ADVANCED MATERIALS

Supporting Information

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Fabricating Continuous Supercapacitor Fibers with High Performances by Integrating All Building Materials and Steps into One Process

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Supporting Information

Supplementary Video

Movie S1. Continuous fabrication of a fiber-shaped supercapacitor.

Supplementary Notes

The calculation of electrochemical parameters. The specific capacitance C was calculated from the equation of $C= I/(dV/dt)$, where I and dV/dt are the discharge current and the slope of the discharge curve, respectively. The volumetric specific capacitance C_V was obtained from the equation of $C_V=C/V$, where V is the volume of the fibrous electrode and calculated from the equation of $V=\pi d^2/4$. Here d is the diameter of the composite fiber electrode. The areal specific capacitance C_A was obtained from the equation of $C_A=C/A$, where A is the area of the fibrous electrode. It is calculated from the equation of $A=\pi dL$, where d and L stand for the diameter and the length of the composite fiber electrode, respectively.

The volumetric energy density of the supercapacitor E_V was derived from the equation of $E_V=C_V\Delta V^2/(8\times3600)$, where ΔV is the operating voltage window. The areal energy density E_A was derived from the equation of $E_A=C_A\Delta V^2/(8\times3600)$. The volumetric power density of the supercapacitor was calculated from the galvanostatic curves at different charge/discharge current densities using the equation of $P_V=E_V\times3600/\Delta t$, where Δt is the discharge time. The areal power density was calculated by equation of $P_A=E_A\times3600/\Delta t$.

Supplementary Figures

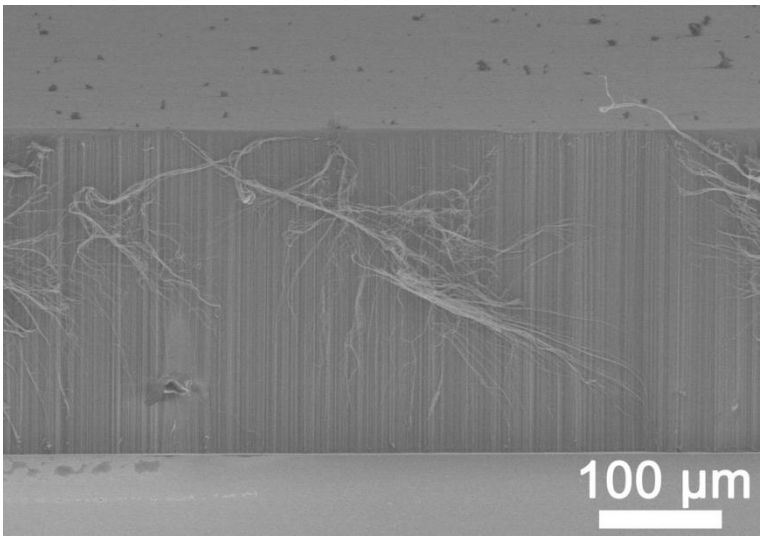

Figure S1. SEM image of the cross-sectional view of a spinnable CNT array. The CNT array was grown on a silicon wafer by chemical vapor deposition.

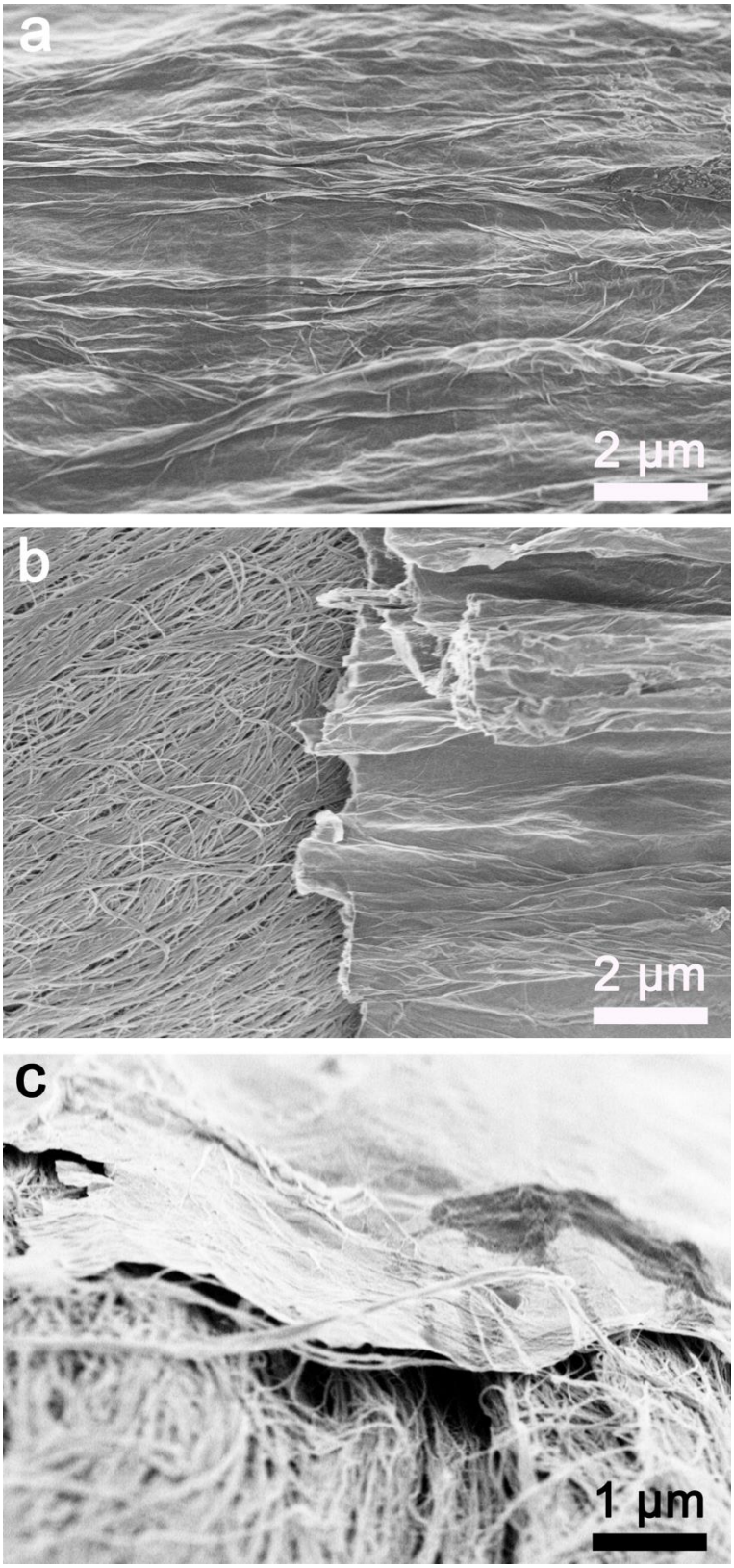

Figure S2. a. High magnification SEM image of the CNT/RGO composite fiber. Part of RGO on the surface was removed to expose the CNTs. **b** and **c.** High magnification SEM images of the RGO layer wrapped on the CNT fiber. The deposition time for this CNT/RGO composite fiber was 120 s.

