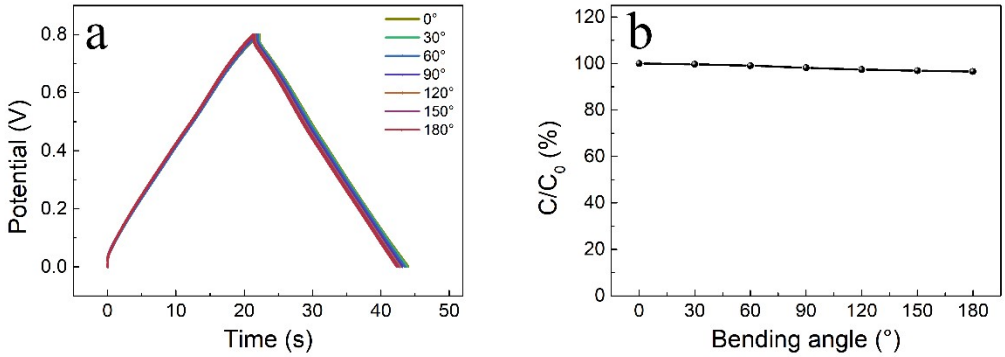

Figure S11. Electrochemical characterization of PANI/N-CNT@CNT fiber electrode under different bending angles. (a) GCD profiles of fiber electrode bending at different angles. (b) Capacitance retention of fiber electrode under different bending angles.

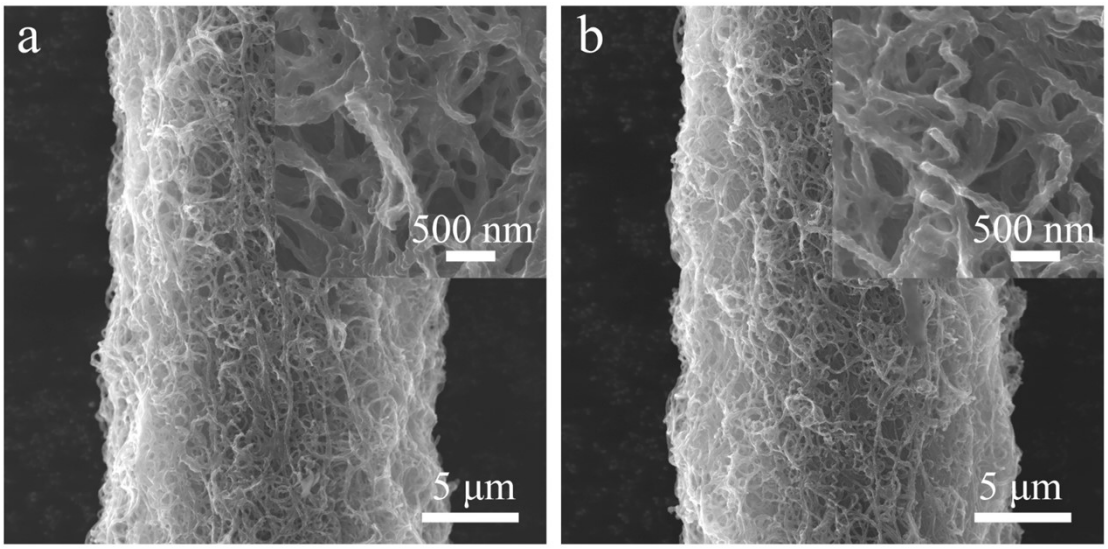

Figure S12. SEM images of PANI/N-CNT@CNT fiber electrode (a) before and (b) after 1000 cycles of GCD processes under 10 A g^{-1}, the insets are the corresponding SEM image under higher magnification.

