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Supporting Information

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Self-Healable Electrically Conducting Wires for Wearable Microelectronics**

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Supporting Information

Experimental Section

Preparation of SHP fibers. A modified Leibler's method was used to synthesize the SHP.[1] Briefly, 22.8 g of DM-80 (85 wt% diacids and 10 wt% triacids, donated by Demand Chemical Co., Ltd, Shanghai) was firstly reacted with 9 g of diethylenetriamine at 160 ^{o}C in an argon atmosphere under stirring. The resulting product was dissolved in 100 mL of chloroform and washed with 100 mL of deionized water and 50 mL of methanol, followed by removal of the residual chloroform by a rotary evaporation. The purified product (1 g) was further dissolved in chloroform (10 mL) to form a uniform solution. This solution was dip-coated onto pre-cleaned glass slides, followed by evaporation of the solvent at 25 ^{o}C for 2h and heated to 80 ^{o}C for 30 min to completely remove the solvent and form a uniform film. The film was cut into narrow strips (typically with a width of 2 mm) that were further scrolled into fibers.

Preparation of aligned CNT/SHP, random orientated CNT/SHP and AgNW/CNT fibers. Aligned CNT films were directly drawn from spinnable CNT arrays (with a height of 200 μm) synthesized by chemical vapor deposition.[2,3] An aligned CNT film showed a thickness of appropriately 0.02 μm, and it was further overlapped along the length direction to form thicker films on a pre-cleaned glass slide. The SHP fiber was carefully attached onto the CNT film, followed by a scrolling process to uniformly wrap the CNT film on the fiber. The thickness of the CNT film on the SHP fiber can be controlled by varying the layer number of the stacked CNT films. Here the layer number of 2, 4, 6, 8 and 10 produced the thicknesses of 0.15, 0.27, 0.38, 0.47 and 0.59 μm, respectively. CNTs were dispersed in ethanol at a concentration of 1 mg/mL, and poly(vinylpyrrolidone) was added to the dispersion with a weight percentage of 3% relative to the CNT to improve the dispersity. Ag nanowires were also dispersed in ethanol with a concentration of 3 mg/mL. Both CNT and Ag nanowire dispersions were spray-coated on the surface of the SHP fiber, followed by drying in air for 2 h.

Electro-polymerization of PANI on aligned CNT/SHP fibers. PANI was electro-deposited onto CNT films. Briefly, the CNT-wrapped SHP fiber was firstly immersed in the electrolyte containing 0.1 M aniline and 1.0 M H_2SO_4 for 20 min to improve the infiltration of electrolyte into CNT films, and electro-polymerization of aniline was then conducted at 0.75 V vs. SCE. The mass of PANI was calculated from the total Faradic charge consumed in the reaction by assuming that an average of 2.5

electrons corresponded to one monomer.[4] The resulting fiber was then washed with de-ionized water and dried in air for 8 h.

Fabrication of self-healable wire-shaped supercapacitors. The PVA-H_2SO_4 gel electrolyte was firstly prepared by dissolving PVA powder (1 g) in deionized water (9 mL) and H_2SO_4 (1 mL). Two CNT-wrapped fibers were then coated with the PVA-H_2SO_4 gel electrolyte (mass ratio of 1/1) and dried in vacuum at room temperature. The resulting two fiber electrodes were twisted together, followed by coating another layer of electrolyte. The two electrodes were then extracted by Cu wires (diameter of 100 μm) and modified with indium for the convenience of the measurement. For the self-healing characterization, the fibers and wire-shaped supercapacitors were cut by a sharp knife, followed by contacting the two cross sections together.

Calculation of specific capacitances. The specific capacitance (C) was calculated from the equation of C=I/(dV/dt), where I and dV/dt correspond to the discharge current and slope of the discharge curve, respectively. The mass-specific capacitance C_m was obtained from the equation of C_m=2C/m, where m is the mass of active material (CNT or PANI/CNT) on one electrode. The length-specific capacitance C_L was calculated from the equation of C_L=2C/L, where L is the length of a wire-shaped supercapacitor.

Characterization. The structures were characterized by SEM (Hitachi FE-SEM S-4800 operated at 1 kV) and optical microscopy (Olympus BX51). The stress-strain curves were conducted on a Shimadzu Table-Top Universal Testing Instrument with the strain rate of 100 mm/min. The resistance was measured on a Keithley Model 2400 Source Meter. The cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and electro-polymerization were performed on an electrochemical workstation (CHI 660a). The EIS was conducted at a frequency range from 0.1 Hz to 1 MHz with an amplitude of 0.05 V. Galvanostatic charge-discharge was conducted on an Arbin multi-channel electro-chemical testing system (Arbin, MSTAT-5 V/10 mA/16 Ch).

