

# Bamboo-pulp-derived super-flexible hierarchically porous carbon film electrode prepared via environment-friendly ice-microcrystal mild pore-forming for supercapacitors

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## Supporting Information

### Experimental details

#### Materials

Dried bamboo pulp was friendly provided by Sichuan Yingde Bamboo Pulp Paper Co., Ltd. 50 wt% NMMO aqueous solution was purchased from Macklin Chemicals Co., Ltd. All reagents were analytically pure and used as received without further purification. Deionized water was used in all experiments.

#### Preparation of flexible carbon film electrode

According to the literature<sup>S1</sup>, (70-75) wt% of NMMO aqueous solution can dissolve cellulose while lower concentration of solution only can swell cellulose and make the crystallinity of cellulose decrease when above 50 °C. Thus, we employ 10 wt% of NMMO aqueous solution and 70 °C to swell bamboo pulp. 0.5 g of dried bamboo pulp washed with deionized water was dispersed in 80 g of 10 wt% NMMO aqueous solution, and swelled for 12 h at 70 °C in an electrothermal thermostatic oven. Next, the excess solution was removed by filtration and correspondingly the swollen bamboo pulp residue became swollen paper. The swollen paper was frozen for 8 h at -16 °C, following by freeze-dried in a vacuum freeze dryer (FD-1A-80, Biocool, Beijing, China) for 48 h. Subsequently, the freeze-dried paper was heated to 900 °C at a heating rate of 2 °C min<sup>-1</sup> and maintained at 900 °C for 2 h in a tube furnace (GSL-1400X, HF-Kejing, Hefei, China) under nitrogen atmosphere, and finally the targeted flexible BFC-N film electrode was obtained.

For comparison, with the same procedure and conditions as the preparation of BFC-N, deionized water instead of NMMO was used to swell dried bamboo pulp and then carbonized to obtain comparison sample BFC-W. In addition, dried bamboo pulp film with no swollen and freeze-dried processes was directly carbonized at 900 °C under nitrogen atmosphere to obtain comparison sample BFC-0.

#### Assembly of sandwich symmetrical supercapacitor

A PVA/KOH gel electrolyte was prepared according to the following: 3 g of PVA and 2 g of KOH were dissolved in 40 mL of deionized water and stirred for 1 h at 90 °C. Using nickel foam (NF) as current collectors, BFC (1×2 cm<sup>2</sup>, about 1 mg) was pressed at 15 MPa on one end of NF (1×3 cm<sup>2</sup>) to prepare BFC/NF composite electrode. PVA/KOH gel electrolyte was used to coat onto the surface of BFC/NF composite electrode and naturally dried at room temperature for 2 h. Then, two BFC/NF electrodes were stacked and bonded together by the coated sides into a symmetric sandwich-type supercapacitor, and dried further at room temperature for 6 h to remove excess water. We called this supercapacitor BFC-SSS.

### Sample characterization

The morphology of BFC was characterized by a scanning electron microscope (S-4800, Hitachi, Japan). Raman spectra data were collected on a micro-Raman spectrometer (Aramis, Horiba-Jobin Yvon). X-Ray Diffraction patterns were recorded on a Bruker diffractometer (D8 Advance) with a  $\text{CuK}\alpha$  ( $\lambda=0.154$  nm) radiation operating at a scan rate of  $5^\circ \text{ min}^{-1}$ . The nitrogen adsorption and desorption isotherms were measured by a Micrometrics ASAP 2020 analyzer at 77k, and based on the BJH method, the pore size distribution analysis was performed from the desorption isotherm.

### Electrochemical performance

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) were measured by a GHI660C electrochemical workstation (Shanghai Chenhua Instrument Company, China) and cycle stability was measured by a Land battery test system. In three-electrode test system, BFC was cut into  $1 \times 1 \text{ cm}^2$  and pressed on between two pieces of  $1 \times 2\text{-cm}^2$  NF under 15 MPa as the working electrode, a platinum electrode and Hg/HgO electrode were respectively served as the counter and reference electrodes, and  $6 \text{ mol}\cdot\text{L}^{-1}$  of KOH solution was used as the electrolyte. The applied potential window range was  $-1\sim 0$  V. The specific capacitance  $C$  is calculated based on the following formula<sup>19</sup>:

$$C = \frac{I \cdot t}{m \cdot V} \quad (1)$$

where  $I$ ,  $t$ ,  $m$  and  $V$  are the discharge current density (A), discharge time (s), mass of BFC in the working electrode (g), and potential change in discharge (V), respectively.

BFC-SSS was directly used for two-electrode test systems. The energy density  $E$  and power density  $P$  are calculated based on the following formulas<sup>19</sup>:

$$C_m = \frac{2I \cdot t}{m \cdot V} \quad (2)$$

$$E = \frac{C_m V^2}{2 \times 4 \times 3.6} \quad (3)$$

$$P = \frac{3600E}{t} \quad (4)$$

Where  $I$ ,  $t$ ,  $m$  and  $V$  are the discharge current density (A), discharge time (s), mass of single PCF electrode (g), and potential change in discharge (V), respectively.

