

## Electronic Supporting Information

### Flexible and Wearable Fiber Shaped High Voltage Hybrid Supercapacitor Based on Copper Hexacyanoferrate and Porous Carbon Coated Carbon Fiber Electrodes

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#### S1. Preparation of porous carbon and copper hexacyanoferrate

Copper hexacyanoferrate (CuHCF) nanoparticles were synthesized via one-step co-precipitation reaction. First, 5.5 mmol of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 20 ml of distilled water under stirring to get a transparent solution (solution A). At the same time, 2.75 mmol of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was dissolved in 20 ml of distilled water (solution B). Afterwards, solution B was added into solution A dropwisely under sonication using a syringe and the mixed solution was kept under sonication for 1 h. After that, the mixed solution was kept at room temperature for 24 h without any interruption. The resulting precipitates were washed several times with absolute ethanol and water, and finally dried in an oven at 60 °C.

To prepare the porous carbon, cleaned *banana peel* waste and 80 mL distilled water were placed into a Teflon-lined stainless steel autoclave and sealed, heated at 180 °C for 24 h, followed by cooling to room temperature. Then, the resulted sample was washed with distilled

water and dried at 60 °C overnight. After that, the hydrothermally treated sample was carbonized in a tube furnace at 800 °C for 3 h under N<sub>2</sub> atmosphere. Afterwards, the carbonized sample was thoroughly washed with desired amount of HCl and distilled water until the pH reaches 7. Finally, the washed sample was dried at 60 °C overnight.

## **S2. Preparation of fiber electrodes and fabrication of the fiber hybrid supercapacitor (HFSC)**

Copper hexacyanoferrate and porous carbon coated fiber electrodes (CuHCF@CF and PC@CF, respectively) were prepared by dip-coating. In details, the porous carbon or copper hexacyanoferrate (80 wt%), SuperP carbon (10 wt%) and polyvinylidene fluoride (PVDF, (10 wt%)) were mixed using mortar. Then, the N-methyl-2-pyrrolidone (NMP) was added drop-by-drop to form a slurry. The slurry was coated on the carbon fiber (10 cm in length) by dip-coating and then dried at 80 °C overnight.

The PVA-KCl gel electrolyte was prepared to fabricate the HFSC. 1 g of PVA was mixed with 40 mL of hot (80°C) water with constant stirring and was kept for 1 h to form a clear solution. Then, 3g of KCl was dissolved in 20 ml distilled water and added to above PVA solution. The mixed solution was then kept at the same temperature under stirring until the formation of a gel-like solution. The prepared fiber electrodes were coated with PVA-KCl gel electrolyte for three repeated times by dipping into the gel electrolyte and drying at 80 °C for 2 min. Subsequently, the electrolyte coated fiber electrodes were twisted together to obtained the HFSC.

## **S3. Characterizations**

Powder X-ray diffraction (XRD) patterns were recorded on a Japan Rigaku D/MAX-CAX-ray diffractometer equipped with Cu<sub>Kα</sub> radiation over the 2θ range of 10-80°. Transmission

electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope, using an acceleration voltage of 200 kV. Field emission scanning electron microscopy (FE-SEM) images were performed on a JEOL JSM-6700 M scanning electron microscope. Specific surface areas and pore size analysis were calculated from the results of N<sub>2</sub> physisorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer–Emmet–Teller) and BJH (Barrett–Joyner–Halenda) methods. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an MgK $\alpha$  excitation source (1253.6 eV).

The electrochemical performances of the individual fiber electrodes (PC@CFs and CuHCF@CFs) were tested by using a three-electrode system in 1 M of KCl electrolyte at room temperature, where Ag/AgCl electrode and Pt-plate were used as reference and counter electrodes, respectively. A two-electrode setup was used to study the electrochemical performances of the fabricated HFSC with PC@CFs as the negative electrode and CuHCF@CFs as the positive one. The cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and cyclic life measurements were conducted on a Biologic VMP3 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were also performed by applying an AC voltage with 10 mV amplitude in the frequency range of 10 mHz to 7 MHz at open circuit voltage (OCV).

