ADVANCED MATERIALS

Supporting Information

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A Fiber Supercapacitor with High Energy Density Based on Hollow Graphene/Conducting Polymer Fiber Electrode

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Supporting Information

Supporting Video

The gases deriving from the reduction reaction of GO were finally accumulated in the void space at the two ends of the pipes. When the pipe was broken by a tweezer, the accumulated gases quickly sprayed out and made the water-drop spurted on the white wall.

Experimental Section

Fabrication of fiber supercapacitor. PEDOT:PSS and VC particles were added to a GO aqueous solution with a weight ratio of VC/GO to be 1/1, followed by an ultrasonic treatment. The resulting mixture solution was injected into glass pipes with a diameter of 0.9 mm, followed by sealing at both ends. After the GO was reduced to RGO at 90 ^{o}C in an oven, the two ends of the pipe were opened, followed by drying and reducing the wet fibers at the same temperature. Both RGO/PEDOT:PSS and RGO fibers were prepared from the mold pipes. To prepare the electrolyte, H_3PO_4 (~1 mL) was dropped to de-ionized water (10 mL), followed by addition of a PVA powder (1 g). The above mixture was then heated to 85 ^{o}C under vigorous stirring until it became clear. The same two fibers were fixed on a substrate in parallel and covered with the PVA/H_3PO_4 gel electrolyte to fabricate a fiber supercapacitor. A PEDOT:PSS weight percentage of 25% was used for the composite fiber unless specified otherwise.

Calculation of specific capacitance. The practical capacitance (C) of an entire fiber supercapacitor was calculated by $C = Q/U = I \times t/U$, where Q, U, I and t are the storage charge, voltage between two electrodes, discharge current and discharge time, respectively. For the convenience in comparison, specific capacitance (C_X) based on individual fiber was used and calculated by $C_X = 2 \times C/X$ for a symmetric supercapacitor, where X could be surface area (A), effective length (L) or effective volume (V) for area-specific capacitance (C_A), length-specific capacitance (C_L) and volume-specific capacitance (C_V), respectively. A and V are equal to the circumference and area of the cross section multiplied by the L (the length of overlapped portion of two electrodes), respectively. 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. In terms of specific energy (or energy density, E_X) and specific power (or power density, P_X), they could be obtained from $E_X = E/(2\times X)$ and $P_X = E_X/t$. Here “2” stands for the same two fiber electrodes in a symmetric supercapacitor. The areal energy density (E_A) may be calculated by $E_A = E/(2\times A) = 0.5\times C\times U^2/(2\times A) = 0.125\times(2\times C/A)\times U^2 = 0.125\times C_A\times U^2$. Unfortunately, for some previous reports, E_A was confusingly calculated by $E_A = E/A = 0.25\times C_A\times U^2$ or $E_A = E/(0.5\times A) = 0.5\times C_A\times U^2$. The specific capacitance was calculated on the basis of fiber electrode.

Characterization. CV and EIS measurements were performed on a VSP (Bio-Logic SAS) electrochemical workstation. Galvanostatic charge/discharge were tested using a CT2001A battery program controlling test system (China-Land Co., Ltd). The structures were characterized by scanning electron microscopy (SEM, CamScan Apollo-300). Nitrogen adsorption–desorption measurements were conducted on a JW-BK 300 instrument (Beijing-JWGB Co., Ltd). The tensile stress-strain curves had been recorded from a HY-0350 instrument (Shanghai-HY Co., Ltd). Fourier transform infrared (FT-IR) spectra were obtained from a Nicolet Nexus (Thermo Scientific) with the KBr pellet technique.