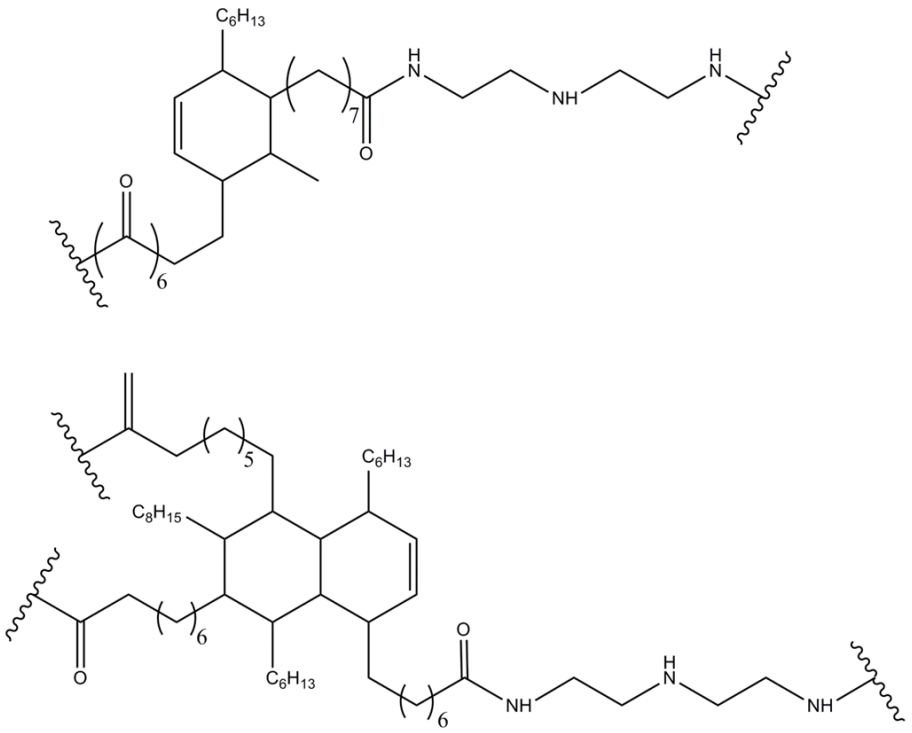

Figure S1. Chemical structure of the self-healing polymer.

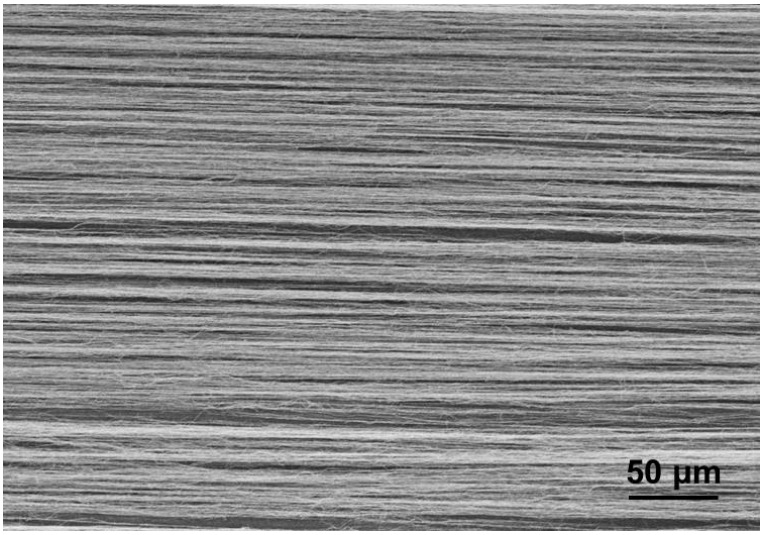

Figure S2. SEM image of a highly aligned CNT film.

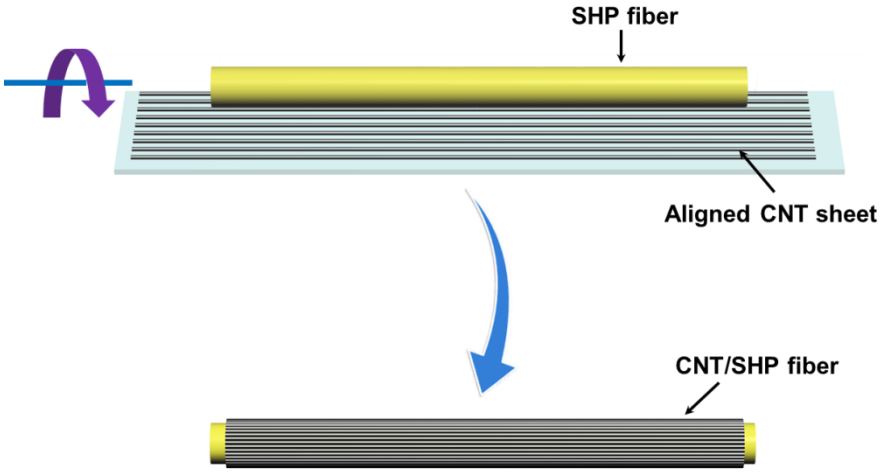

Figure S3. Schematic illustration to the preparation of the CNT/SHP fiber by a scrolling process.

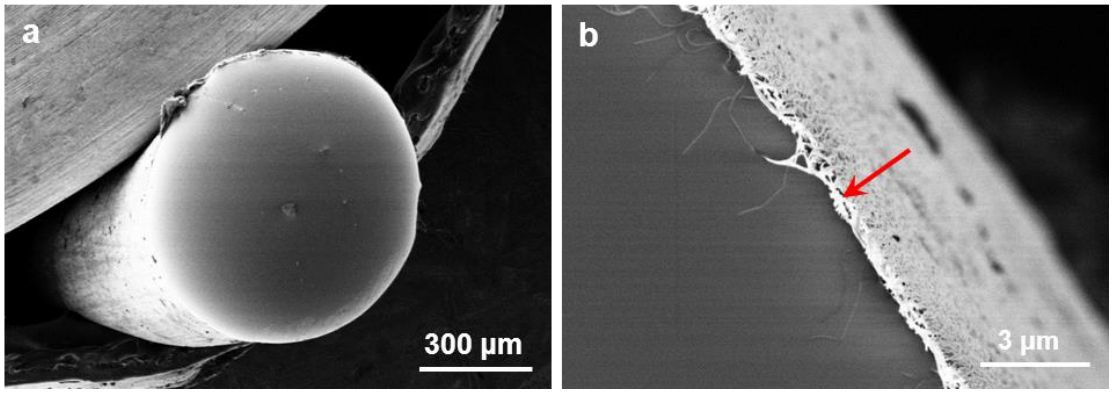

Figure S4. Cross-sectional SEM images at low and high magnifications. The arrow at **b** indicates the interface between aligned CNT and SHP. A cutting process was conducted in liquid nitrogen to get the neat cross section.