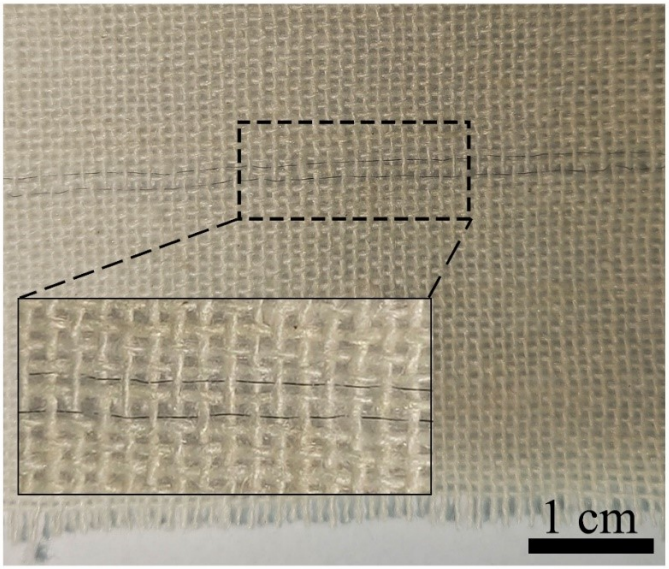

Figure S13. The picture of the hierarchical core-sheath fiber based supercapacitors woven into a textile.

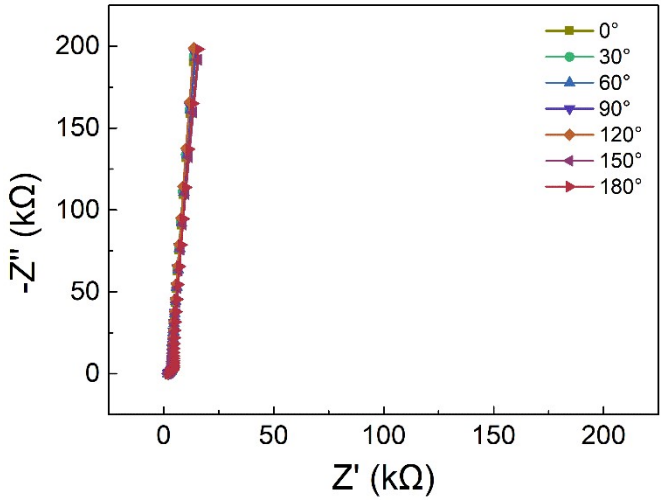

Figure S14. Nyquist plots of the FCS bending at different angles.

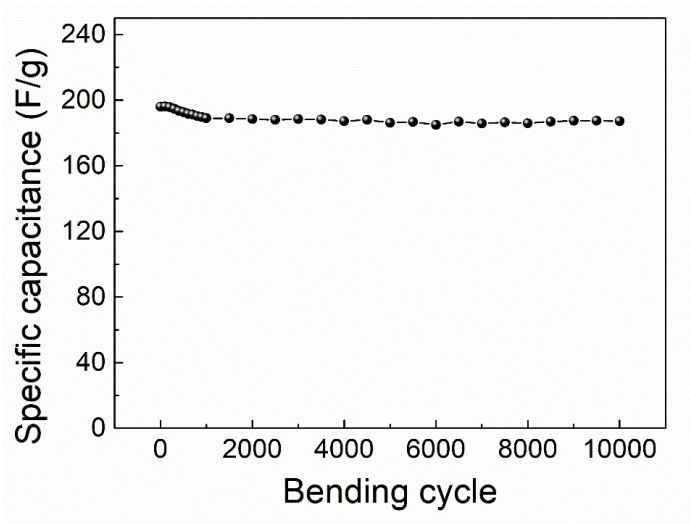

Figure S15. FSC capacitance values after different bending cycles of 0°-to-180°-to-0° .

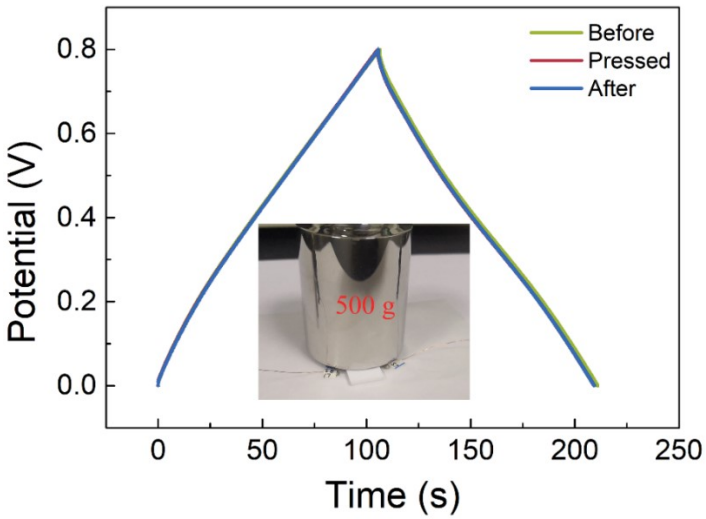

Figure S16. GCD profiles of the FCS before, during and after pressing process, and the inset is the

optical photograph of the test under compression.