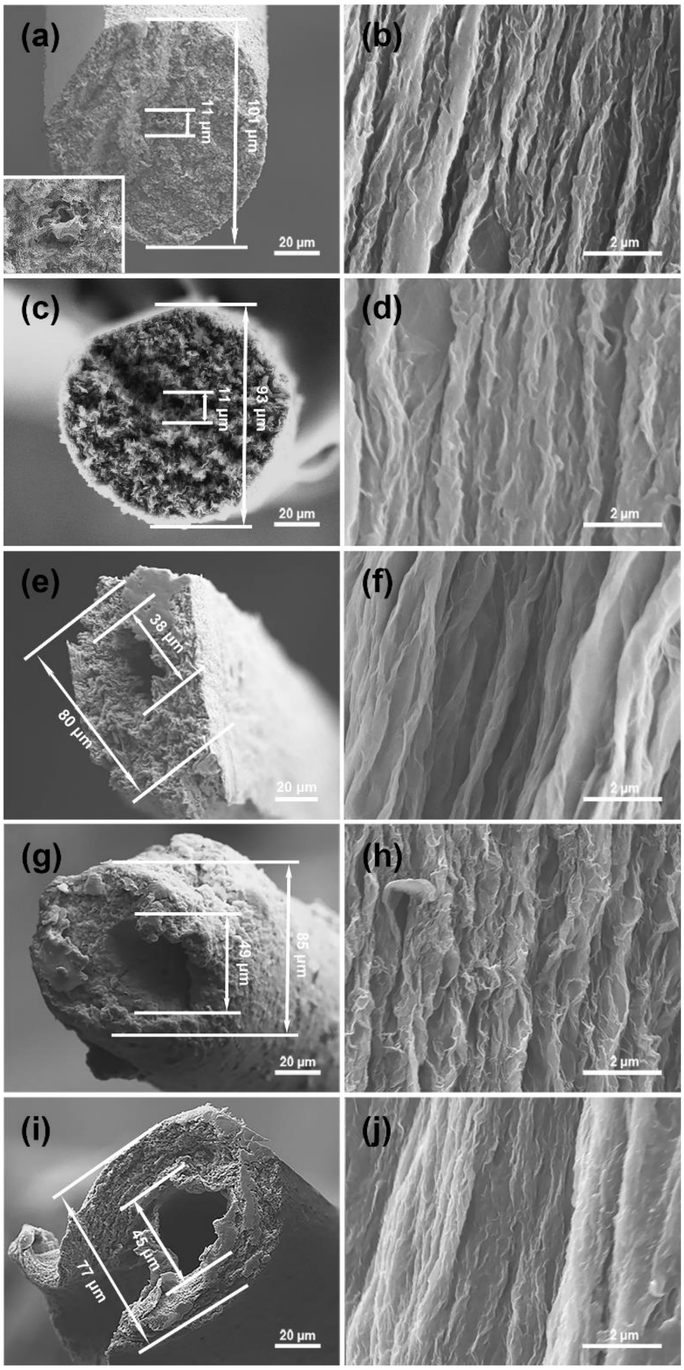

Figure S1. SEM images of HPFs without (**a**, **b**) and with increasing PEDOT:PSS weight percentages from 10% (**c**, **d**), 20% (**e**, **f**) and 25% (**g**, **h**) to 33% (**i**, **j**). The left and right columns correspond to top and side views, respectively. The diameter ratios of the inner to the outer are approximately 11%, 12%, 47%, 58% and 59% for both HPFs and HCFs with increasing PEDOT:PSS weight percentages from 10% to 33%.

