Supplementary Information

Making Commercial Carbon Fiber Cloth Having Comparable Capacitances to Carbon Nanotube and Graphene in Supercapacitors through a "Top-Down" Approach

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Experimental Details

Materials and methods: Carbon fiber cloth used in this work was single weave Zorflex woven cloths purchased from Chemviron Carbon (Calgon Carbon Corporation, PA, USA). Threads of the cloth are bundles of activated carbon fibers with diameter ranging from 15 μm to 20 μm. The cloth has a thickness of 300 μm and an areal density of 12 mg/cm². Potassium hydroxide pellets (KOH), sulfuric acid (H_2SO_4), hydrochloride acid (HCl) and phosphoric acid (H_3PO_4) were purchased from Fisher Scientific. Anhydrous sodium sulfate (Na_2SO_4) and polyvinyl alcohol (PVA, MW 86,000) were purchased from ACROS Organics. Deionized water was used for all experiments.

In a typical experiment of KOH activation, 1.0 g of the as-purchased CFC was immersed in 4.0 M aqueous KOH solution (mass ratio of CFC to KOH was 1 to 4). The solution was then transferred into a vacuum desiccator to ensure access of KOH to the pores of CFC and was then dried inside an oven (80°C, 12 hours). The dried KOH/CFC mixture was heated in a tubular furnace under N_2 atmosphere at 800 °C for 0.5 hr, 1 hr, 2 hrs and 3.5 hrs. After activation, the mixture was washed with 2.0M HCl and was rinsed with deionized water to completely remove KOH. The activated CFC was dried inside an oven at 110°C for 4 hours. Thermal annealing of activated CFC was conducted at 1100°C for 2 hours under N_2.

Material Characterization: The morphology of CFC was studied using a scanning electron microscope (SEM, FEI XL30) operated at 5~ 10 kV and a transmission electron microscope (TEM, FEI Tecnai G2) operated at 200kV. The surface area and pore characteristics were analyzed using a Tristar 3000 (Micrometritics) Analyzer. The analysis was performed at the temperature of 77K. The specific surface area was determined by the 5-point BET (Brunauer–Emmett–Teller) method at the nitrogen relative pressure (P/P_o) of 0.05-0.3. Pore size distribution was obtained from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) model. Electrical conductivity was analyzed using a Keithley 2400 meter and a Fluke 115 multimeter.

Electrochemical Measurements: The EDLC performance of CFC electrodes was studied using a two electrode setup with a Biologic Potentiostat (model SP-300), using cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) techniques. The EIS analysis was performed with a frequency range of 200 kHz to 20 mHz. Supercapacitor cells were assembled as symmetric cells using type 2032 coin cells. Electrolytes tested were 1M H_2SO_4, 6M KOH or 0.5M Na_2SO_4. Flexible solid-state EDLC devices were assembled using a PVA/H_3PO_4 gel electrolyte. This electrolyte was prepared by adding 2g H_3PO_4 and 2g PVA powder into 30 ml water. The mixture was stirred

and heated at 80°C until PVA was completely dissolved. The solution was then cooled to room temperature and was used as the gel electrolyte.

The specific capacitance was determined from CV results (equation S1) and galvanostatic charge-discharge results (equation S2) using the following two equations: [1-3]

$$C = \frac{\int I \, dU}{mvU} \qquad \text{(S1)}$$

$$C = \frac{I \times \Delta t}{m \times \Delta U} \qquad (\Delta U = U - IR) \quad \text{(S2)}$$

Specific energy density (E) and power density (P) were calculated based on the charge-discharge results using equations as follows:

$$E = \frac{1}{2} \times C \times \Delta U^2 \qquad \text{(S3)}$$

$$P = \frac{E}{\Delta t} = \frac{1}{2} \times \frac{I \times \Delta U}{m} \qquad \text{(S4)}$$

where m is the mass of electrode materials, I is the current, v is the CV sweep rate, U is the voltage window, ΔU is the voltage change during galvanostatic discharging processes, and Δt is the discharging time. When calculating areal specific capacitance, the geometric area of the electrode (cm^2) was used instead of m in equation S1.