#### **S4. Calculations**

The specific capacitances (in F/g) of the electrodes are calculated using the following equation [1],

$$C = \frac{I\Delta t}{m\Delta V}$$

Where,  $I$  is the applied current (mA),  $\Delta t$  is the discharge time (s),  $m$  is the mass of active electrode material (mg) and  $\Delta V$  is the potential window (V).

To ensure equal amounts of charges (capacitances) on both electrodes in HFSC, the optimal mass ratio of copper hexacyanoferrate (CuHCF) and porous carbon (PC) is calculated based on the equation [2],

$$\frac{m^-}{m^+} = \frac{C^+ \times \Delta V^+}{C^- \times \Delta V^-} \quad 2$$

Where,  $m$  (mg),  $C$  (F/g) and  $\Delta V$  (V) are the mass of active material, gravimetric capacitance and potential window of the electrode, respectively (+ and – refer to positive and negative electrodes, respectively). According to this equation, the optimal mass of the electrodes should be  $m^+$  (CuHCF)/ $m^-$  (PC) = 0.4412. Therefore, the total mass of the active material is (3 mg (CuHCF) + 6.8 mg (PC)) 9.8 mg.

The capacitance (in F) of the HFSC was calculated from charge-discharge curves using the following equation,

$$C = \frac{I\Delta t}{\Delta V} \quad 3$$

Where,  $I$  is the applied current (mA),  $\Delta V$  is the cell voltage (V) and  $\Delta t$  is discharge time obtained from discharge curve (s). Then, the specific capacitance (in F/g or F/cm or F/cm<sup>2</sup> or F/cm<sup>3</sup>) of the HFSC were obtained by dividing the capacitance  $C$  by the length (L) of device or the total mass (M) of the active material or areal (A) of the device or volume (V) of the device, i.e.,  $C_M=C/M$  or  $C_L=C/L$  or  $C_A=C/A$  or  $C_V=C/V$ . The area (A) and volume of electrode or HFSC is calculated by [3],

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

$$V = \pi D^2 L / 4 \quad 5$$

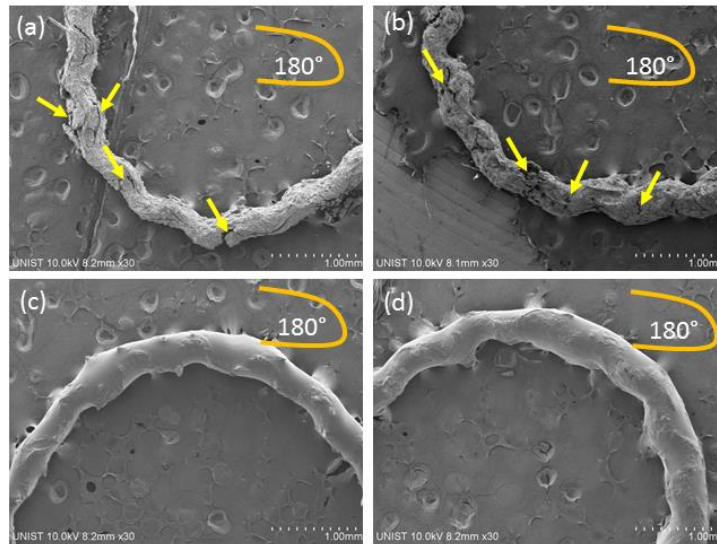
where, L and D are the length and diameter of the electrode or HFSC, respectively.