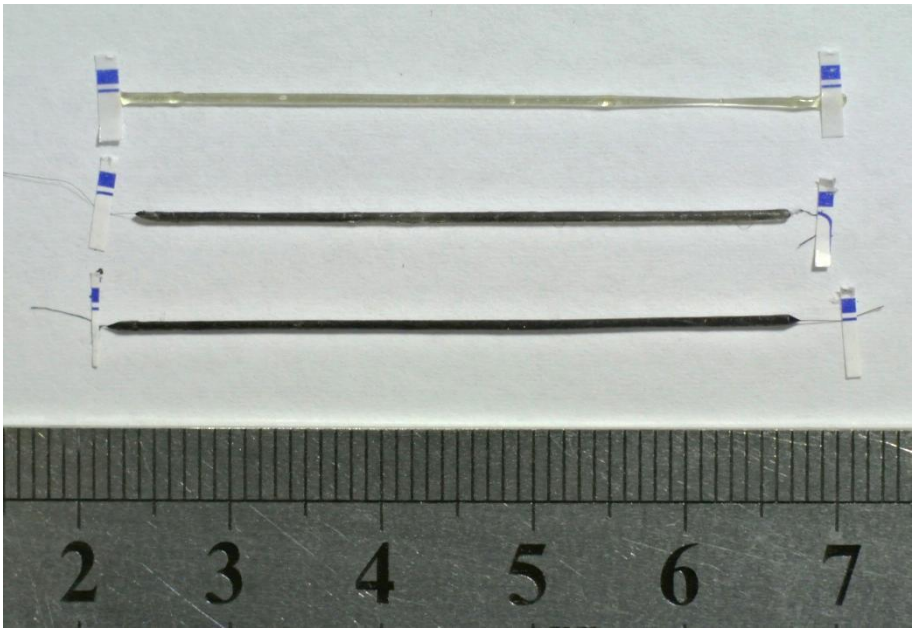

Figure S5. Photographs of a self-healing polymer fiber before (the top) and after being wrapped with CNT films with thicknesses of 0.15 μm (the middle) and 0.38 μm (the bottom).

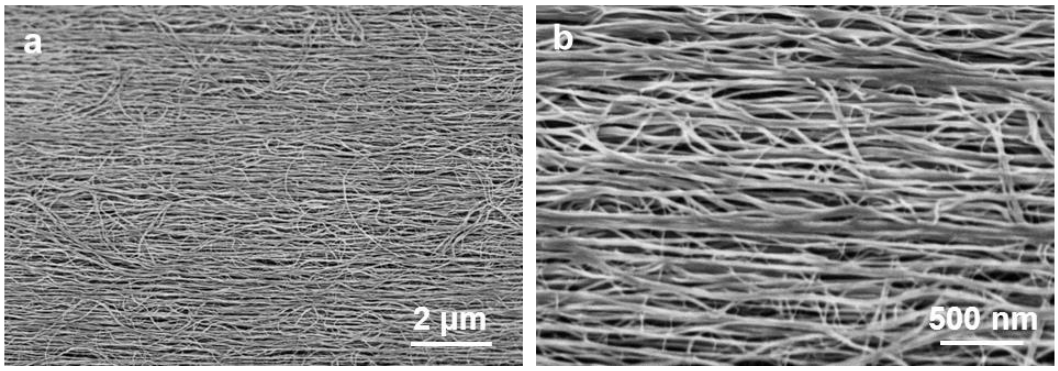

Figure S6. SEM images of the wrapped CNT film at low and high magnifications, respectively. The thickness of CNT film is 0.38 μm.

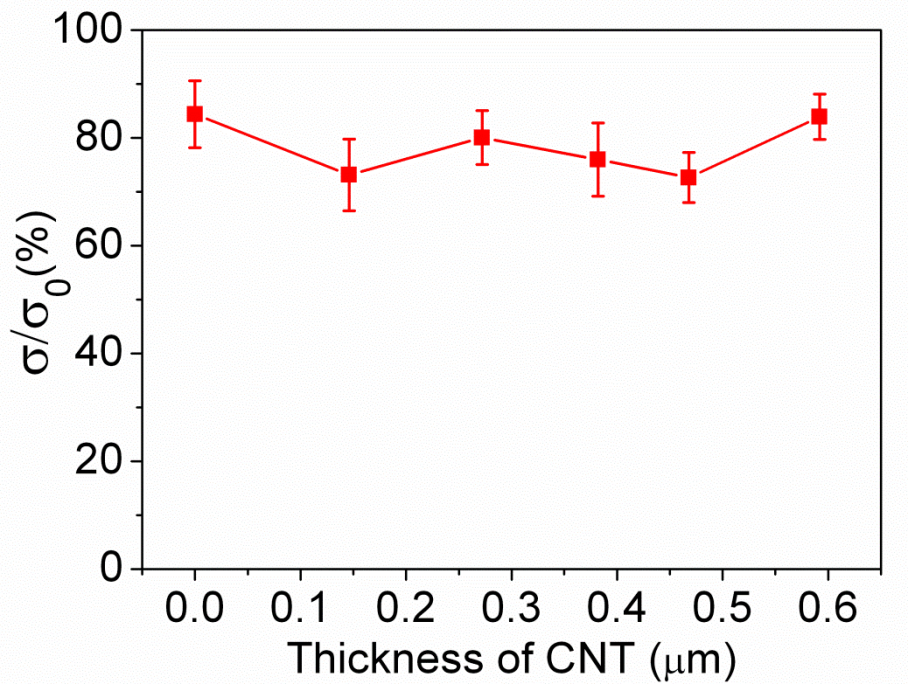

Figure S7. Tensile strengths of CNT-wrapped SHP fibers with different thicknesses of CNT films. Here σ_0 and σ correspond to the tensile strengths before breaking and after healing.