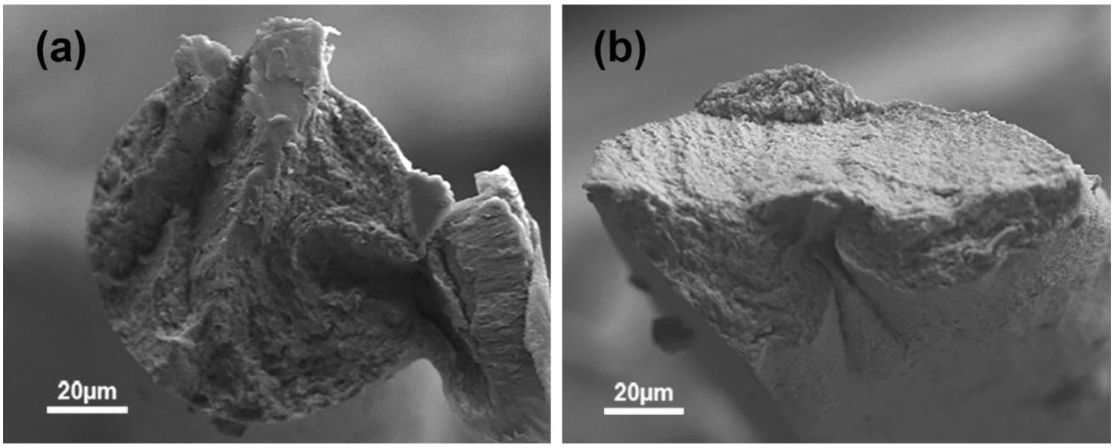

Figure S2. a) Cross-sectional SEM image of a solid RGO/PEDOT:PSS composite fiber. **b**) Cross-sectional SEM image of a solid RGO fiber.

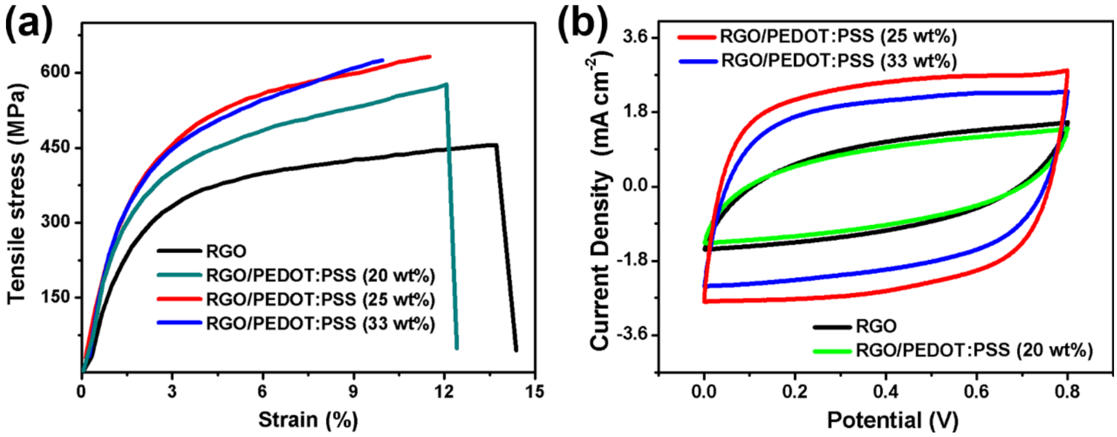

Figure S3. a) Typical stress-strain curves of hollow RGO fibers obtained with increasing PEDOT:PSS weight percentages. **b**) CV curves of the hollow RGO fiber-based supercapacitors obtained with increasing PEDOT:PSS weight percentages.