The gravimetric or length or area or volume energy ( $E_M$  or  $E_L$  or  $E_A$  or  $E_V$  and power ( $E_M$  or  $E_L$  or  $E_A$  or  $E_V$ ) densities were calculated using the following equations [2],

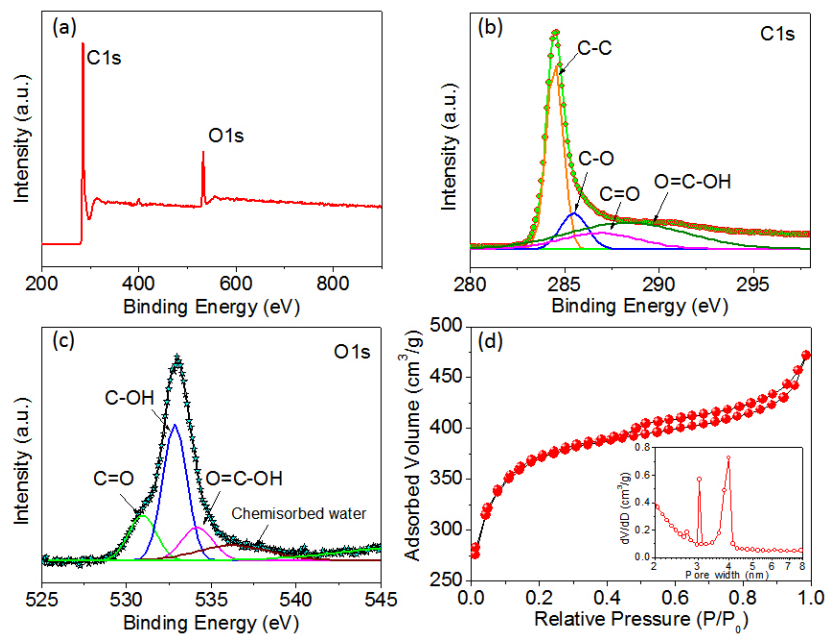
$$\text{Energy density, } E_X = \frac{C_X V^2}{2} \quad 6$$

$$\text{Power density, } P_X = \frac{E_X}{\Delta t} \quad 7$$

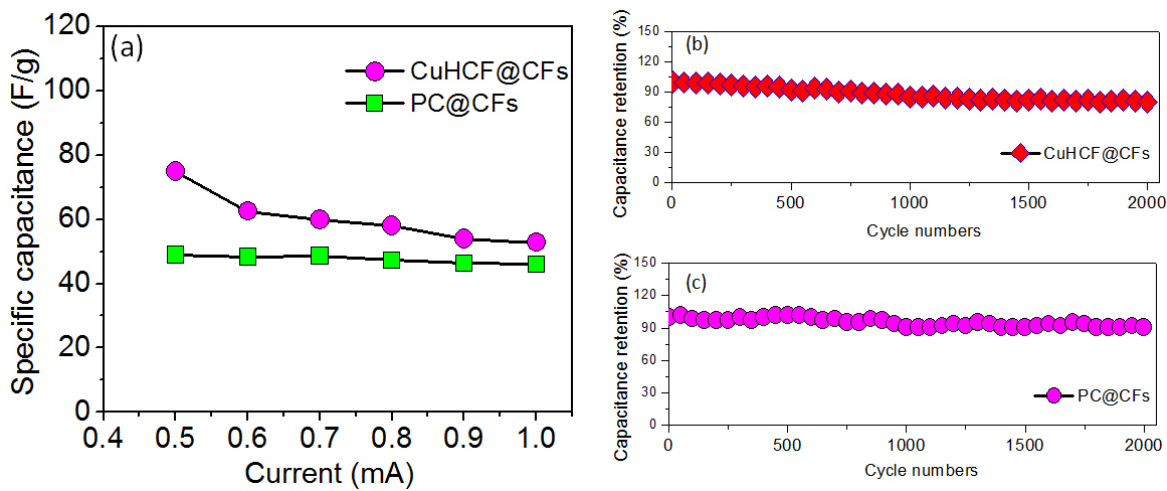
where, X=M (mass) or L (length) or A (area) or V (Volume), V is the cell voltage and  $\Delta t$  is discharge time obtained from discharge curve (s).



