## Supporting Information

# Multi–synergistic Regulation of Hard Carbon via Green Bioengineering Strategy Achieving High–capacity Sodium–ion Storage

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# 1. Experimental Section

## 1.1 Preparation of hard carbon

Natural bamboo (Phyllostachys edulis) from Huaihua, Hunan is used as raw materials in this study. First, bamboo was crushed and screened through a 120–mesh sieve. Subsequently, 2.5 g of bamboo powder was aseptically placed in a sterile, and *Coriolus versicolor* (CV) (No.cui 7233, from Institute of Microbiology, Beijing Forestry University) as a kind of fungus was inoculated onto bamboo powder. The bamboo powder was autoclaved at 121°C for 40 min (MJ–54A, STIK Co., Ltd) before inoculation. Then, 1 $cm^2$ of fungal material was taken, and 4000 µL of water was added. The mixture was ground to obtain a fungal suspension. Next, 200 µL of the suspension was injected into a culture dish. Sterilized bamboo powder was then added and spread evenly. Then the pre–inoculated samples were placed in Petri dish and incubated at 28±0.5 °C (SPX–150BIII, Faithful lnstrument Co., Ltd.) for different durations (0, 1, 3, 5, and 10 days) to promote mycelial growth. After the corresponding incubation period, bamboo powder after fungal erosion with CV hyphae was collected. The samples were dried overnight at 40 °C. The samples were labeled as CV–0 Bamboo, CV–1 Bamboo, CV–3 Bamboo, CV–5 Bamboo, and CV–10 Bamboo, respectively. The obtained precursors were subjected to pyrolysis and carbonization (GSL–1400X, Hefei Kejing Material Technology Co., Ltd.) . Treatment at 500 °C with a heating rate of 10 °C/min for 2 hours under argon gas flow, followed by carbonization at 1300 °C with a heating rate of 10 °C/min for 2 hours. The carbonized samples were labeled as CV–0 HC, CV–1 HC, CV–3 HC, CV–5 HC, and CV–10 HC, corresponding to the samples treated with CV for 0, 1, 3, 5, and 10 days, respectively. Additionally, sample treated with *Aspergillus niger* (AN) (No.33.2915, from China General Microbiological Culture Collection Center) for 10 days by similar method was labeled as AN–10 HC, while the sample treated with CV for 20 days was labeled as CV–20 HC.

## 1.2 Characterizations

Images of bamboo and hyphae were obtained using an optical microscope (H550S, Nikon, Tokyo, Japan). The morphology of the hard carbon materials was observed by scanning electron microscopy (SEM, ZEISS Sigma 300, Jena, DE) and high–resolution transmission electron microscopy (HRTEM, JEOL JEM−F200, Tokyo, JP). Fourier transform infrared spectra (FTIR, Nicolet iS20, Waltham, USA) were characterized on a Thermo Scientific Nicolet iS20 instrument, and the samples were tabulated with KBr as the support. Inductively Coupled Plasma Mass Spectrometry (ICP–MS, Agilent 5110OES, Santa Clara, USA) was used to test total content of main mineral elements. An asynchronous thermal analyzer (TG 6000, PerkinElmer, Hopkinton, MA, USA) was used to test the thermal stability of the samples in an argon atmosphere at a heating rate of 10 ℃/min, with a temperature range of 30 to 800 ℃. The crystalline structures of materials were characterized by X–ray diffraction (XRD, Rigaku SmartLab SE, Tokyo, JP) using Cu–Kα radiation (1.54056 Å). Raman spectrum was obtained using a laser micro–Raman spectrometer (Horiba LabRAM HR Evolution, Kyoto, JP) with a wavelength of 633 nm. Small–angle X–ray scattering (SAXS, Xenocs Xeuss 2.0, Grenoble, FR) data was acquired with an X–ray diffractometer in a transmission and parallel beam geometry with Cu–Kα radiation and a point detector (Pilatus 3R 300K). N2 adsorption–desorption equipment was utilized to determine the Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2460, Norcross, USA) surface area and pore parameters. X–ray photoelectron spectroscopy (XPS, Thermo Scientific K–Alpha, Waltham, USA) experiment was carried out on a Thermo Scientific K–Alpha spectrometer using Al Kα radiation. The content of cellulose, hemicellulose and lignin in samples were determined by National Renewable Energy Laboratory (NREL) method. The starch content in bamboo was determined using the acid hydrolysis method as specified in GB 5009.9-2023, the National Food Safety Standard. For in situ XRD tests, the 2θ range was 10~45°, and the scanning speed was 3 degrees/min. In situ batteries composed of CV–0 HC and CV–10 HC anodes, with Na as the opposite electrode, were charged and discharged at 30 mA/g, respectively.