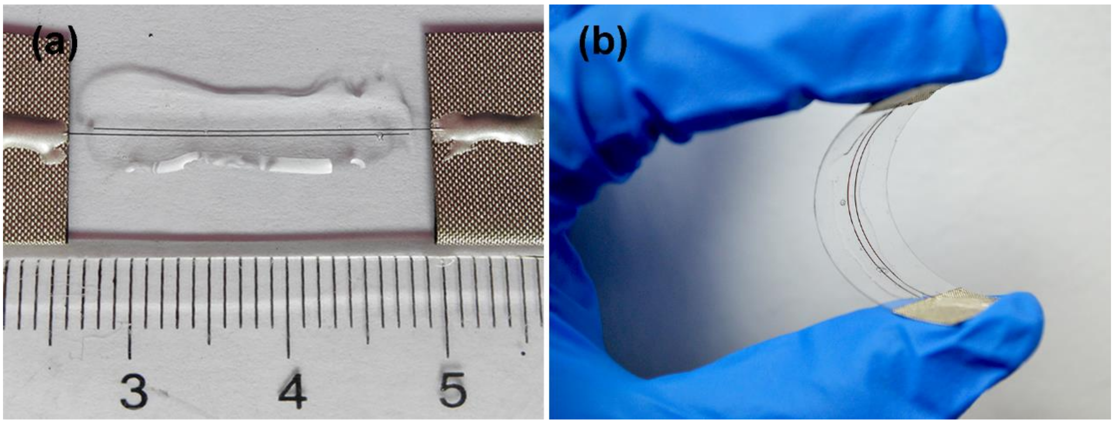

Figure S4. a) Photograph of a fiber supercapacitor on glass substrate. **b**) Photograph of a flexible solid-state fiber supercapacitor.

