Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

All-biomaterial Supercapacitor Derived from Bacterial Cellulose

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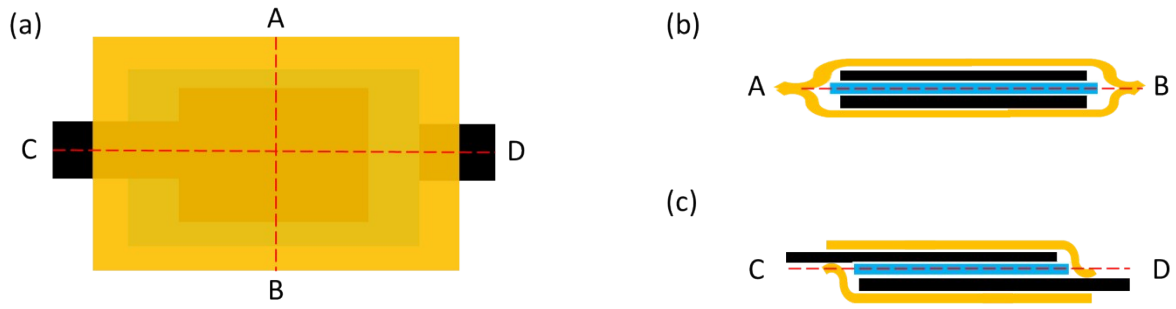

Scheme S1 The schematic of the vertical section for the all bio material supercapacitors

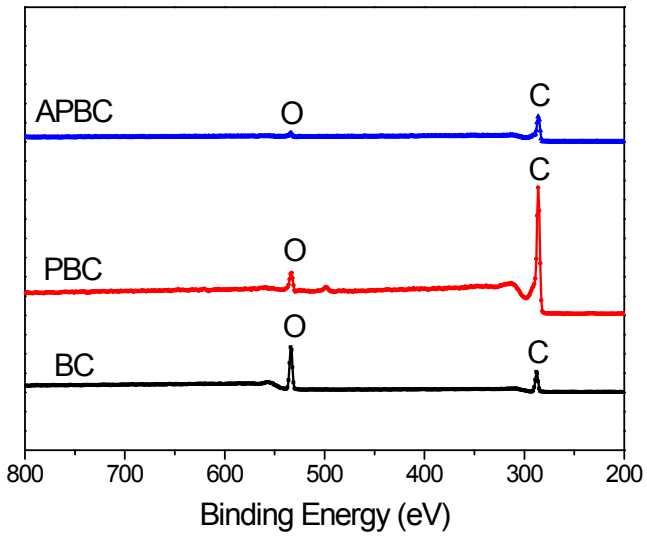

Figure S1 The XPS spectra of BC and APBC

As shown in Figure 4, the X-ray photoelectron spectroscopy (XPS) clearly shows that both PBC and APBC were mainly composed of two elements, carbon and oxygen without any other inorganic substance.

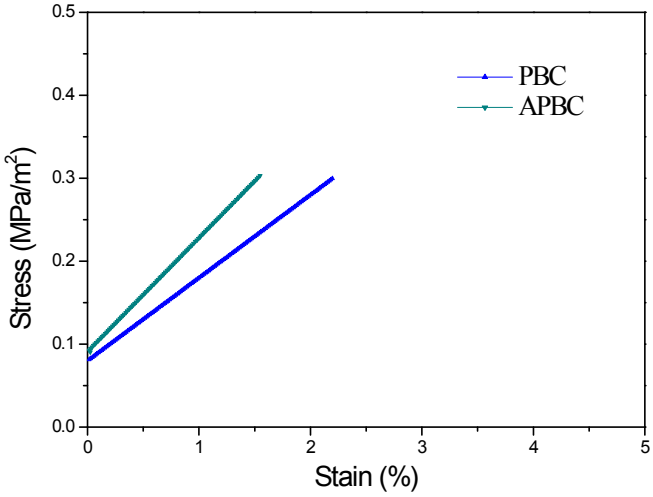

Figure S2 Tensile stress–strain curves of the BC derived materials

As shown in Figure S2, it can be seen that the stress-strain behavior of the PBC and APBC presented a brittle fracture model with elongations before break of 1.5% and 2.2% respectively, which are fairly close to the reported carbon nanofibers[4], meaning the mechanical properties of the BC derived electrodes are sufficient for the flexible devices.