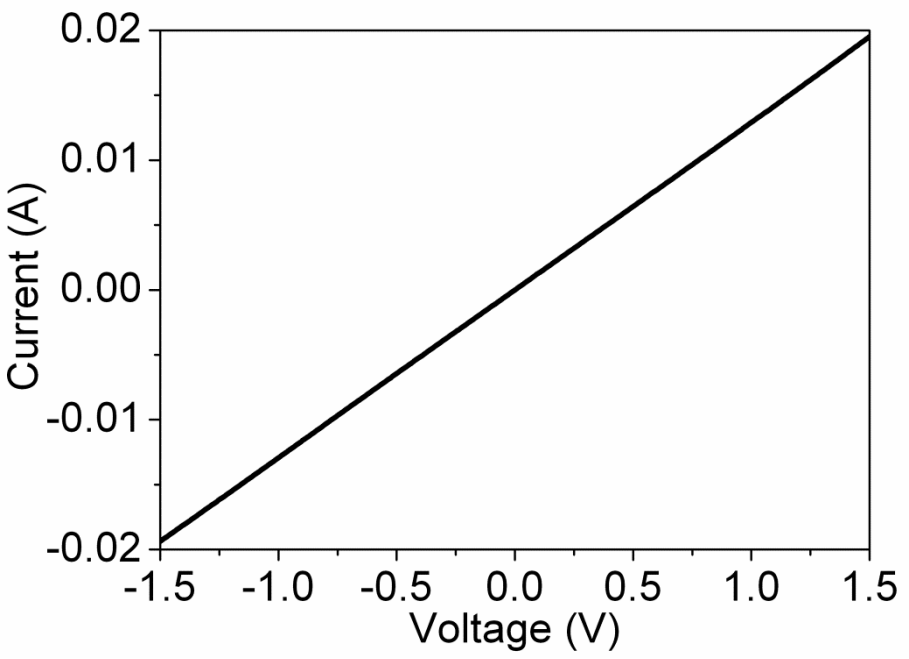

Figure S8. Typical I-V curve of an aligned CNT/SHP fiber with the length of 1 cm.

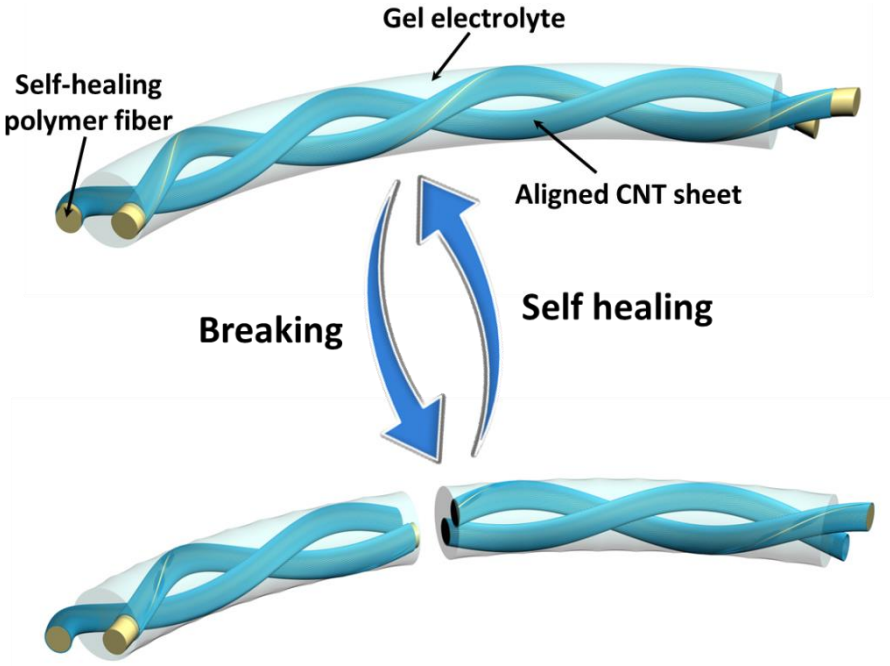

Figure S9. Schematic illustration to the self-healing of the wire-shaped supercapacitor wire.

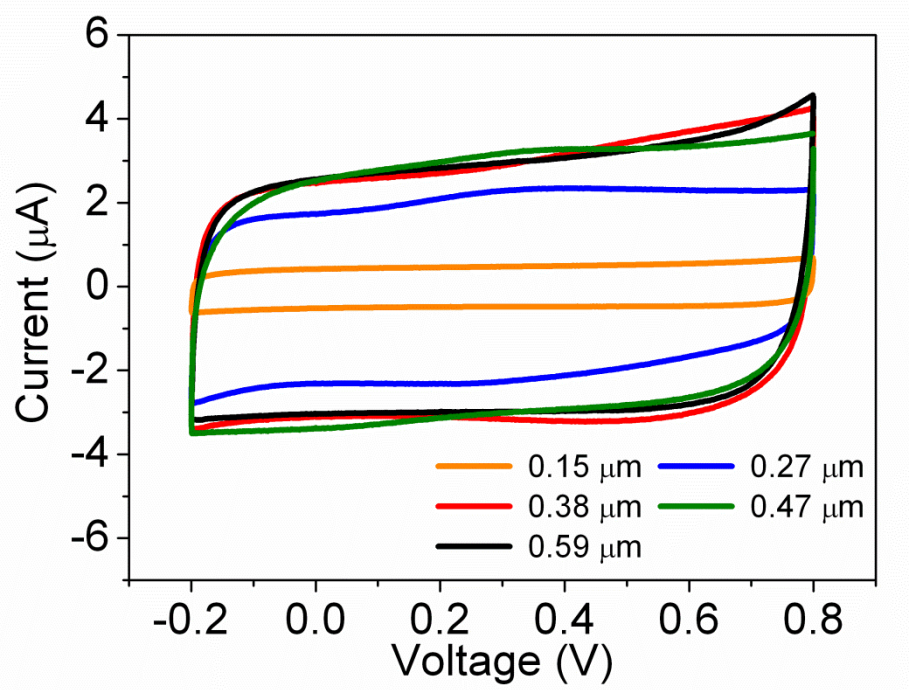

Figure S10. CV curves of self-healable wire-shaped supercapacitors with different thicknesses of aligned CNT sheets. The measurement was conducted in PVA-H_2SO_4 electrolyte at a scan rate of 100 mV s^{-1} with the potential range from -0.2 to 0.8 V.