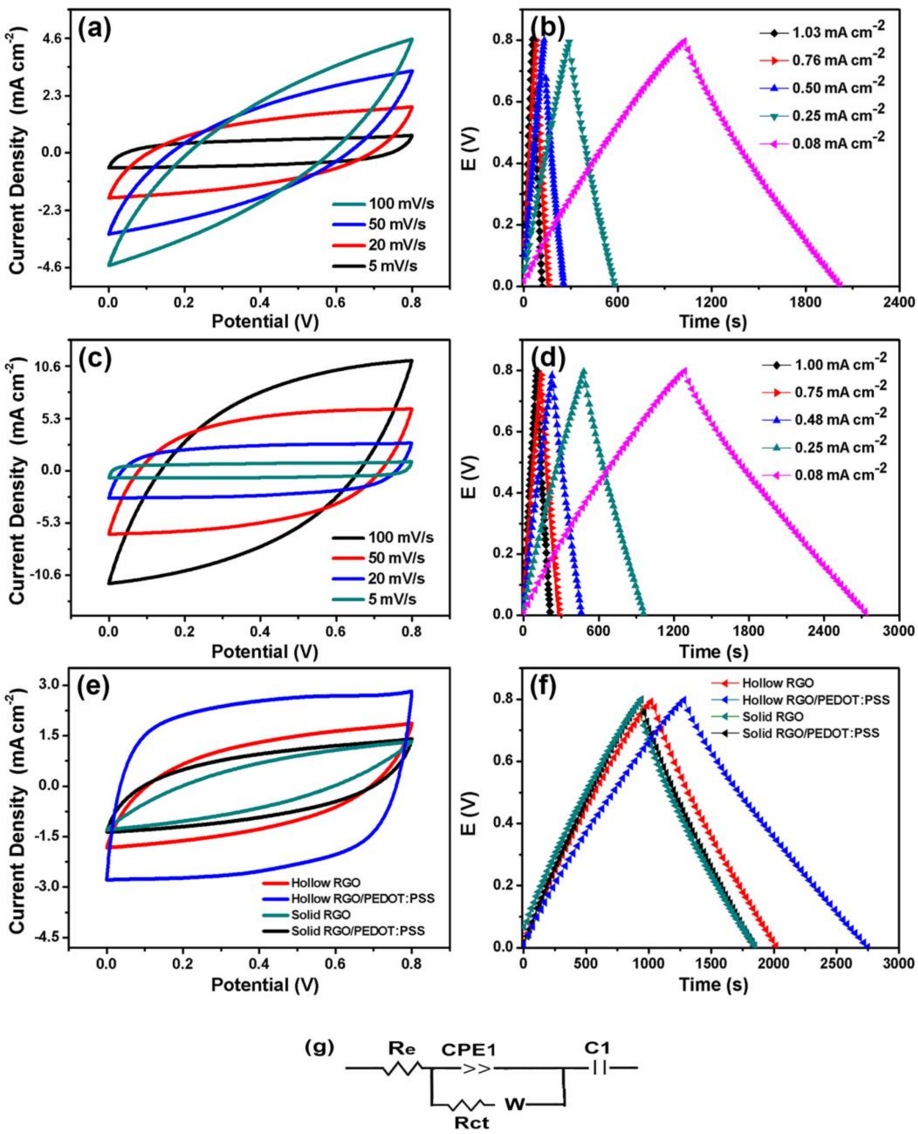

Figure S5. CV curves and galvanostatic charge/discharge profiles of the fiber supercapacitors. **a**) and **b**) CV curves and galvanostatic charge/discharge profiles of the HPF-based supercapacitor, respectively. **c**) and **d**) CV curves and galvanostatic charge/discharge profiles of the HCF-based supercapacitor, respectively. **e**) CV curves for different fiber electrodes at 20 mV s^{-1}. **f**) Galvanostatic charge/discharge profiles for different fiber electrodes at 0.08 mA cm^{-2}. **g)** The equivalent circuit for EIS of the fiber supercapacitor. Re, CPE, Rct, W and C stand for the equivalent resistance, constant phase element, charge transfer resistance, Warburg resistance and capacitor, respectively.

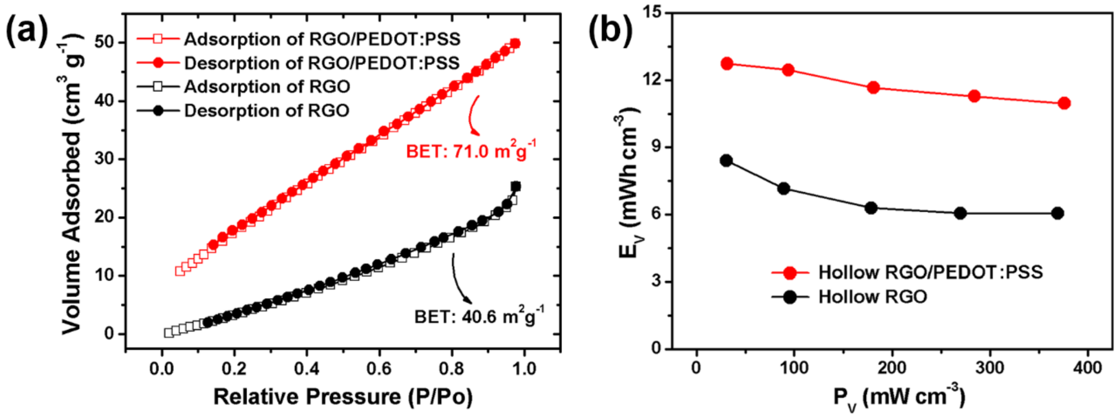

Figure S6. a) Nitrogen adsorption-desorption isotherms of HCFs and HPFs. **b)** Ragone plot of the fiber supecapacitors based on the volume of single fiber.