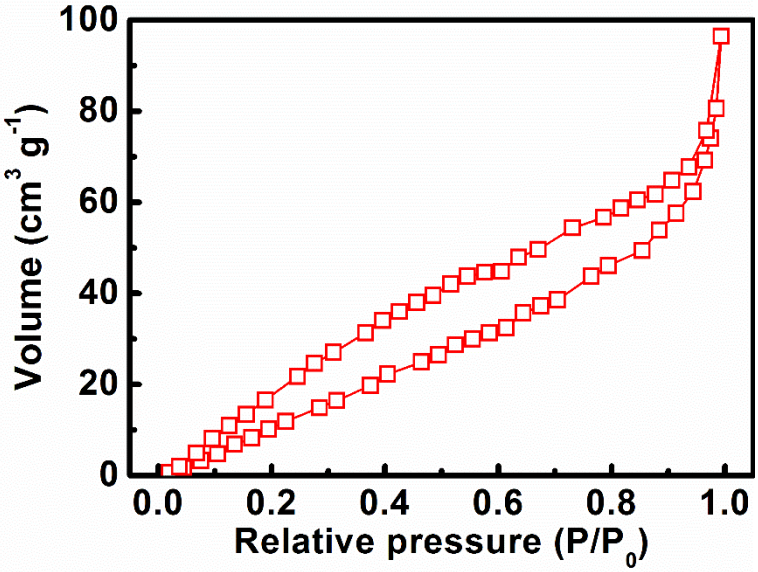

Figure S3. Nitrogen adsorption–desorption isotherm of RGO sheets. The RGO samples were peeled from the CNT/RGO composite fibers.

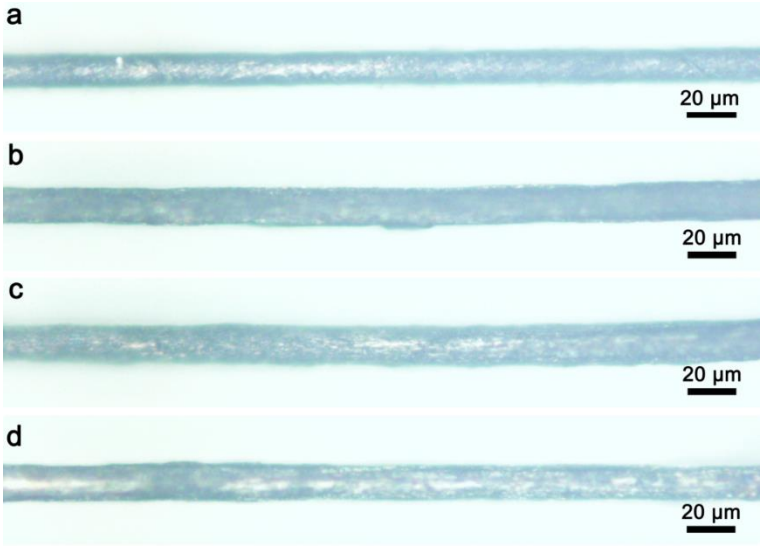

Figure S4. Optical microscopic images of a CNT/RGO composite fiber. The deposition time for this CNT/RGO fiber was 180 s. Four sections were taken from a 1 m composite fiber at four points: 20 cm, 40 cm, 60 cm and 80 cm. Each section had a length of 5 mm and was observed under an optical microscope. The four sections of the CNT/RGO composite fiber had a uniform diameter and morphology.

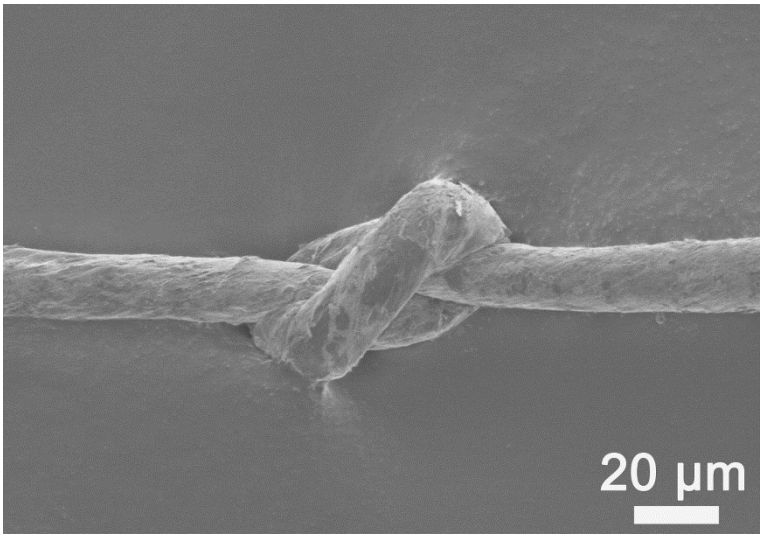

Figure S5. SEM image of a knotted CNT/RGO composite fiber. The deposition time for this sample was 180 s.

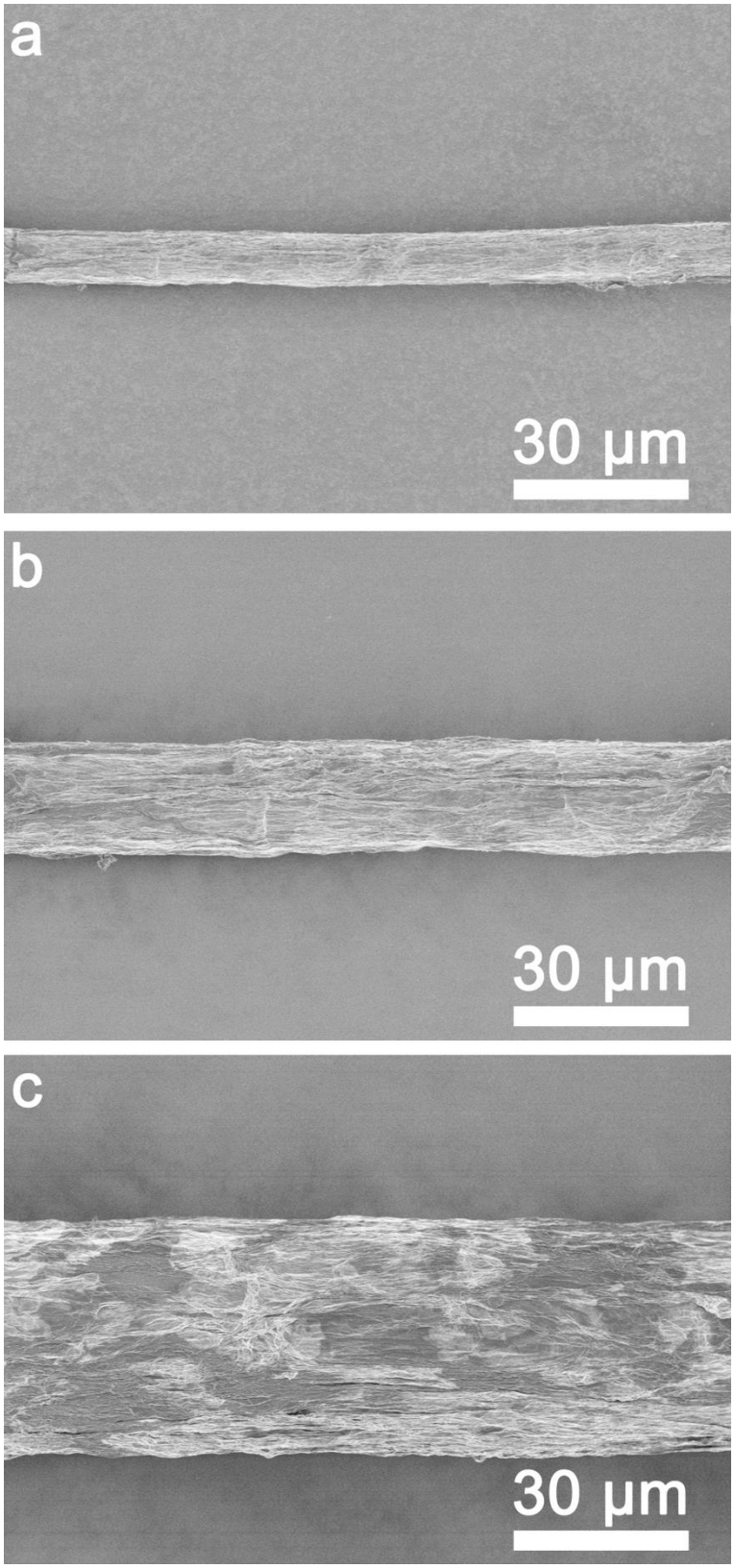

Figure S6. SEM images of CNT/RGO composite fibers of different diameters. The initial diameters of CNT fibers were 10 μm (**a**), 20 μm (**b**) and 35 μm (**c**). The deposition time for these samples was 180 s.