Table S1. Surface area of fiber electrodes with length of 1 cm and the corresponding areal specific capacitance.

Fiber electrode	CNT fiber	N-CNT@CNT fiber	PANI@CNT fiber	PANI/N-CNT@CNT fiber
Surface area (cm^2)	4.71×10^{-3}	7.76×10^{-3}	5.97×10^{-3}	7.85×10^{-3}
Areal specific capacitance ($mF\ cm^{-2}$)	1.50	3.08	108.83	121.38

Table S2. Equivalent series resistance (R_s) and charge transfer resistance (R_{ct}) of the fiber electrodes with different structures.

Fiber electrode	CNT fiber	N-CNT@CNT fiber	PANI@CNT fiber	PANI/N-CNT@CNT fiber
R_s (Ω)	19	16	31	25
R_{ct} (Ω)	508	236	370	254

Table S3. Comparison of the Electrochemical Characteristics with Those Observed in Other Studies.[20, 21, 25, 26, 55-62]

	Electrode material	Electrolyte	Capacitance	Cycle life	Bending cycle life
This work	PANI/N-CNT@CNTF	PVA/H_3PO_4	264.8 F g^{-1} (1 A g^{-1})	92.1% (10000 cycles)	95.5% (10000 cycles)
58	PANI/CNTF	PVA/H_2SO_4	221 F g^{-1} (0.3 A g^{-1})	79.9% (10000 cycles)	85.6% (15000 cycles)
59	CNT-Au@OCNT-PANI	PVA/H_3PO_4	324 F cm^{-3} (0.5 A cm^{-3})	80% (2000 cycles)	85% (3000 cycles)
60	CNTF/CNTs/PANI	PVA/H_3PO_4	67.31 mF cm^{-2} (0.5 mA cm^{-2})	90% (5000 cycles)	99.8% (500 cycles)
61	CNT/PANI	PVA/H_3PO_4	394 F g^{-1} (2mV s^{-1})	75.7% (12000 cycles)	–
55	PANI@CNT/G	PVA/H_3PO_4	138 F g^{-1} (1 A g^{-}	77.3% (5000	–

			^{1})	cycles)	
25	CNT/PANI	PVA/H_3PO_4	111.6 F g^{-1} (0.5 A g^{-1})	90% (2000 cycles)	95.2% (5000 cycles)
21	CNT/PANI	PVA/H_3PO_4	255.5 F g^{-1} (1 A g^{-1})	69% (10000 cycles)	94% (1000 cycles)
56	IR-CNT@PANI	PVA/H_3PO_4	78 F g^{-1} (2 A g^{-1})	89% (1000 cycles)	98% (200 cycles)
57	CNT/PANI	PVA/H_3PO_4	272.7 F g^{-1} (1 A g^{-1})	90% (2000 cycles)	96.4% (200 cycles)
62	PANI/CNT	PVA/H_2SO_4	6.23 mF cm^{-2} (0.2 A g^{-1})	86% (800 cycles)	–
26	PANI/CNTF	PVA/H_3PO_4	274 F g^{-1} (1 A g^{-1})	–	97% (50 cycles)
20	PANI/CNTF	PVA/H_2SO_4	38 mF cm^{-2} (0.01 mA cm^{-2})	91% (800 cycles)	–

References

[S1] Hao Sun, Xiao You, Jue Deng, Xuli Chen, Zhibin Yang, Jing Ren and Huisheng Peng, *Adv. Mater.,* 2014, **26**, 2868-2873.

[S2] Zhuanpei Wang, Jianli Cheng, Qun Guan, Hui Huang, Yinchuan Li, Jingwen Zhou, Wei Ni, Bin Wang, Shi He, Huisheng Peng, *Nano Energy*, 2018, **45**, 210–219.

[S3] Guangxi Huang, Ye Zhang, Lie Wang, Peng Sheng, Huisheng Peng, *Carbon*, 2017, **125**, 595-604.

[S4] Yiliang Wang, Huaqiang Xuan, Gaoxin Lin, Fan Wang, Zhi Chen, Xiaoping Dong, *J. Power Sources*, 2016, **319**, 262-270.