### Notes and references

S1 A.J. Sayyed, L.V. Mohite, N.A. Deshmukh and D.V. Pinjari, Carbohydr. Polym., 2019, 206, 220.

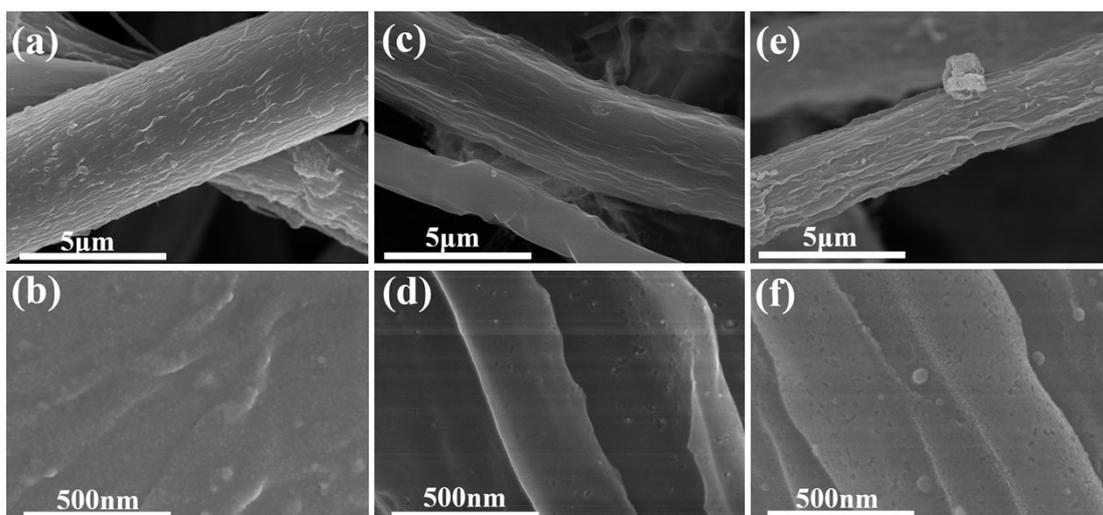


Fig. S1 SEM images of BFC-0 (a, b), BFC-W (c, d) and BFC-N (e, f).

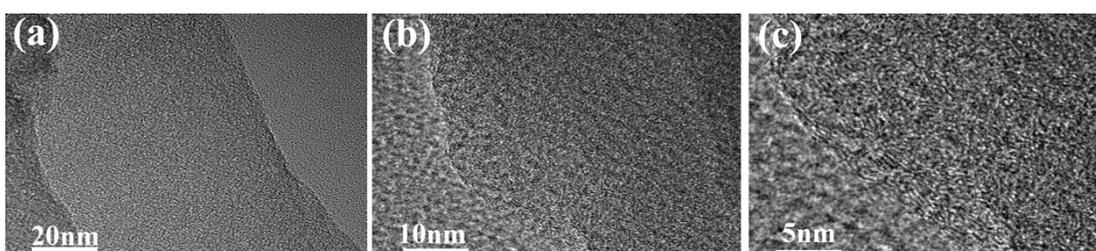


Fig. S2 TEM images of BFC-N.

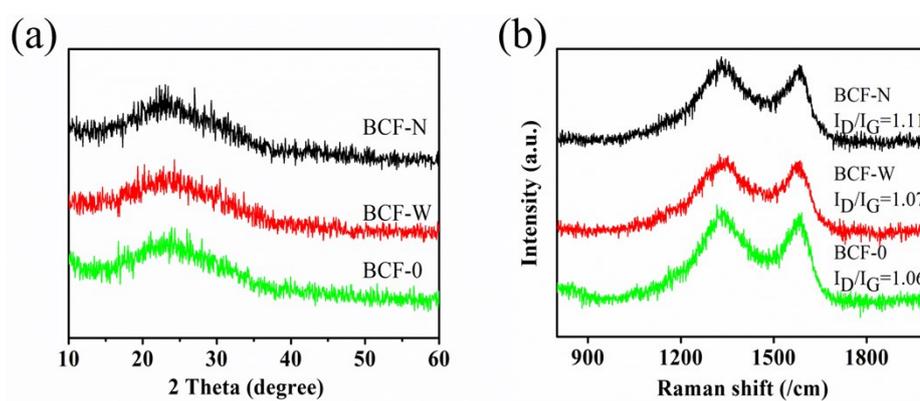


Fig. S3 XRD patterns (a) and Raman spectra (b) for BFC samples.