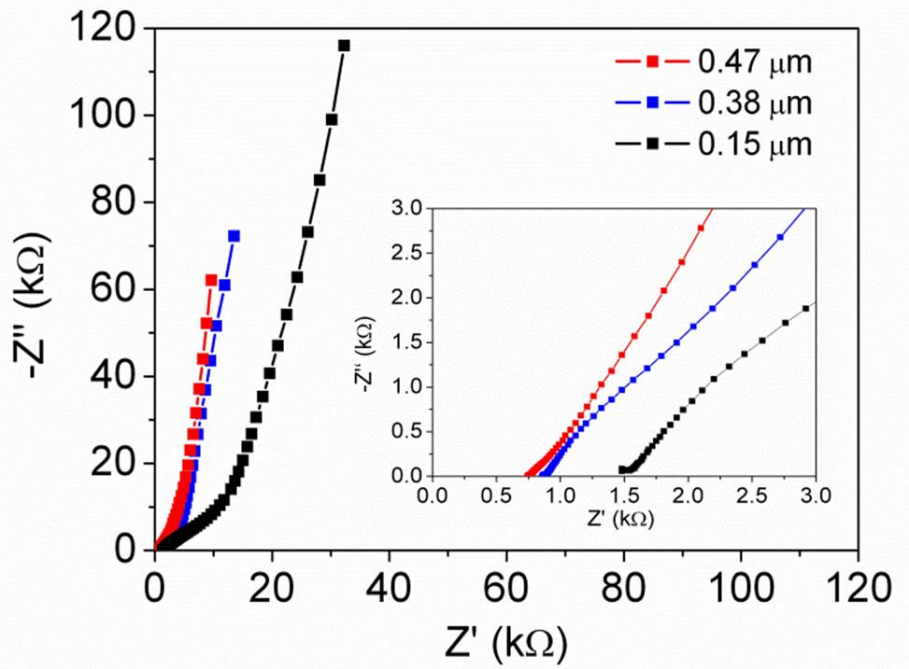

Figure S11. Nyquist plots of wire-shaped supercapacitors with different thicknesses of aligned CNT films. The inserted image represents the high-frequency region.

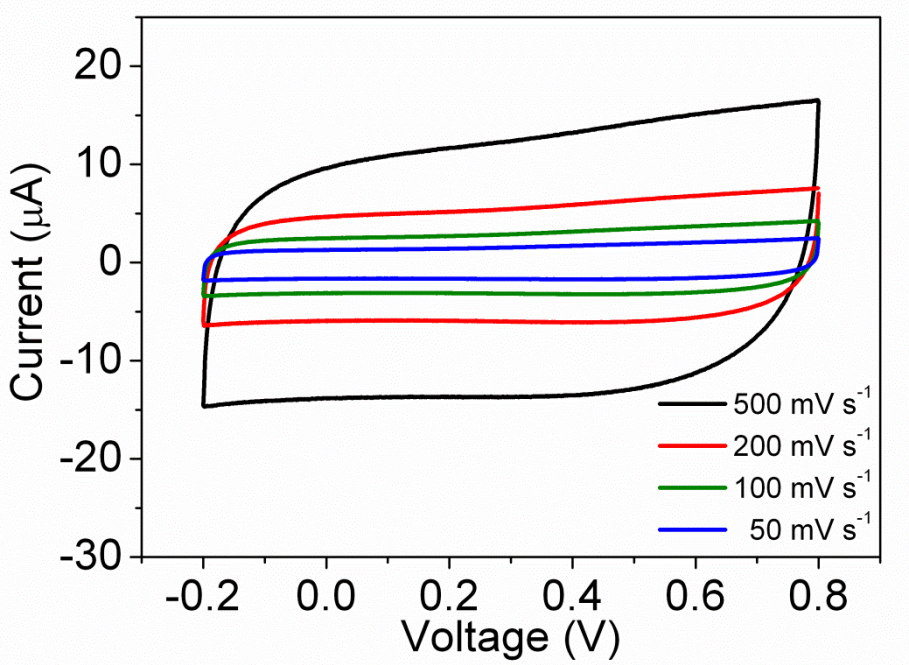

Figure S12. CV curves of a wire-shaped supercapacitor based on aligned CNT/SHP fibers with increasing scan rates from 50 to 500 mV s^{-1} at the CNT thickness of 0.38 μm.

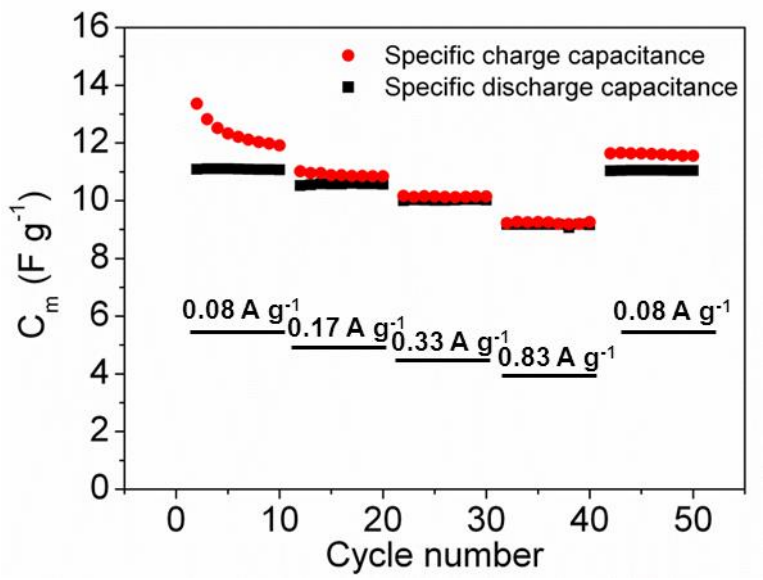

Figure S13. Dependence of specific capacitance on current density for a wire-shaped supercapacitor based on aligned CNT/SHP fibers. The thickness of CNT sheet was 0.38 μm.