Table S1 The BET surface area and the average pore diameter of PBC and APBC

	$S_{BET}(m^2g^{-1})$	Average pore diameter (nm)
PBC	337	4.03
APBC	491	3.23

The electrical conductivity of the BC derived materials were shown in the table S1. Dried BC and BC-H_3PO_4 are dielectric and thus applied for separator, while PBC and APBC hold good electrical conductivity which is used for electrode materials.

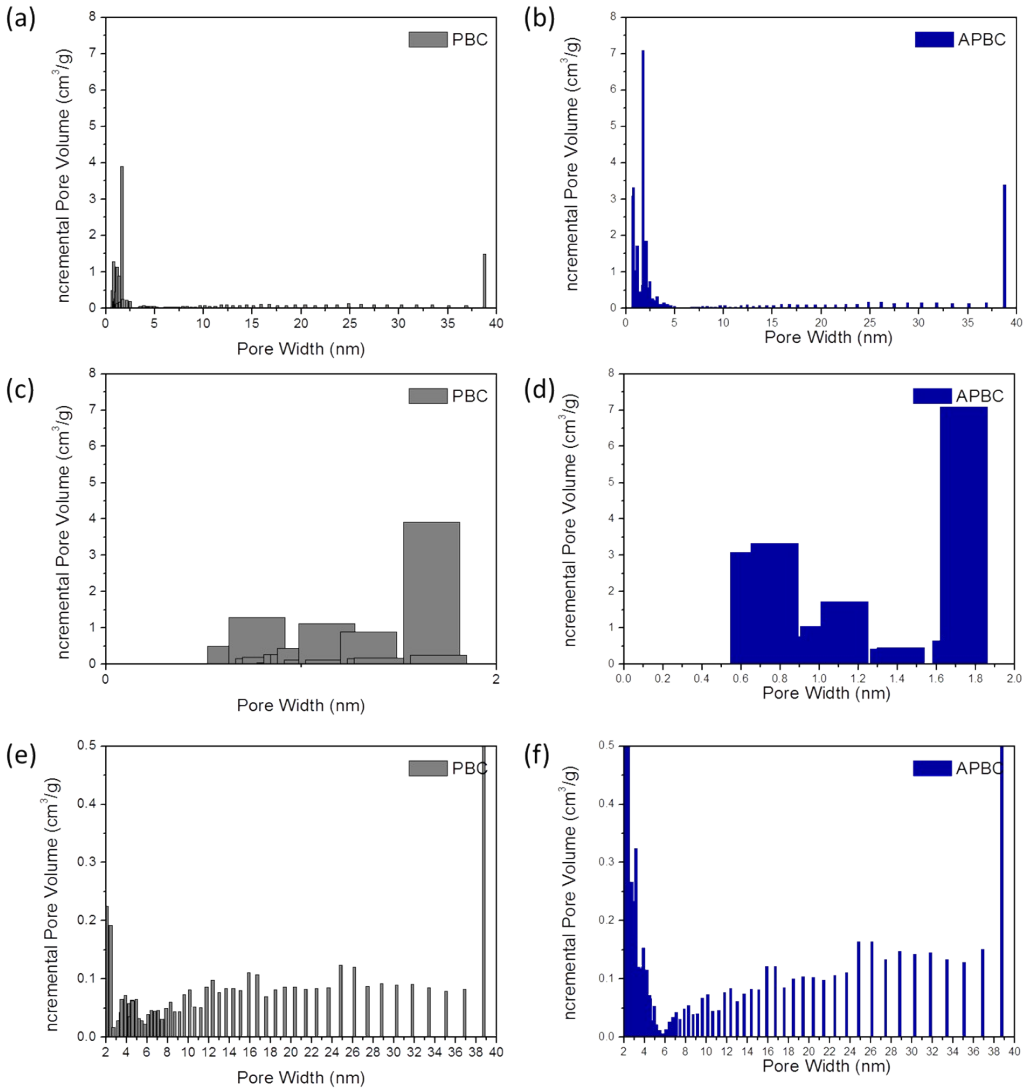

Figure S3 the pore width distribution of the PBC (a, c, e) and APBC (b, d, f)