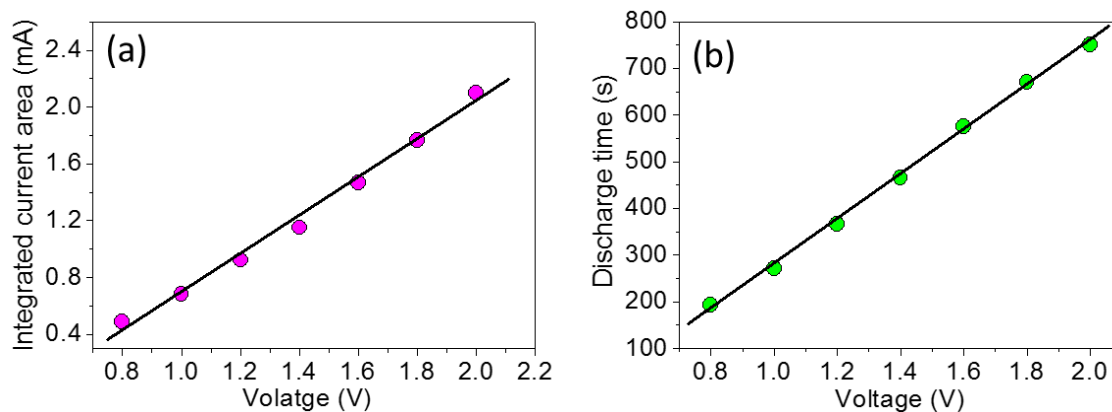
**Figure S1.** SEM image of the fiber electrodes at bending condition ( $\sim 180^\circ$ ): (a) CuHCF@CFs electrode, (b) PC@CFs electrode, (c) PVA/KCl coated CuHCF@CFs electrode and (d) PVA/KCl coated PC@CFs electrode (arrow indicates the presence of cracks).



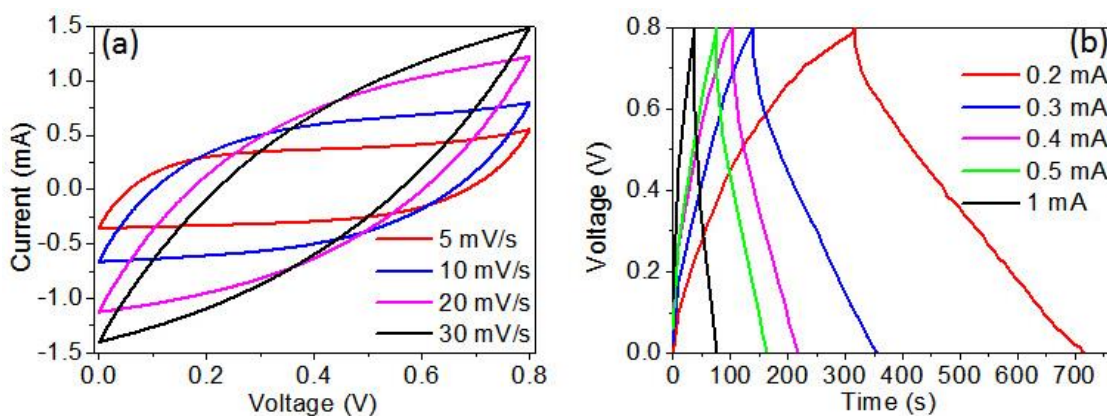
**Figure S2.** (a) XPS survey spectra, (b) C1s core level XPS spectra, (c) O1s core level XPS spectra and (d) N<sub>2</sub> adsorption-desorption isotherm of PC.



**Figure S3.** (a) Rate capability and (b and c) cyclic tests of the electrodes.



**Figure S4.** (a) Voltage vs. integrated area of CV curve and (b) voltage vs. discharge time.



**Figure S5.** (a) CV curves and (b) GCD curves of a symmetric supercapacitor (PC@CFs//PC@CFs).

#### References:

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- [3] D. Yu, Q. Qian, L. Wei, W. Jiang, K. Goh, J. Wei, J. Zhang, Y. Chen, *Chem. Soc. Rev.* **2015**, *44*, 647.