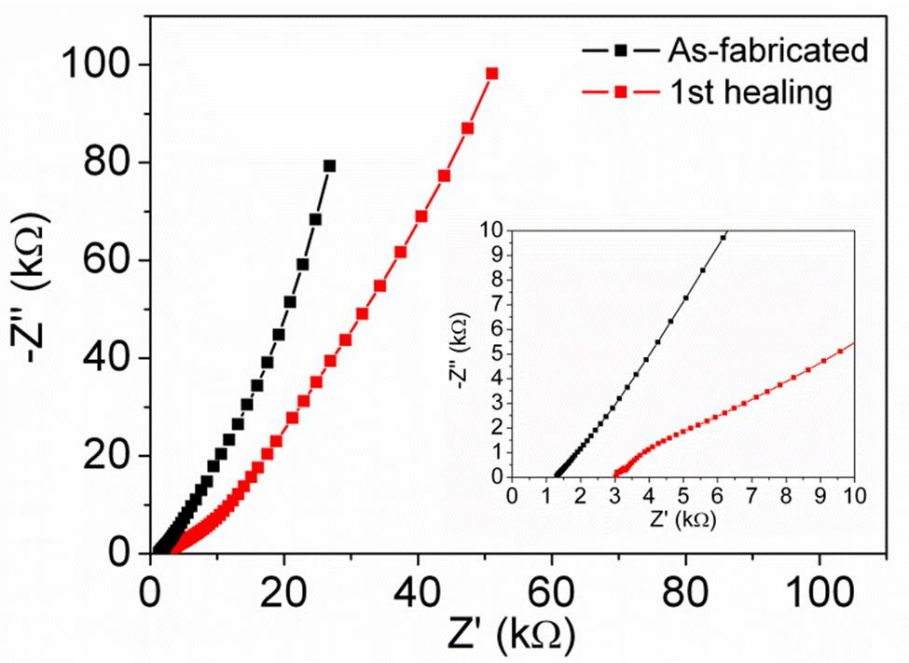

Figure S14. Nyquist plots of a wire-shaped supercapacitor based on aligned CNT/SHP fibers before and after healing. The inserted image represents the high-frequency region. The thickness of CNT sheet was 0.38 μm.