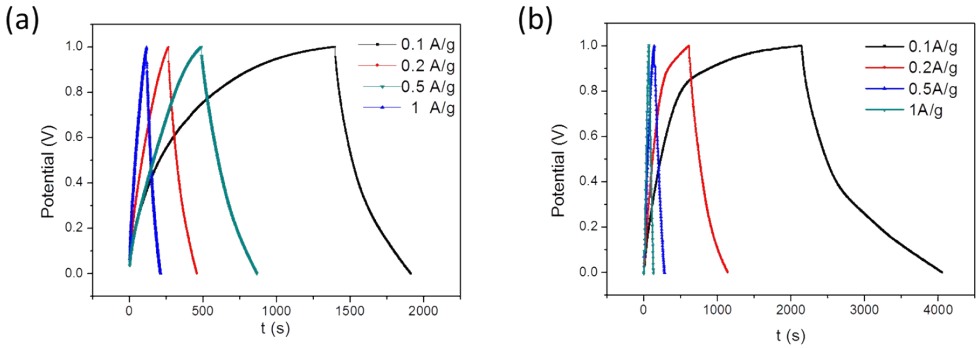

Figure S4 The Charge-discharge curves for the coin-type supercapacitors. (a) the PBC supercapacitor with glass fiber as the seperator; (b) the APBC supercapacitor with glass fiber as the seperator.

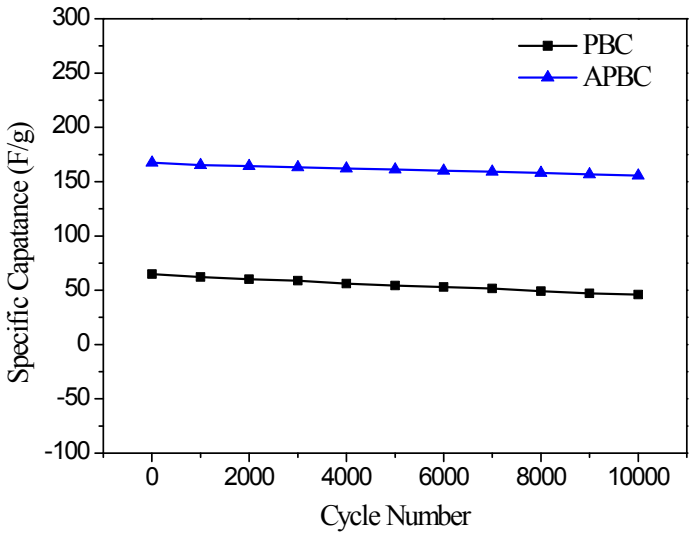

Figure S5. Cycling capabilities of PBC electrodes and APBC electrodes.

Another important requirement for supercapacitor applications is cycling capability. To further highlight the superior electrochemical capacitance of APBC, the cycling life tests for PBC and APBC electrodes were carried out at 1 Ag^{-1}, as shown in **Figure S5**.

Table S2 The electrical conductivity of the BC derived materials

	Conductivity (S cm^{-1})
Dried BC	/
BC-H_3PO_4	7.8×10^{-3}
PBC	0.25
APBC	0.23

Table S3 The electrical conductivity of the BC-H_3PO_4 gel electrolyte

	% of H_3PO_4	Conductivity (S cm^{-1})
Sample 1	0.61	7.8×10^{-3}
Sample 2	0.28	5.2×10^{-3}
Sample 3	0.16	2.9×10^{-3}