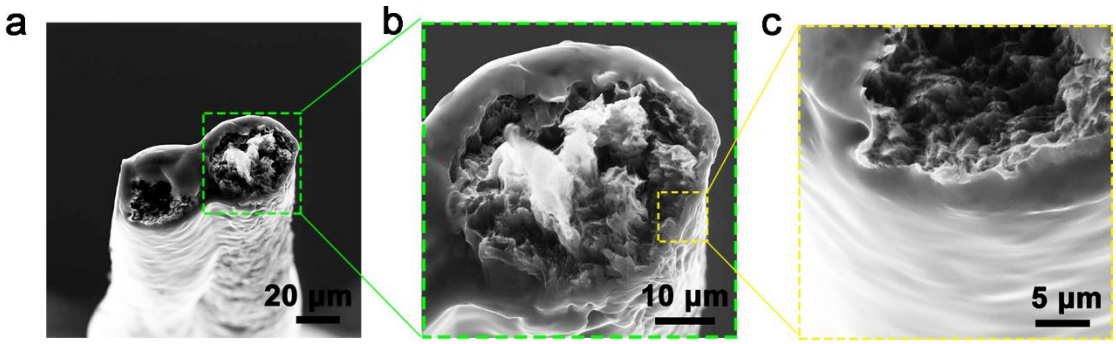

Figure S7. Cross-sectional SEM images of fiber-shaped supercapacitor made from CNT/RGO composite fibers by a localized view of the interface between the electrolyte and electrode. **a.** The fiber-shaped supercapacitor. **b.** Magnified image of **a**, displaying a CNT/RGO composite fiber externally coated with electrolyte. **c.** Magnified image of **b**. The fiber-shaped supercapacitor was broken up in a liquid nitrogen.

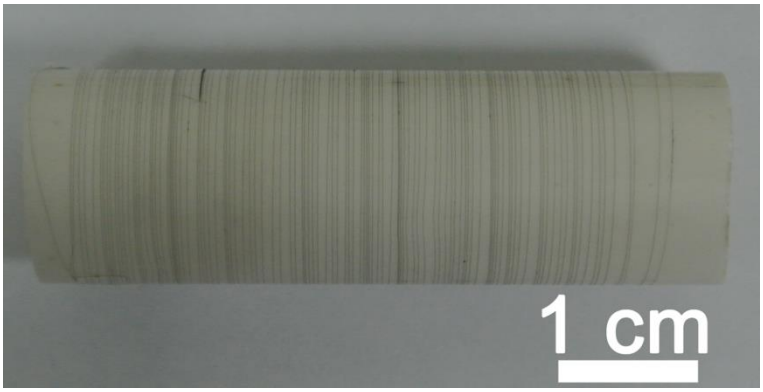

Figure S8. Photograph of a 5 m-long fiber-shaped supercapacitor wrapped on a plastic tube. The supercapacitor was made by twisting two CNT/RGO composite fibers.

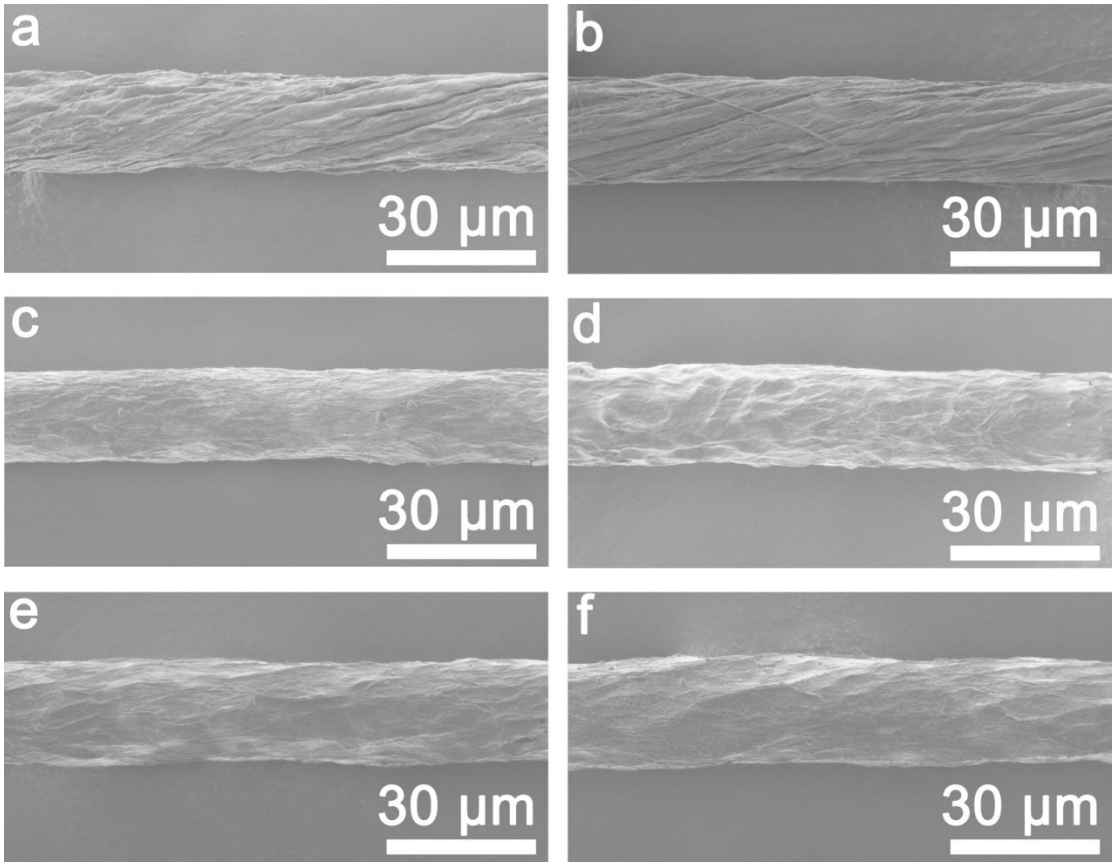

Figure S9. SEM images of CNT/RGO composite fibers prepared under different deposition time. **a.** 30 s. **b.** 60 s. **c.** 120 s. **d.** 180 s. **e.** 240 s. **f.** 300 s. The original diameter of CNT fiber was 20 μm.