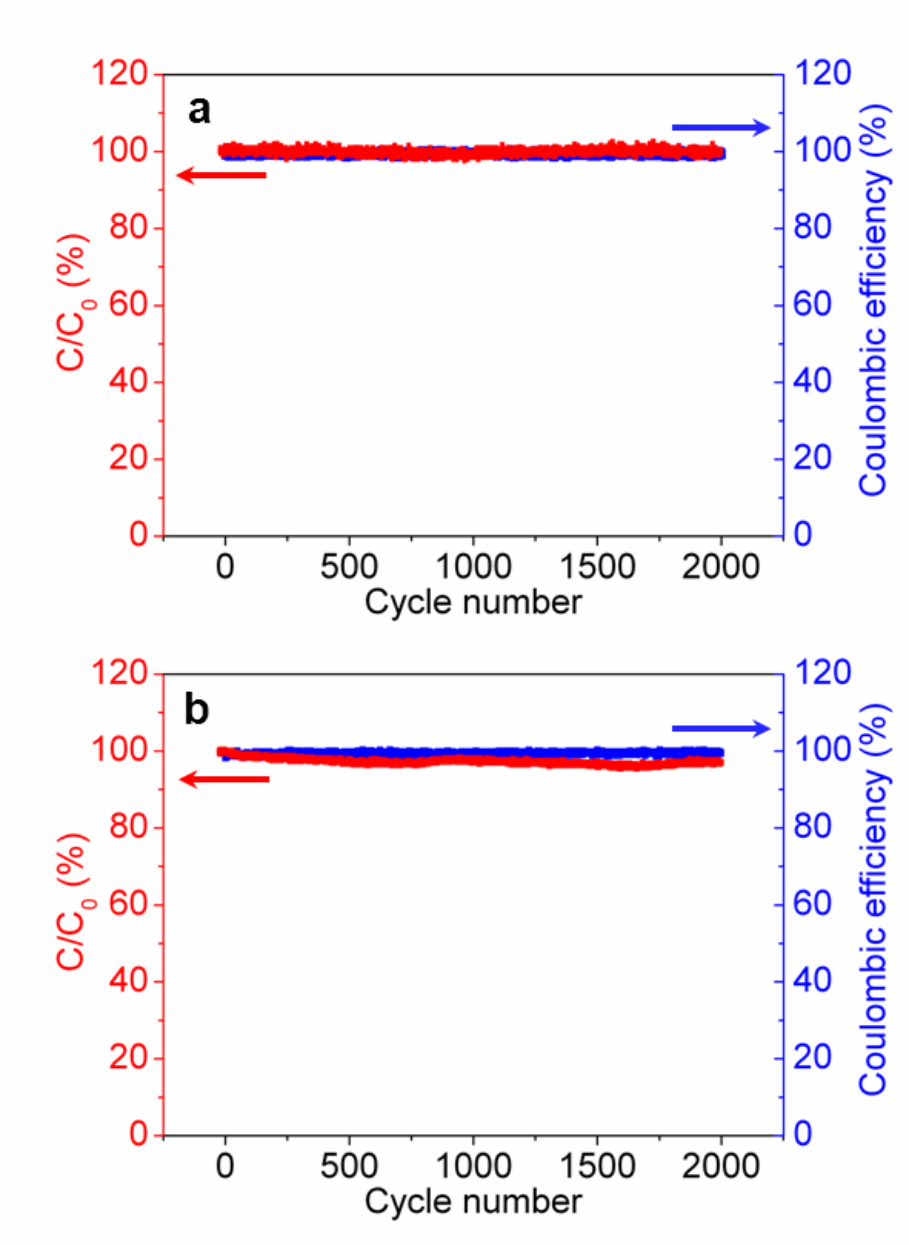

Figure S15. Specific capacitances and Coulombic efficiencies of a wire-shaped supercapacitor based on aligned CNT sheet before breaking (**a**) and after self-healing (**b**) during 2000 charge-discharge cycles. Here C_0 and C correspond to the specific capacitances before breaking and after self-healing, respectively. The specific capacitances are calculated from the galvanostatic charge-discharge results at a current density of 0.17 A g^{-1}. The aligned CNT sheet shows a thickness of 0.38 μm.

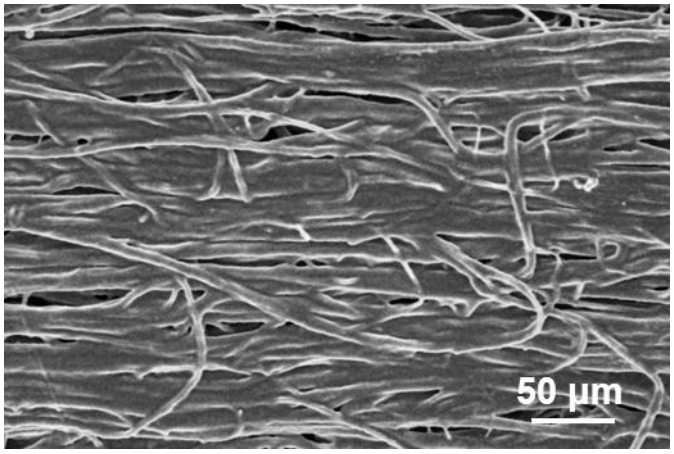

Figure S16. SEM image of an aligned CNT/SHP fiber after deposition of PANI. The thickness of CNT film is 0.27 μm with the PANI/CNT mass ratio of 1/1.

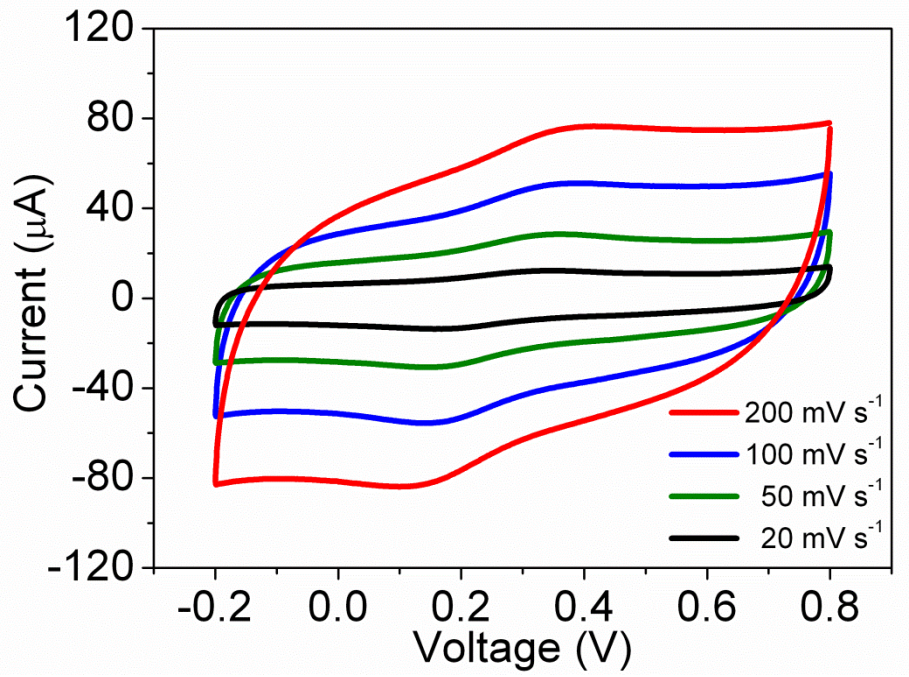

Figure S17. CV curves of a self-healable wire-shaped supercapacitor with the incorporation of PANI.