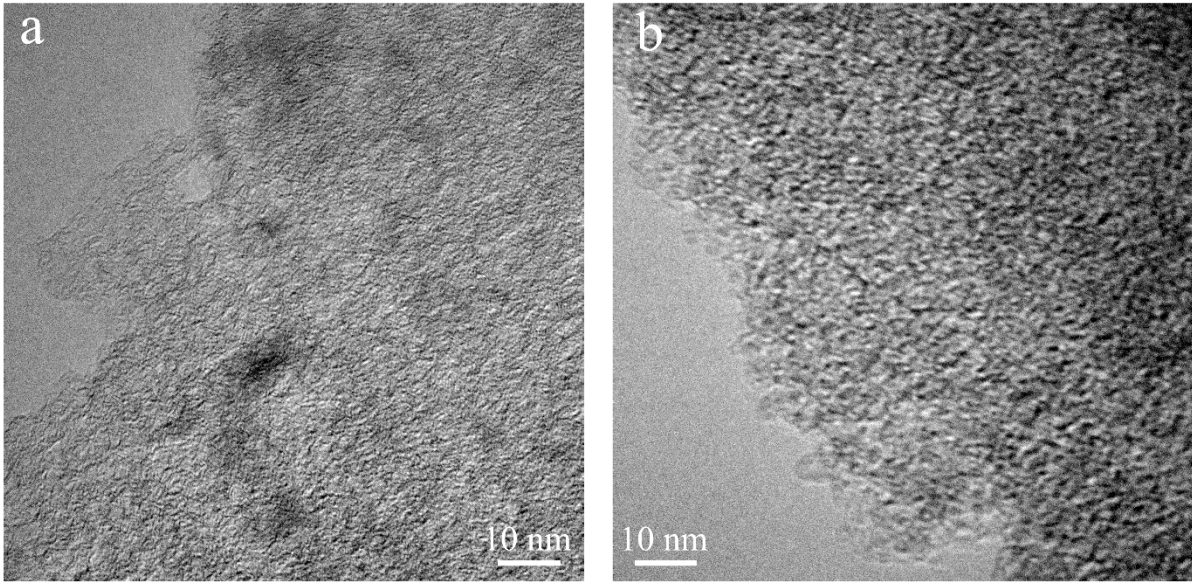**Morphology of CFC after Thermal Annealing:**