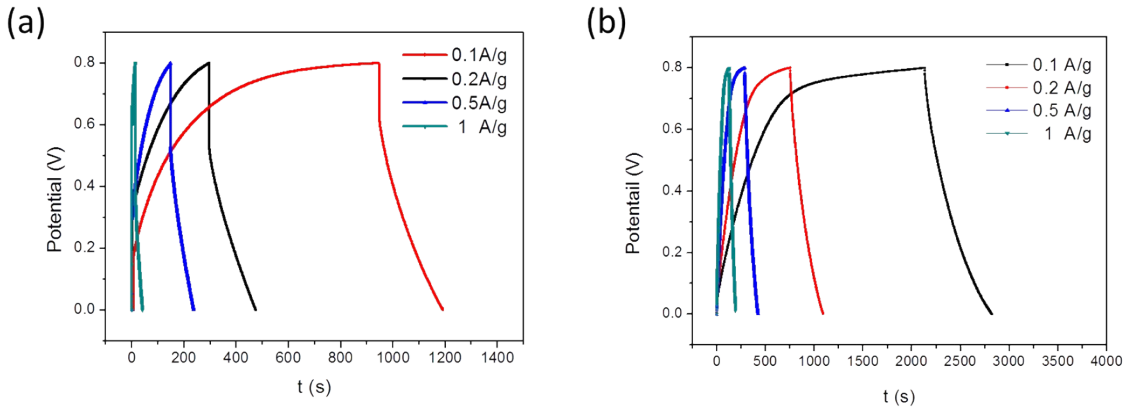

Figure S6 The Charge-discharge curves for the film supercapacitors. (a) the APBC supercapacitor with PVA-H3PO4 as the seperator; (b) the APBC supercapacitor with BC as the seperator.

Table S4 The areal specific capacitance and mass specific capacitance of the all-biomaterial supercapacitor

Current density ($mAcm^{-2}$)	Areal specific capacitance ($mFcm^{-2}$)	Mass specific capacitance (Fg^{-1})
0.1	289	72.25
0.2	259	64.75
0.5	235	58.75
1	225	56.25
2	217	54.25
5	209	52.25
10	204	51

Typically, the weight of a single electrode is around 4 mg with the density of ~201 mg cm^{-3}. According to the areal specific capacitance, detailed mass specific capacitances at different current density were calculated and further exhibited in the Table S4.

Experimental details

Material preparation

Pretreatment of BC: Purified bacterial cellulose (BC) pellicles were friendly supplied by Hainan Nanye Industry Company. The obtained BC pellicles were first washed by distilled water at 70℃ for 3h, then washed in 0.1M aqueous NaOH at 70℃ for 90min to remove the bacteria and their residues, and thoroughly washed in distilled water until neutral pH was reached. The X-ray photoelectron spectroscopy (XPS) (Figure S1) shows that the purified BC was mainly composed of two elements, carbon and oxygen.

Preparation of PBC and APBC: The BC pellicles were frozen in liquid nitrogen, followed by vacuum dying at -54 °C for 48h. The obtained freeze-dried BC aerogel was pyrolysed under flowing argon to get pyrolysed BC (namely, PBC). Briefly, there were four temperature stages at 180, 230, 520, 900 °C respectively and 1 h at each stage. The activated pyrolysed bacterial cellulose (APBC) was obtained by activating with KOH as an activation agent during the following processes, and the mass ratio of KOH and PBC was 1:1. After sufficient mixing, the KOH/PBC slurry was prepared at 120 °C for 48 h in air, and then heated in tubular resistance furnace at a heating rate of 5 °C min^{-1} from room temperature to 900 °C. Finally, the etched products were washed, and dried in vacuum at 60 °C for 24 h. The X-ray photoelectron spectroscopy (XPS) (Figure S1) shows that the APBC was mainly composed of two elements, carbon and oxygen.