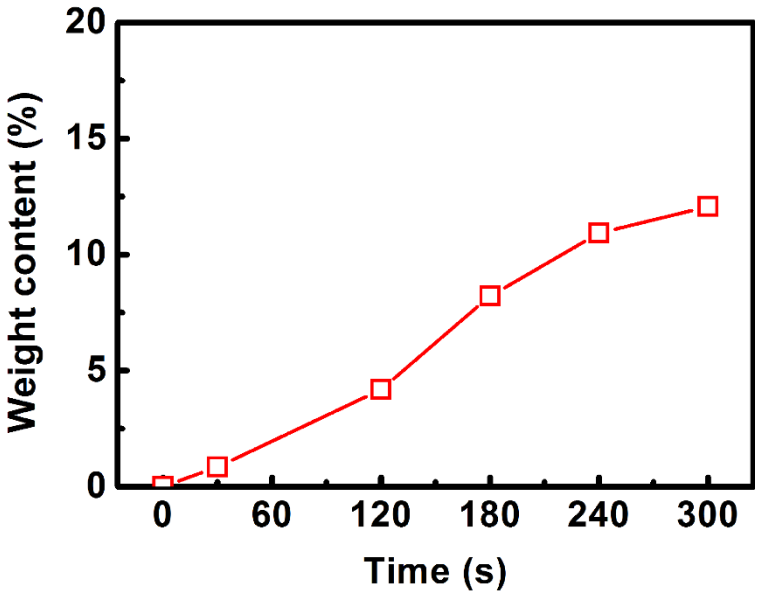

Figure S10. The weight content of RGO in CNT/RGO composite fibers prepared under different deposition time. The masses of CNT fibers and CNT/RGO composite fibers were defined by an element analytical balance.

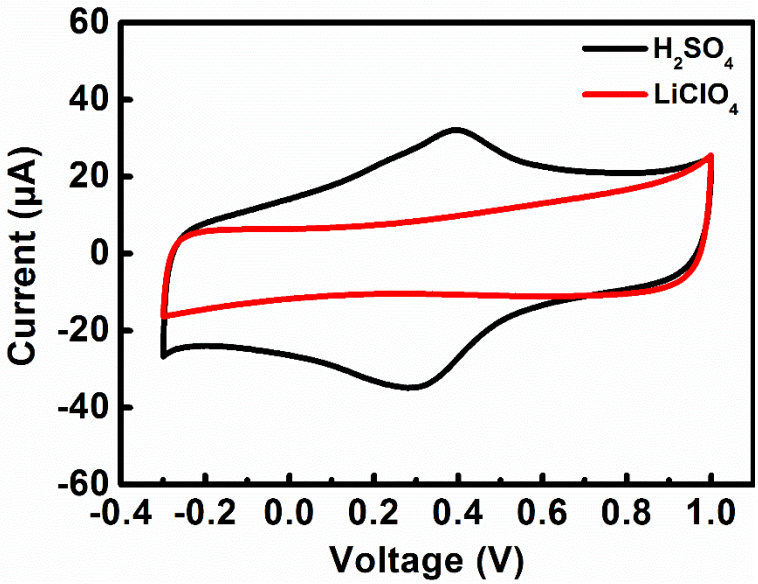

Figure S11. Cyclic voltammograms of a CNT/RGO composite fiber prepared in 1 M H_2SO_4 and $LiClO_4$ solutions. The CV tests were performed through a three electrode system with the CNT/RGO composite fiber as the working electrode, platinum wire as the counter electrode and Hg/Hg_2Cl_2 as the reference electrode. The voltage was scanned between –0.3 to 1.0 V at a scanning rate of 50 mV s^{-1}. The deposition time for the composite fiber was 180 s.

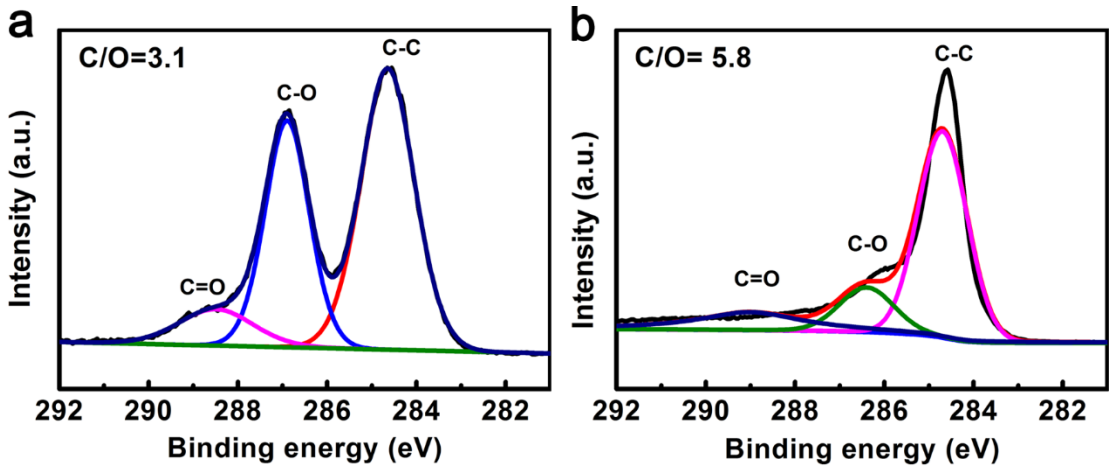

Figure S12. X-ray photoelectron spectra of CNT/GO composite fiber (**a**) and CNT/RGO composite fiber (**b**). The deposition time for the CNT/RGO composite fiber was 180 s. The carbon/oxygen ratio was increased from 3.1 to 5.8 after reduction, indicating that the GO was partially reduced during the process.

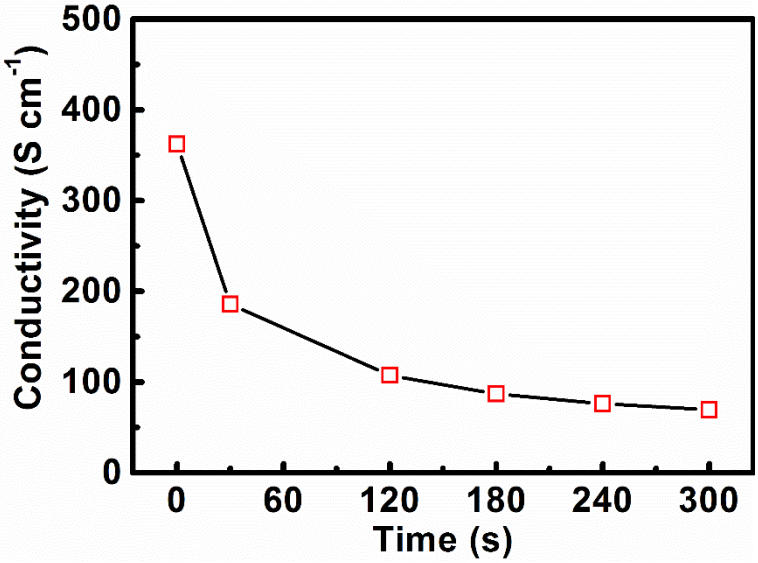

Figure S13. Electrical conductivities of CNT/RGO composite fibres prepared at different depositing times. The original diameter of CNT fiber was 20 μm.

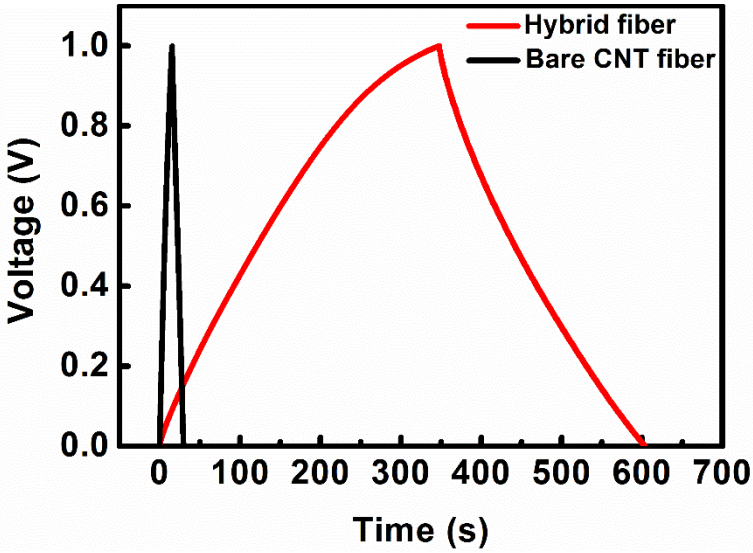

Figure S14. Galvanostatic charge-discharge curves of fiber-shaped supercapacitors based on bare CNT and CNT/RGO composite fibers at 62 mA cm^{-3}. The deposition time for CNT/RGO composite fiber here was 180 s.