## 1.3 Electrochemical measurements

The hard carbon anodes were prepared by mixing the hard carbon with super P and carboxy methyl cellulose (CMC) binder at a weight ratio of 8:1:1. The obtained slurry was coated on an Al foil followed by drying in a vacuum oven at 80 ℃ overnight. Distilled water was used as the dispersant for the slurry. The average loading of the active material in the electrode was about 1.0 mg/cm2. The electrochemical tests were conducted in 2016–type coin cells using sodium foil as a counter electrode, 1.0 M $NaPF_6$/Diglyme as the electrolyte, generic polypropylene separator for SIBs. The coin cells were assembled in an argon–filled glove box with the moisture and oxygen concentration below 0.01 ppm. The cells were galvanostatically charged and discharged at various current densities on the LAND battery testing systems at 25 ℃ (Wuhan, China). The cyclic voltammetry curves and electrochemical impedance spectroscopy (EIS) tests were performed with the coin cells at the electrochemical station (Ivium Technologies B.V., Netherlands). The cyclic voltammetry curves were tested in a voltage range of 0–3.0 V at a scan rate of 0.1 mV/s, with other scan rates used depending on the specific test. The test frequency range of EIS was 0.01~100 kHz.

## 2. Supplementary Fig.s and Table.s

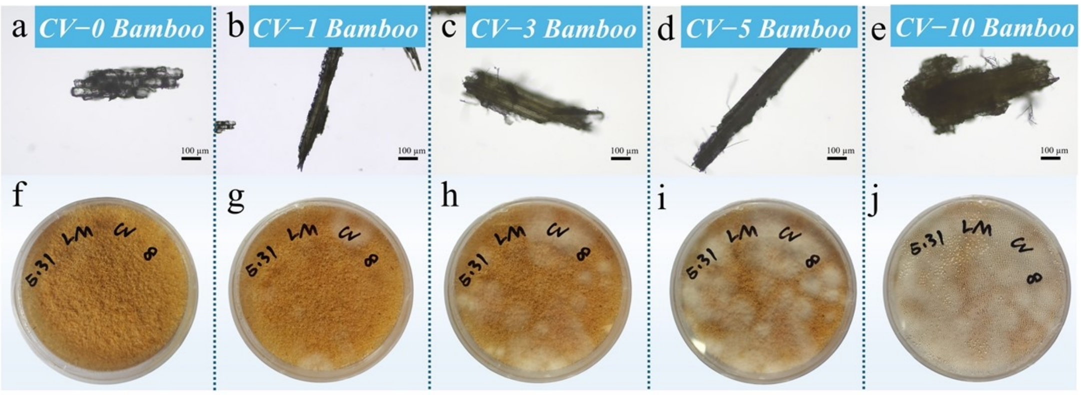

**Fig. S1** The growth process of CV on bamboo powder with the extension of the incubation time from (a–e) optical microscope and (f–j) digital photographs.