The chemical component and types of functional groups of BFC-N were detected via XPS and the XPS spectra are shown in Fig S3. In Fig S3 (a), there are three apparent peaks observed at binding energy of 287, 399 and 532eV, standing for carbon, nitrogen and oxygen atoms, respectively. The high resolution C 1s spectrum in Fig S3 (b) present four peaks at 283.8, 284.5, 286.6 and 289.9 eV, which represent the C-C, C-N, C-O and C=O, respectively. The N 1s spectra exhibit four major peaks at the 398.2 (pyridinic N, N-6), 399.7 (pyrrolic N, N-5), 400.5 (quaternary N, N-Q) and 402.44 eV (oxidized N, N-X), respectively. The high resolution O 1s spectra reveal four characteristic peaks, dispatching to C=O quinone-type oxygen (531.3 eV, O-I), C-OH phenol groups and/or C-O-C ether groups (532.2 eV, O-II), and chemisorbed oxygen and/or water (533.5 eV, O-III), respectively.

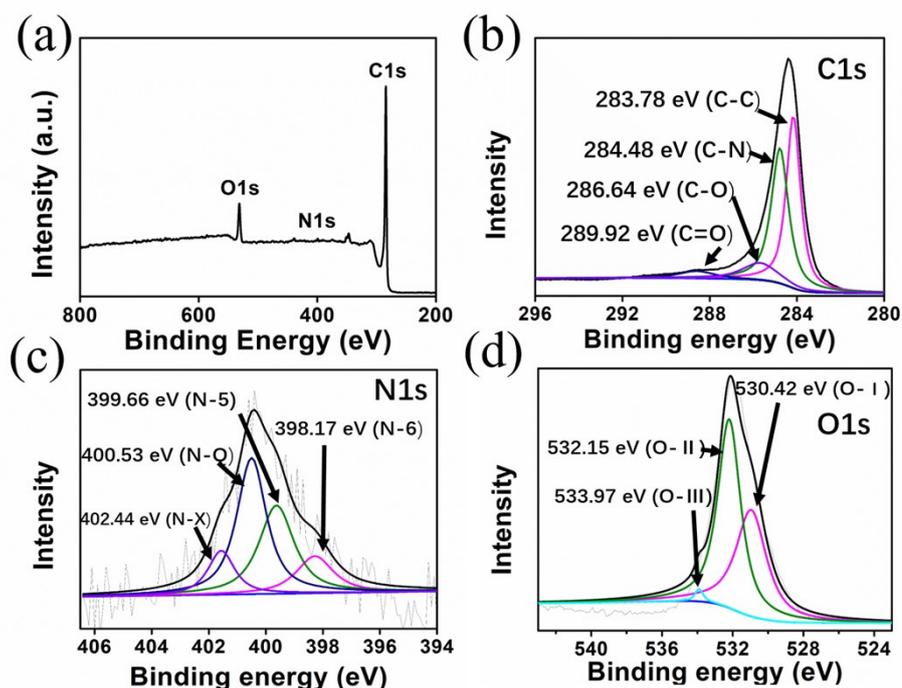


Fig. S4 XPS spectra of BFC-N sample. (a) XPS full spectrum, (b) C1s spectrum, (c) N1s spectrum, (d) O1s spectrum.

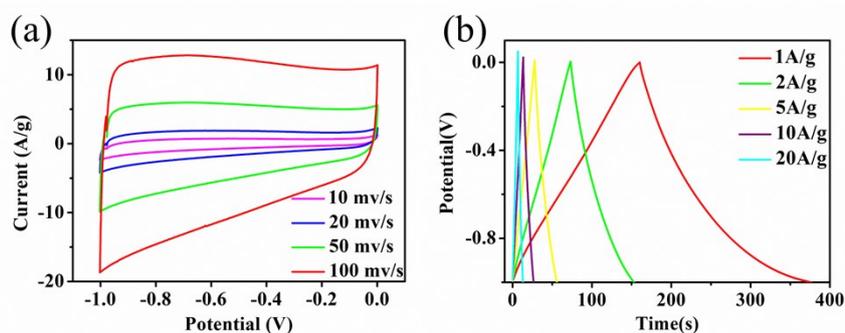


Fig. S5 CV curves at various scan rates (a) and GCD curves at various current densities (b) for BFC-N sample.

**Table S1** BET specific surface area and porosity parameters of BFC-0, BFC-W and BFC-N samples

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	$S_{\text{me}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{me}}$ ( $\text{cm}^3/\text{g}$ )	$S_{\text{mi}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{mi}}$ ( $\text{cm}^3/\text{g}$ )	$S_{\text{me}}/S_{\text{BET}}$	$V_{\text{me}}/V_{\text{total}}$	$D_{\text{aver}}$ (nm)
BCF-N	86.7	0.112	38.5	0.0869	2.23	0.0014	0.444	0.776	8.63
BCF-W	181	0.109	18.7	0.0276	8.27	0.0036	0.103	0.253	4.27
BCF-0	4.49	0.0110	1.71	0.0110	0	0	0.381	1	12.5

Note:  $S_{\text{BET}}$ ,  $S_{\text{me}}$  and  $S_{\text{mi}}$  is BET, mesopore, and micropore surface areas, respectively;  $V_{\text{total}}$ ,  $V_{\text{me}}$  and  $V_{\text{mi}}$  is total pore, mesopore, and micropore volumes;  $D_{\text{aver}}$  is pore average width.