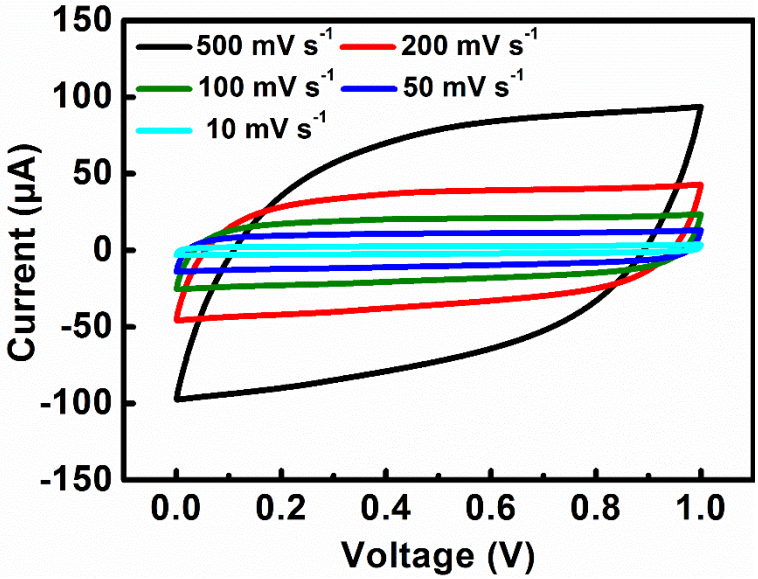

Figure S15. Cyclic voltammograms of fiber-shaped supercapacitors based on CNT/RGO composite fibers at increasing scan rates. The deposition time for CNT/RGO composite fiber here was 180 s.

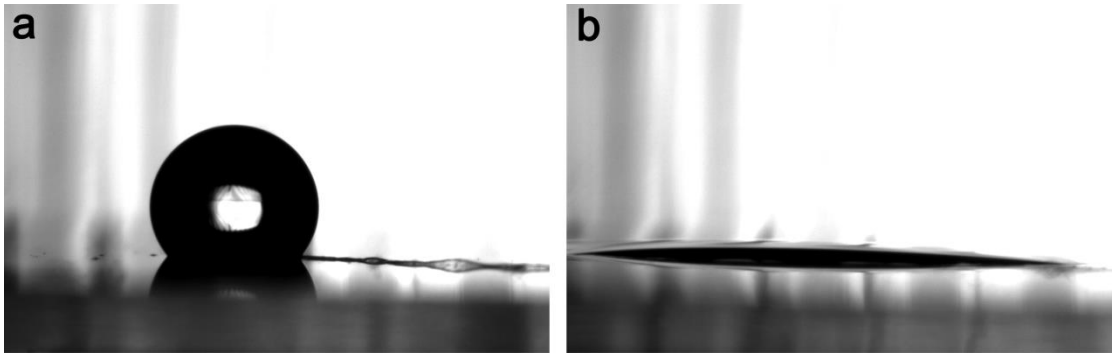

Figure S16. The hydrophilicity of CNT and CNT/RGO composite. The contact angle measurements were conducted on planar samples. **a.** CNT sheets. **b.** CNT/RGO composite sheets. The CNT/RGO composite sheets were prepared through the same electrochemical deposition method. The deposition time was 180 s. The contact angles of CNT and CNT/RGO composite are 137^{o} and 10^{o}, respectively.

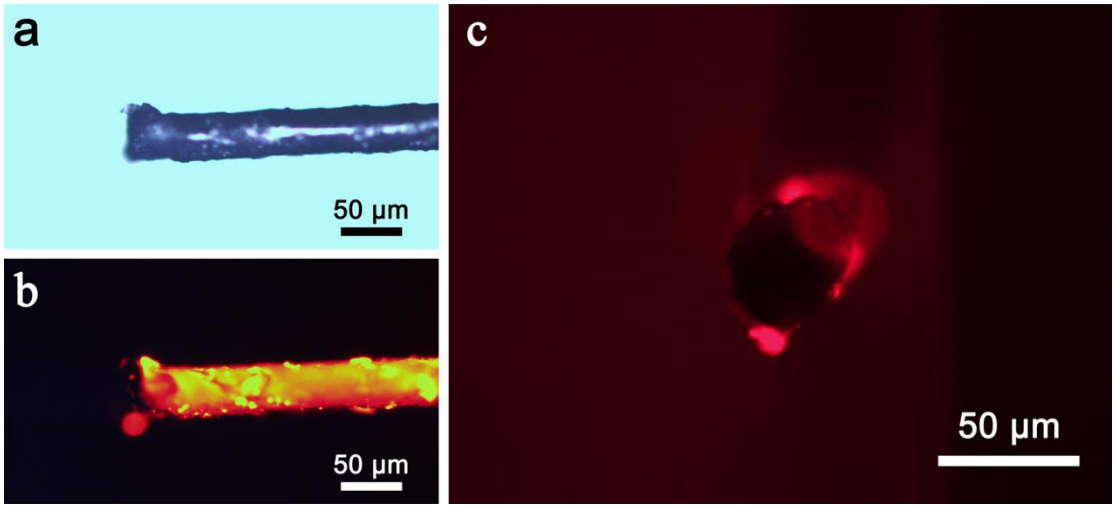

Figure S17. a. Optical microscopic image of a CNT/RGO composite fiber coated with electrolyte. **b.** Fluorescent microscopic image of **a. c.** Fluorescent microscopic image of the cross section of the CNT/RGO composite fiber. The deposition time for the composite fiber was 180 s. To demonstrate the infiltration of electrolyte in the composite fiber, rhodamine was added to the electrolyte as a fluorescent indicator. The CNT/RGO composite fiber was dip-coated with rhodamine-added electrolyte and observed under fluorescent microscope. The red fluorescent signals indicated the distribution of electrolyte. It reveals that the electrolyte mainly gathered on the near surface and was rarely infiltrated inside the electrode.

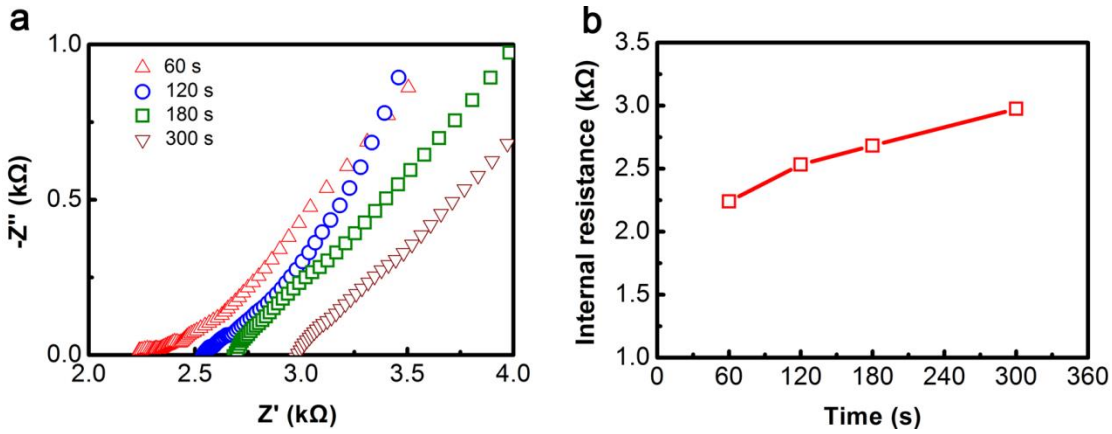

Figure S18. a. Electrochemical impedance spectra of fiber-shaped supercapacitors made from CNT/RGO composite fibers that were prepared under different deposition time. **b.** Internal resistances that derived from the horizontal intercepts of **a**. The electrochemical impedance measurement was conducted from 10 mHz to 1 MHz with a voltage amplitude of 5 mV.