Figure S1: High resolution TEM images of CFC (a) after KOH activation. (b) KOH-activated CFC was annealed at 1100°C. Compared with image (a), annealed CFC showed well-connected and increased graphite crystallites. No cracks, big holes or peeled graphite chips were observed.
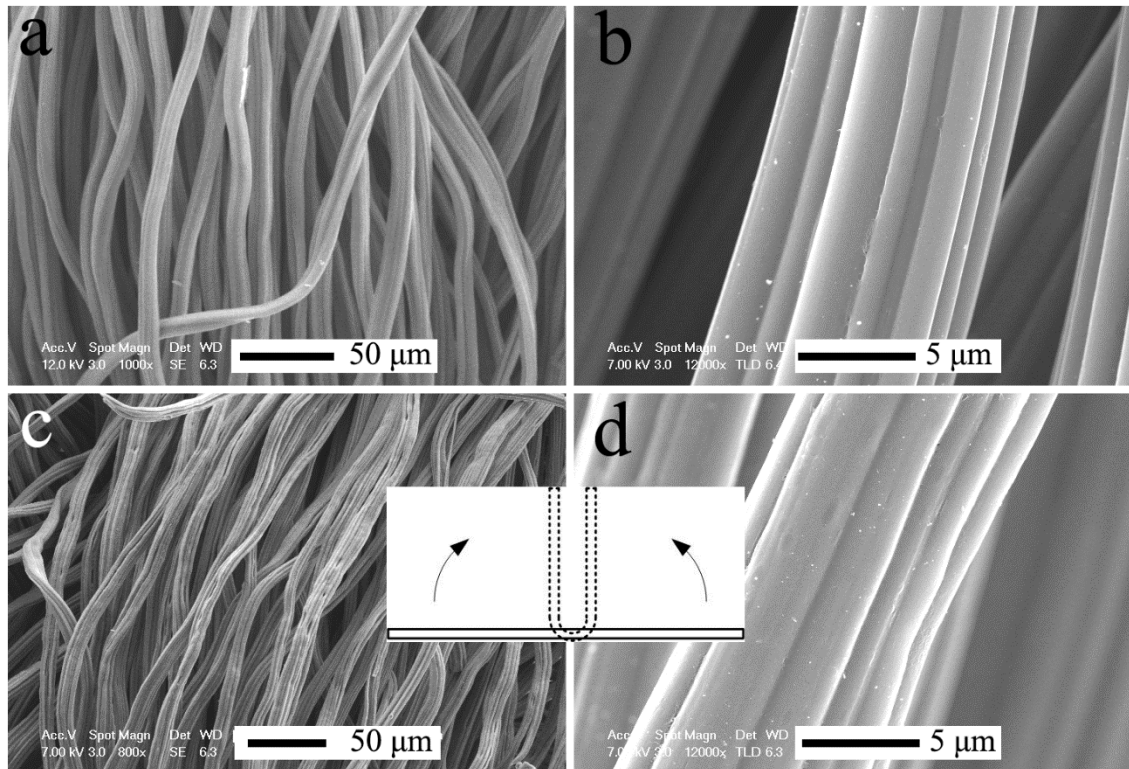
Mechanical Strength of Activated CFC:

Figure S2: Comparisons activated CFC before and after bending test: (a) as-activated CFC (b) individual fiber of the activated CFC. (c) After 20 cycles of 180º bending, SEMs were taken at the bended area of CFC. The performed bending rate was 2 bendings per second. (d) Morphology of the individual fiber in image (c). No distinct broken fibers, cracks, and peeled carbon chips were observed after bending tests. Insert is the schematic illustration of the bending test used in this work.
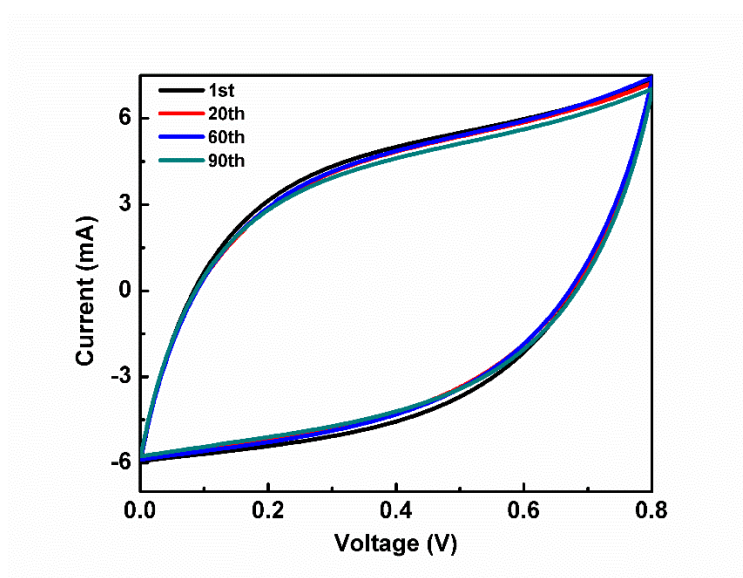
Flexibility of CFC-SC:

Figure S3: Comparison of the CV cycles of the flexible device after the bending cycles as indicated. The CV sweep rate was 5mV/s. The bending was performed from 0º to180º and the rate was 1 bend/second.
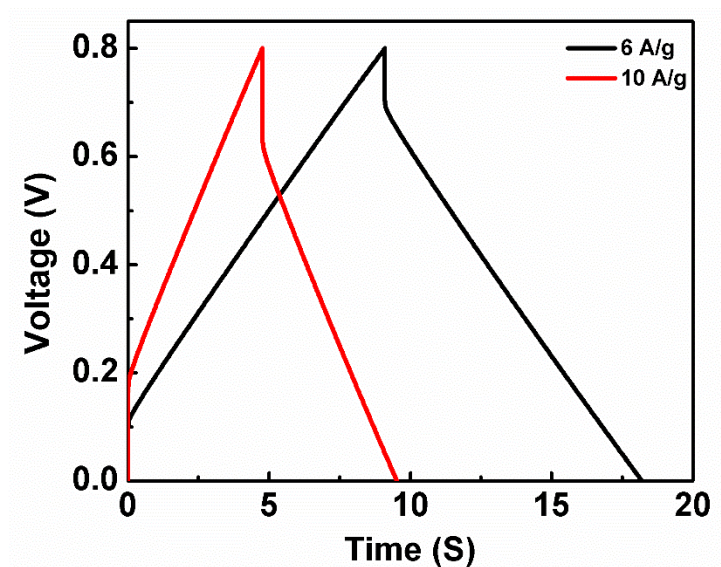
High Rate EC Performance of CFC:

Figure S4: Galvanostatic charge-discharge curves of processed CFC electrodes at current densities of 6 A/g and 10 A/g, respectively.
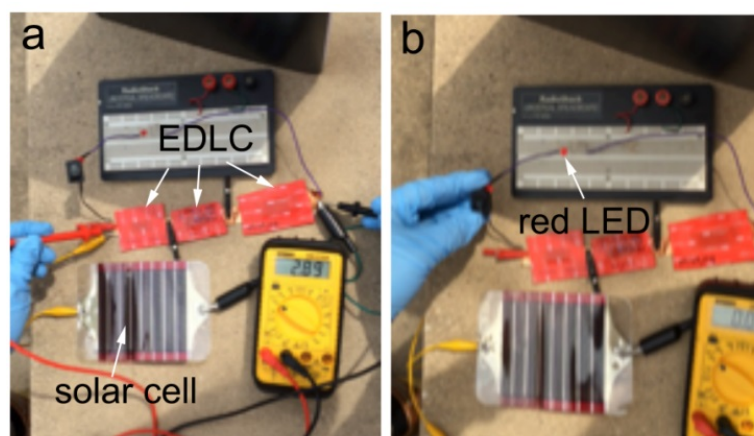
CFC-SC Demonstration:

Figure S5: (a) Charging a set of three flexible EDLC devices connected in series using a solar cell. (b) Lighting a red light-emitting diode (LED) using the charged EDLCs.

Figure S5 shows prototype demonstrations of the flexible solid-state supercapacitors assembled in this work for harvesting and storing solar energy. Three EDLC devices were connected in series and integrated with a commercial solar cell (DTU OPV V1.0, Denmark). After charging the EDLCs by the solar cell with sunlight irradiation, the EDLCs were switched to the discharge circuit that was connected to a red LED and a 30 Ω current limiting

resistor and were able to light the red LED for more than 3 minutes. This demonstration suggests that the EDLC device fabricated with processed CFC has great potentials for practical applications.

References:

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2. L. F. Chen, X. D. Zhang, H. W. Liang, M. G. Kong, Q. F. Guan, P. Chen, Z. Y. Wu and S. H. Yu, *ACS Nano* 2012, 6, 7092-7102.

3. S. Shi, C. Xu, C. Yang, Y. Chen, J. Liu, and F. Kang, *Sci. Rep.* 2013, 3, 2598-2603.