Preparation of BC electrolyte: Purified BC was compressed, dried in an oven at 50 °C for 12h, and then soaked into H_3PO_4 solution. The water content of BC pellicles is 99%. Three pieces of BC pellicles of 30g was dried in an oven for 12h, 10h and 8h. The mass of the BC sample decreased to 1g, 1.21g and 1.37g. Then the BC samples were soaked into the phosphoric acid (85%, 1.69g/ml), for 8h. The liquid on the surface of the BC samples was removed and the mass increased to 1.05g, 1.24g and 1.39g. Thus, the concentration of phosphoric acid in BC-H_3PO_4 gel electrolyte is 0.61, 0.28 and 0.16molL^{-1}. The electrical conductivity has been tested as follows. Thus, sample 1 has been selected as the gel electrolyte of the all-biomaterial supercapacitor. The PVA-H_3PO_4 gel electrolyte was prepared by mixing PVA powder (1 g), H_3PO_4 (0.8 g, 85%), and deionized water (10 mL) together. The mixture was heated to 85℃ with stirring until the solution became clear. Then the mixed liquid was added into a culture dish slowly. The gel electrolyte would be formed under the conditions of 25℃ standing for 7 days.

The concentration of phosphoric acid is 85% and the density is 1.69g/ml. Thus, the concentration of phosphoric acid in the PVA-H_3PO_4 gel electrolyte is calculated to be 0.69 mol L^{-1}.

Characterization

The scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S-4800 instrument. The transmission electron microscopy (TEM) micrographs and electronic diffraction (ED) patterns were obtained using an FEI Tecnai F20 instrument operating at 200 kV. Raman spectra were collected usinga Renishaw inVia Raman microscope with a laser wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB250Xi apparatus at base pressure of 1×10^{-9} mbar, and X-ray source of Al K α .The powder X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2500 instrument with Cu K α irradiation; The nitrogen adsorption was measured using a Micromeritics accelerated surface area porosimetry (ASAP 2020, USA) auto adsorption analyzer to obtain N_2 adsorption isotherms at 77 K, and the specific surface area (SSA) was obtained by Brunauer–Emmett–Teller (BET) analyses of the adsorption isotherms.

Electrochemical Measurements

The electrochemical comparison of PBC and APBC were carried out by the two-electrode symmetric supercapacitor systems, where two electrodes with exactly the same composition and mass were separated by glass fiber soaked with 6 M KOH aqueous solutions, and then assembled into coin-type cells. For all-biomaterial supercapacitors, the electrode materials, i.e. APBC, were cut into rectangle, pasted onto the adhesive tape to be fastened, and then packaged with BC electrolyte or PVA/H_3PO_4 between the two electrodes. All of the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI660D electrochemical station (CH Instrument, Shanghai, China). The EIS plots were tested in the frequency range from 100 kHz to 0.1 Hz at 1 V scanning amplitude. The galvanostatic charge/discharge measurements were made using a CT2001A Battery Program Controlling Test System (China-Land Com. Ltd.). The specific capacitances for coin cell supercapacitors were calculated according to the equation:

$$C_S = \frac{I \cdot \Delta t}{m \cdot \Delta U} \quad (1)$$

and the specific area capacitances for all biomaterial supercapacitor were calculated according to the equation:

$$C_{Sa} = \frac{I \cdot \Delta t}{m \cdot \Delta U} \div \rho \quad (2)$$

The electrodes of the solid film supercapacitor, APBC, were obtained by filtering. The thickness of the APBC film is 0.2mm and the area is 1cm^{-2}, so volume specific capacitance conversion is as follows:

$$C_V = \frac{\int_i^f I(V)dV}{S(V_f - V_i)V} \quad (3)$$

Here, I, S, and V mean the current density, scan rate, and total volume of the electrode material, respectively. V_i and V_f are respectively the initial potential and the end potential.

Where I is the discharge current (A), Δt is the discharge time(s), m is the weight of single electrode, s is the area of the two electrodes at opposite parts, Δ U is the discharge voltage, and ρ is the specific area density of the electrode materials, 5mgcm^{-2} . The specific energy was calculated according to the equation:

$$E_S = \frac{1}{2} C_S V^2 \quad (4)$$

Where V is the discharge potential scope (v). The specific power was calculated according to the equation:

$$P_S = \frac{V}{4R^2} \quad (5)$$

Where R is the quotient of the IR drop and the corresponding discharge current.