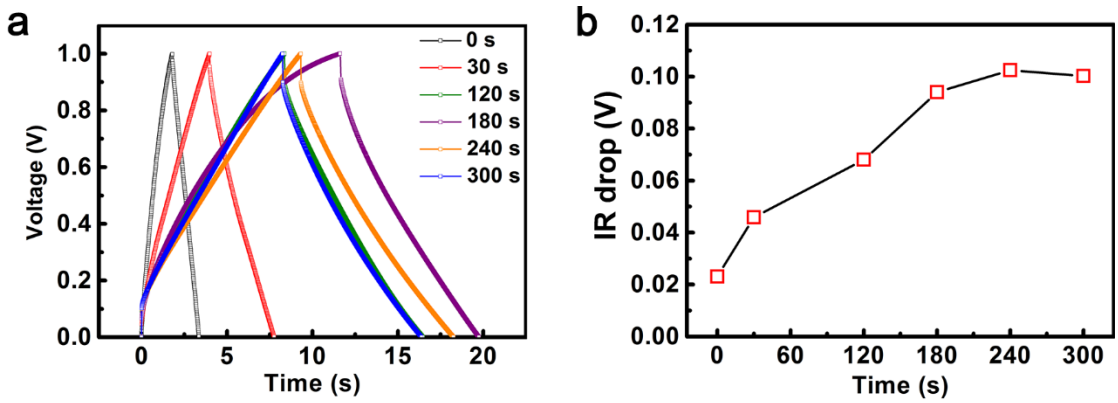

Figure S19. a. Galvanostatic charge-discharge curves of fiber-shaped supercapacitors made from CNT/RGO composite fibers that were prepared under different deposition time. The current density for charge and discharge was 2500 mA cm^{-3}. All the samples for electrochemical tests had the same length. **b.** The relation of voltage drops induced by internal resistance with deposition time. The IR drops were defined from charge-discharge curves in **a.**

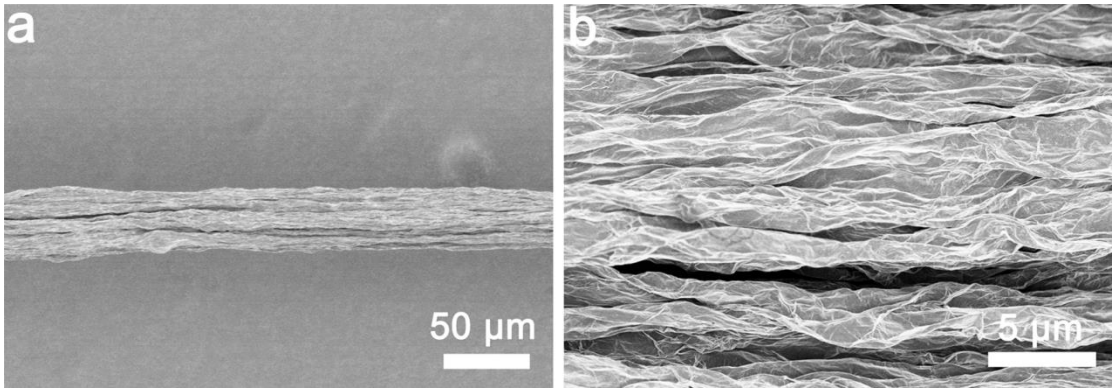

Figure S20. SEM images of graphene fibers at low (**a**) and high (**b**) magnifications. The graphene fiber was prepared through wet-spinning method (C. Gao et al., *Adv. Mater.* 2013, 25, 188.) and had a diameter of 40 μm. The conductivity of the graphene fiber was 48.9 S cm^{-1}.

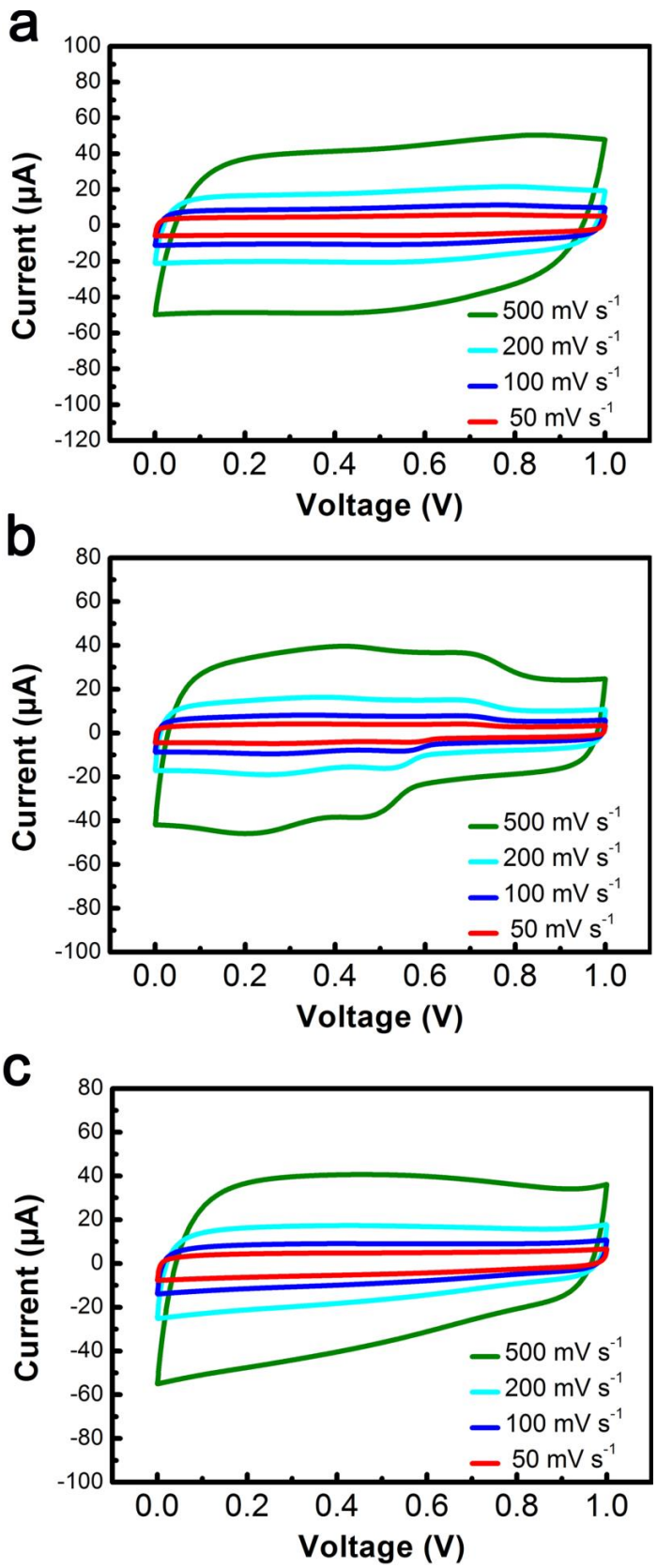

Figure S21. Cyclic voltammograms of fiber-shaped supercapacitors based on CNT/MnO_2 composite fibers (**a**), CNT/PANI composite fibers (**b**) and CNT/PPy composite fibers (**c**).