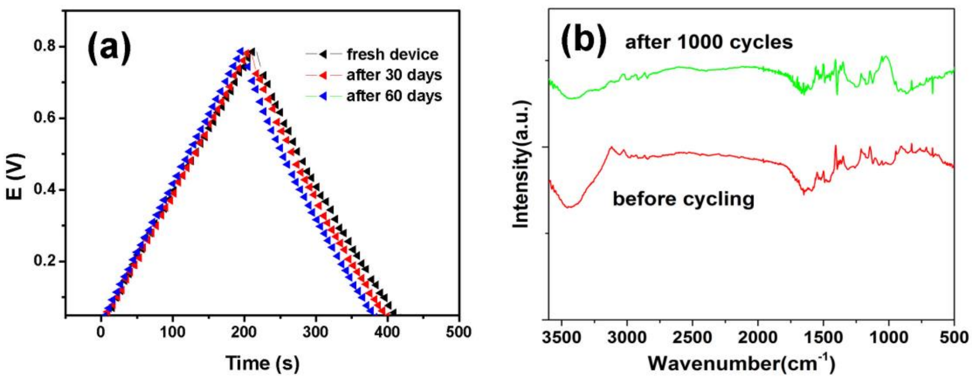

Figure S7. (a) Galvanostatic charge/discharge profiles for the HCF electrode soaked in electrolyte for different times. **(b)** FTIR spectra of the gel electrolyte before cycling and after 1000 cycles. The S=O vibration near 1200 cm^{-1} and O–S–O at 1034cm^{-1} are characteristic peaks of the sulfonic acid group of the PSS chain. However, these characteristic peaks could not be observed from the spectra after 1000 cycles, revealing a high stability of the electrode in gel electrolyte. Therefore, the amount of PSS released from the composite to the electrolyte is negligible.

(Ref: *Macromolecules* 2009, 42, 6741; *Frontier in Energy Research*, 2014, 2, 1)

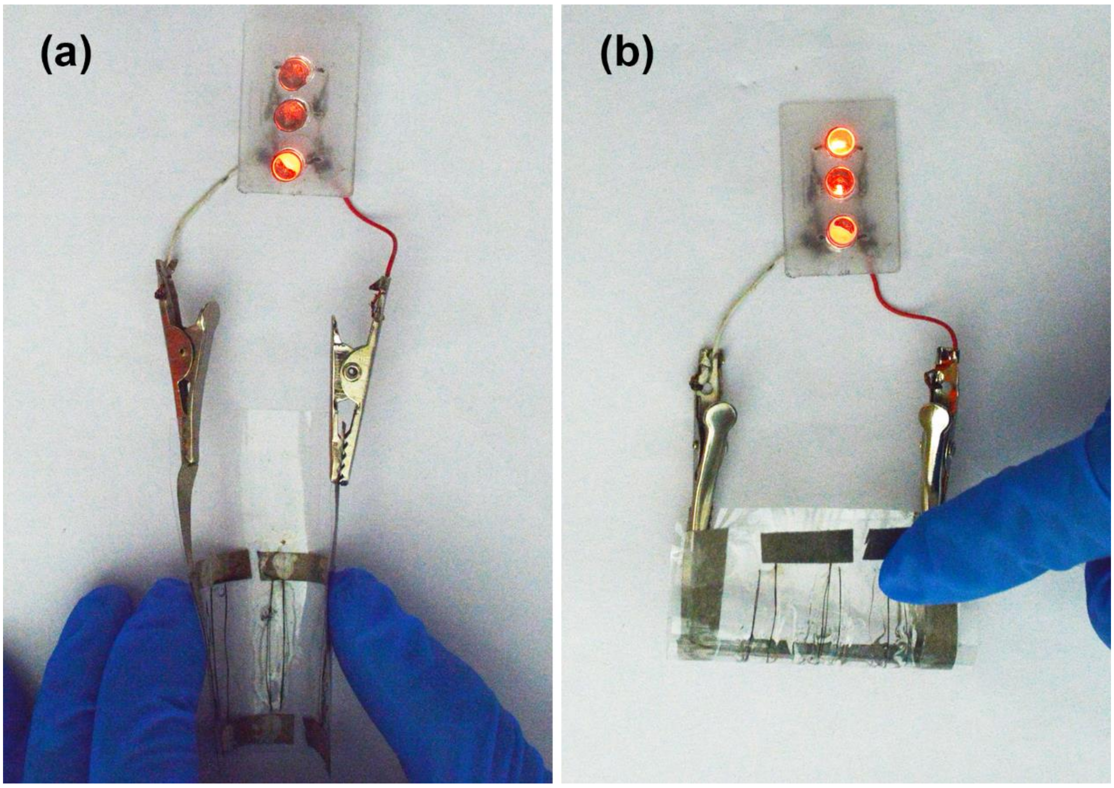

Figure S8. Photographs of a flexible fiber supercapacitor to power three LEDs when it was bent to an angle of 180^{o} in parallel (**a**) and perpendicular (**b**) directions relative to the length of the fiber supercapacitor.