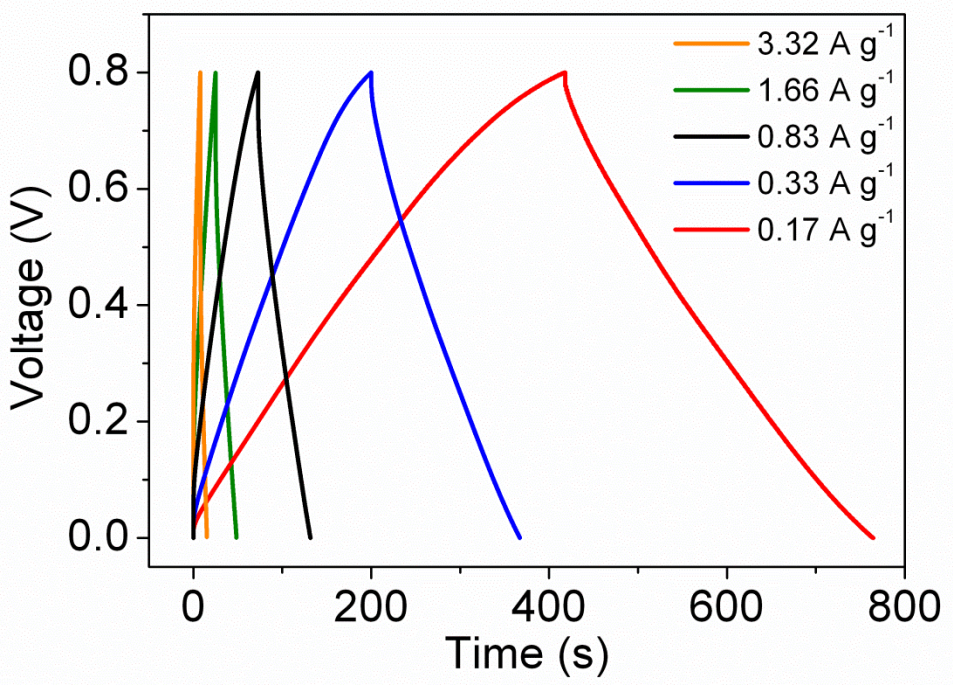

Figure S18. Galvanostatic charge-discharge curves of a wire-shaped supercapacitor with the use of PANI at different current densities.

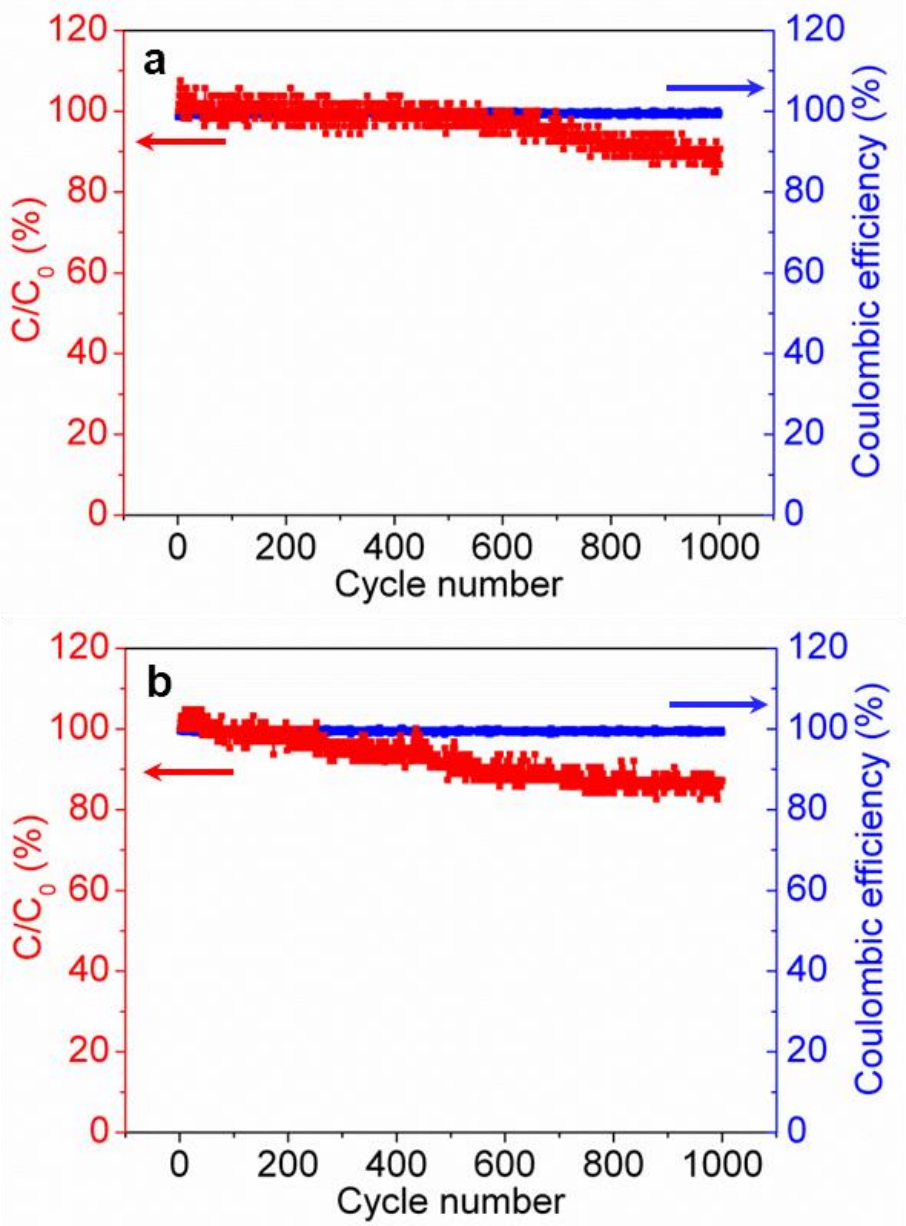

Figure S19. Specific capacitances and Coulombic efficiencies of a wire-shaped supercapacitor with the use of PANI before breaking (**a**) and after healing (**b**) during 1000 charge-discharge cycles. Here C_0 and C correspond to the specific capacitance before breaking and after self-healing, respectively. The specific capacitances are calculated from the galvanostatic charge-discharge results at a current density of 1.66 A g^{-1}. The thickness of aligned CNT sheet is 0.27 μm with PANI/CNT mass ratio of 1/1.

Refencences for the Supporting Information

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[2] W. Wang, X. Sun, W. Wu, H. Peng, Y. Yu, *Angew. Chem. Int. Ed.* **2012**, *124*, 4722-4725.

[3] H. Peng, X. Sun, F. Cai, X. Chen, Y. Zhu, G. Liao, D. Chen, Q. Li, Y. Lu, Y. Zhu, *Nature Nanotechnol.* **2009**, *4*, 738-741.

[4] H. Lin, L. Li, J. Ren, Z. Cai, L. Qiu, Z. Yang, H. Peng, *Sci. Reports.* **2013**, *3*.