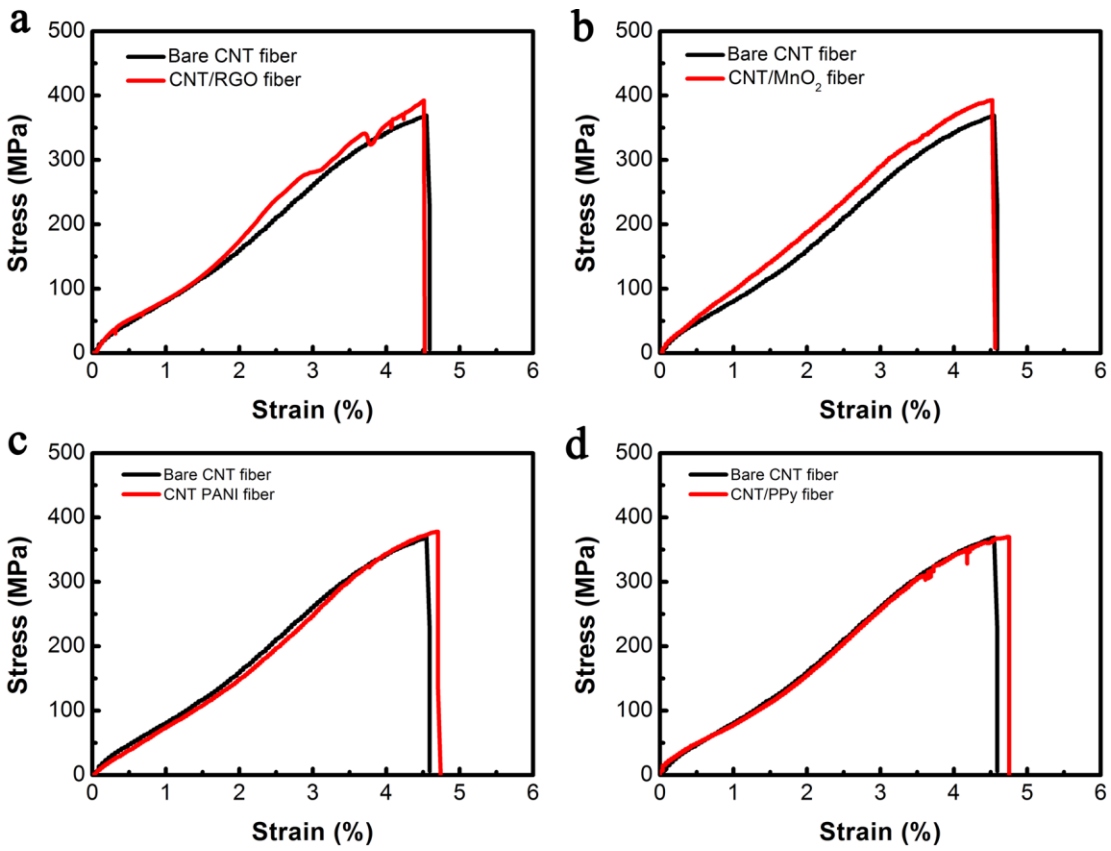

Figure S22. Stress-strain curves of different composite fibers prepared from electrochemical deposition method. **a.** CNT/RGO composite fiber. Deposition time: 180 s. **b.** CNT/MnO_2 composite fiber. **c.** CNT/PANI composite fiber. **d.** CNT/PPy composite fiber. The original CNT fiber had a diameter of 20 μm. Bare CNT fiber was used as a reference. The tensile strengths for different composite fibers are listed below. CNT fiber: 369.3 MPa; CNT/RGO fiber: 392.5 MPa; CNT/MnO_2 fiber: 393.1 MPa; CNT/PANI: 378.1 MPa; CNT/PPy fiber: 369.8 MPa.

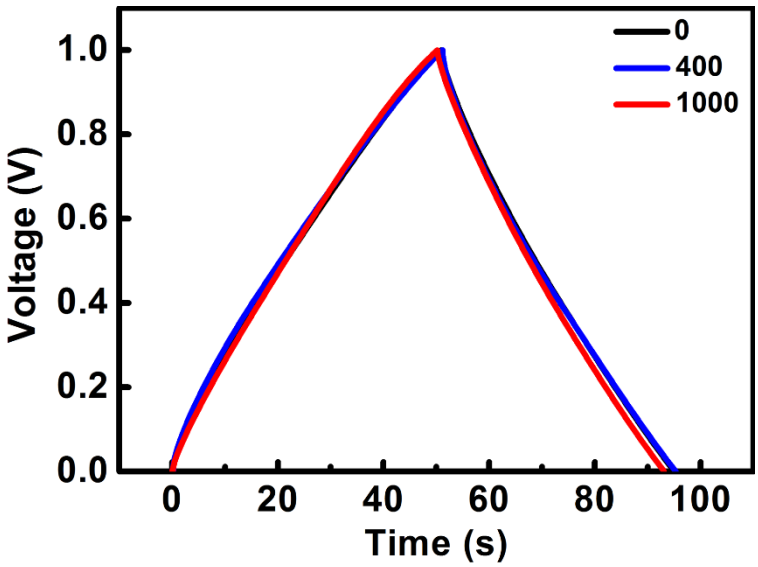

Figure S23. Galvanostatic charge-discharge curves of a fiber-shaped supercapacitor before and after being bent to 180 ^{o} for 400 and 1000 cycles. The supercapacitor was made from CNT/RGO composite fibers. The current density for charge and discharge was 310 mA cm^{-3}.

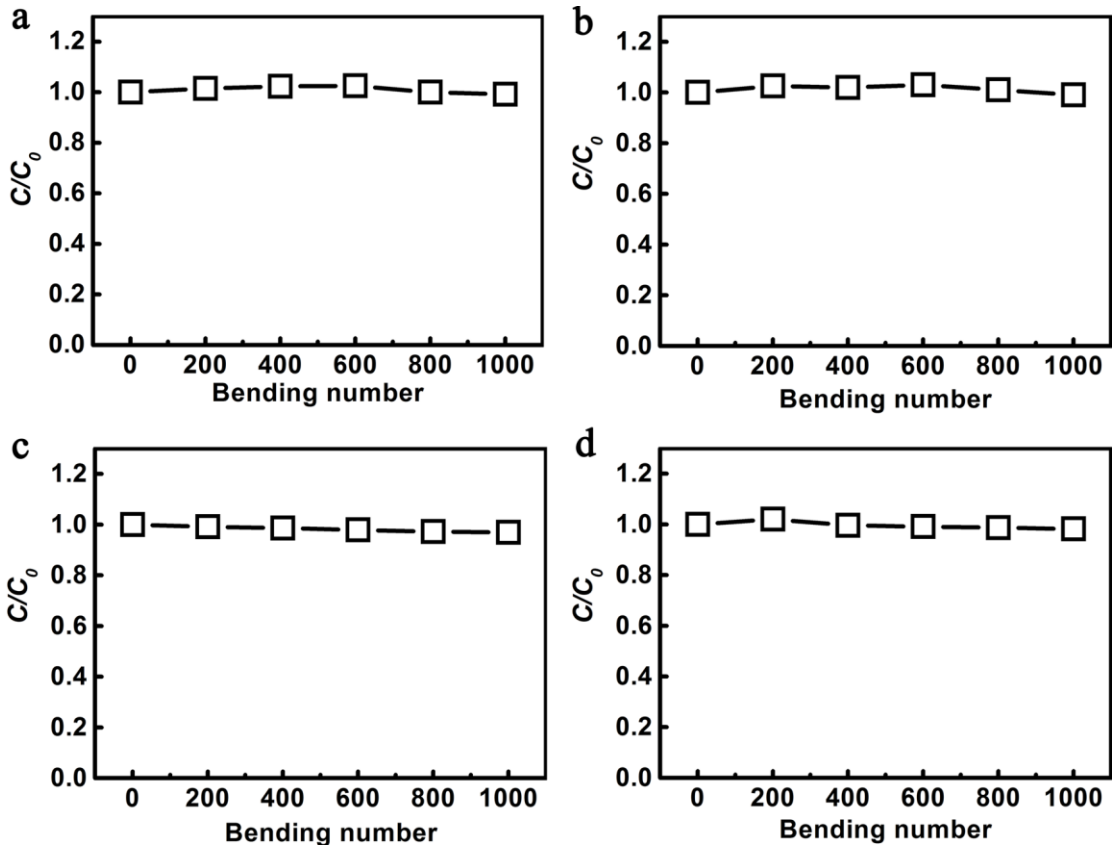

Figure S24. Dynamic bending tests of fiber-shaped supercapacitors made from CNT/RGO composite fibers (**a**), CNT/MnO_2 composite fibers (**b**), CNT/PANI composite fibers (**c**) and CNT/PPy composite fibers (**d**). The bending angle was 180 °.

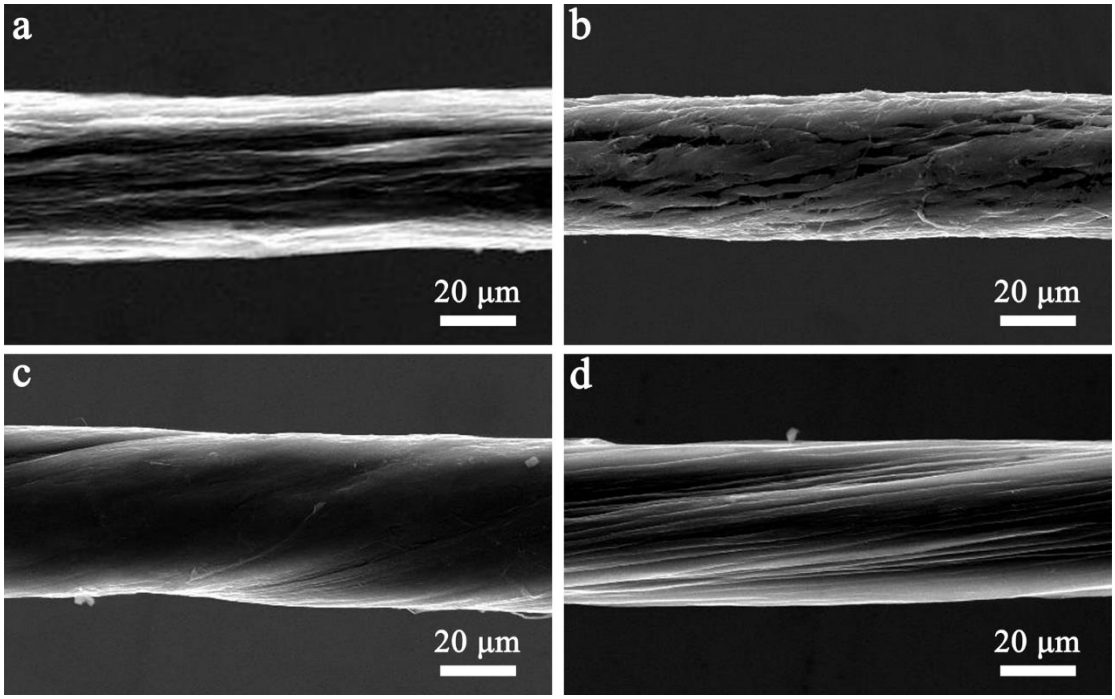

Figure S25. SEM images of different composite fibers after bending for 1000 times. The bending angle was 180° and the bending radius was 0.5 cm. **a.** CNT/RGO composite fiber. **b.** CNT/MnO_2 composite fiber. **c.** CNT/PANI composite fiber. **d.** CNT/PPy composite fiber.

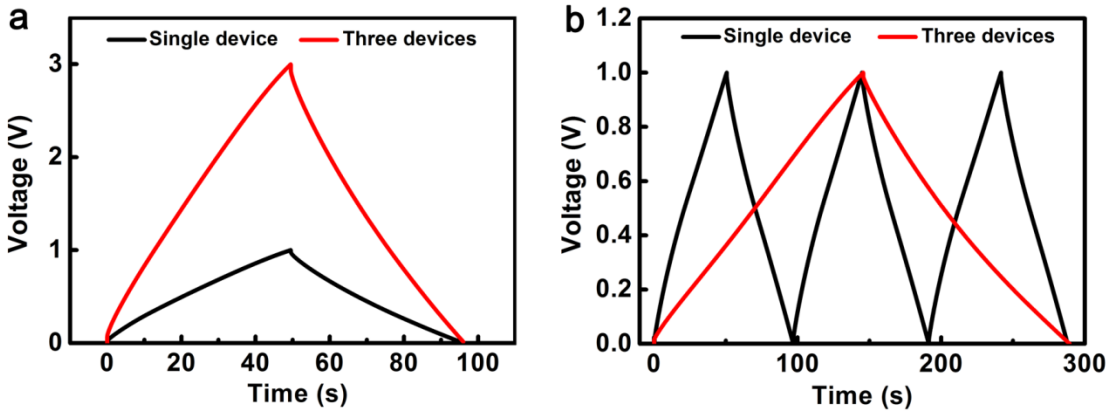

Figure S26. Galvanostatic charge-discharge curves of single supercapacitor and three supercapacitors being connected in series (**a**) and in parallel (**b**). The current density for charge and discharge was 310 mA cm^{-3}. The supercapacitor was made from CNT/RGO composite fibers.

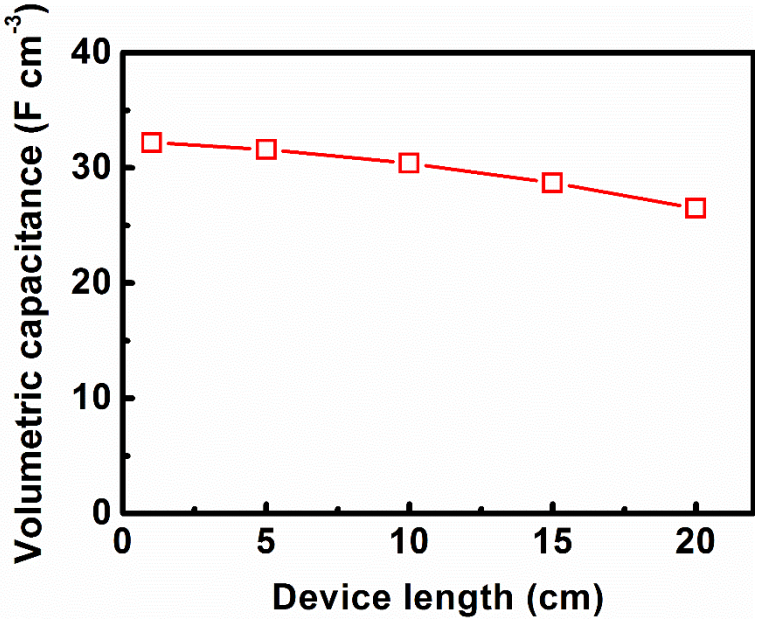

Figure S27. Volumetric capacitances of fiber-shaped supercapacitors in different lengths. The supercapacitors were continuously produced and were assembled from CNT/RGO composite fibers under a deposition time of 180 s. The current density was 1240 mA cm^{-3}.