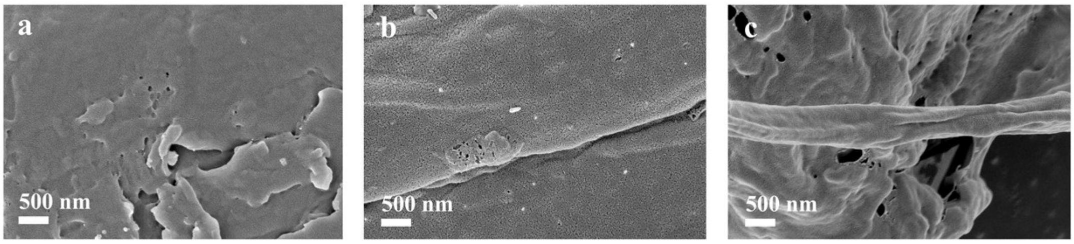

**Fig. S2** SEM images of (a) CV–0 Bamboo, (b) CV–0 HC, (c) CV–10 Bamboo.

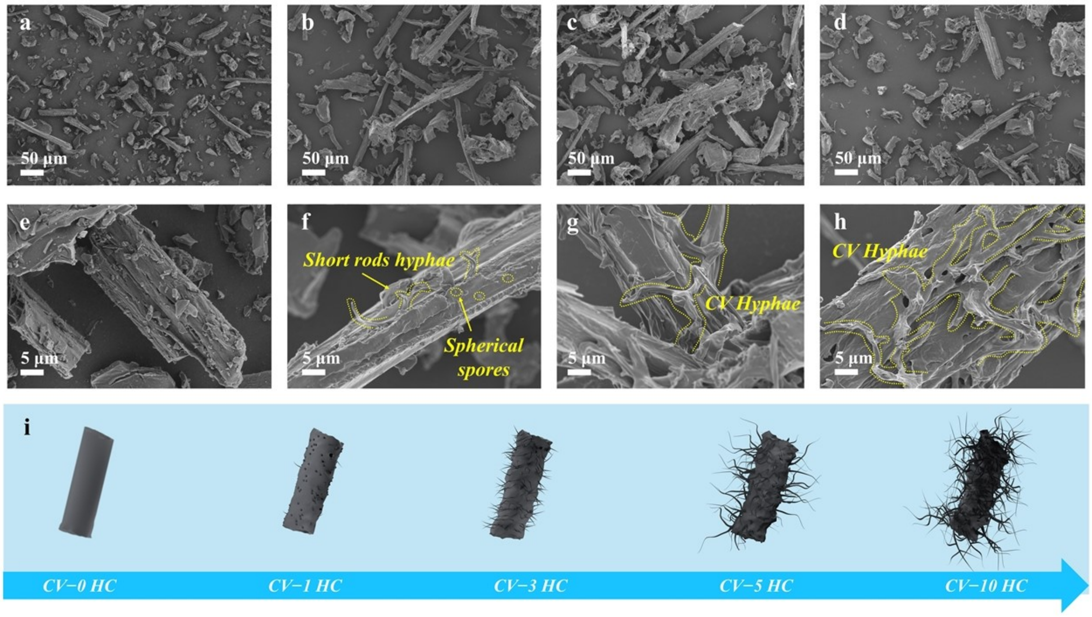

**Fig. S3** SEM images of (a, e) CV–0 HC, (b, f) CV–1 HC, (c, g) CV–3 HC, (d, h) CV–5 HC; (i) Schematic diagram of bamboo–derived HC upon CV growth pretreatment for different times.

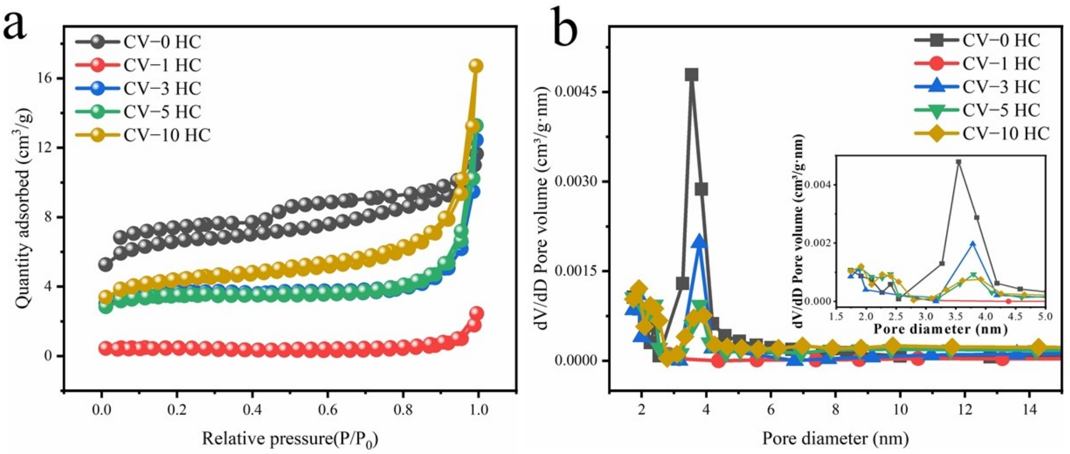

**Fig. S4** (a) $N_2$ adsorption–desorption isotherms; (b) Pore size distribution calculated from the adsorption isotherms.

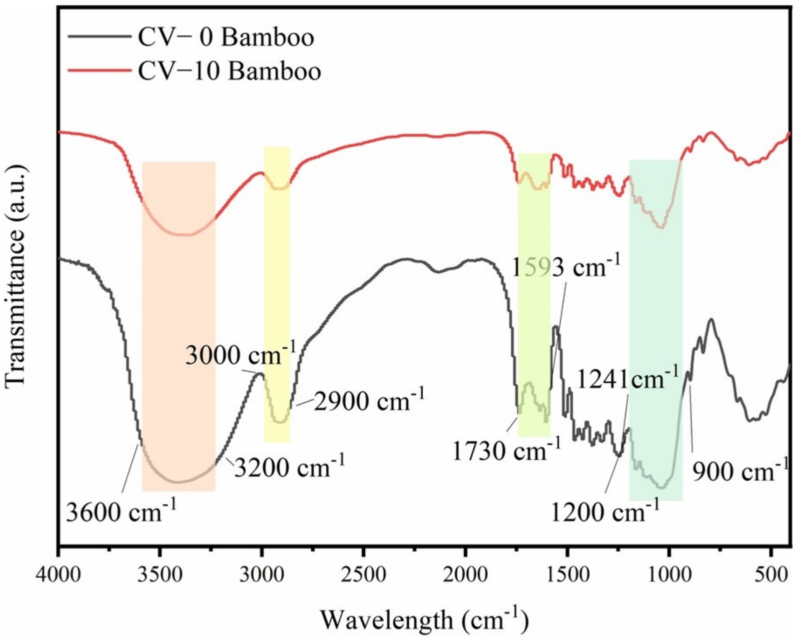

**Fig. S5** FTIR spectra of CV–0 Bamboo and CV–10 Bamboo.

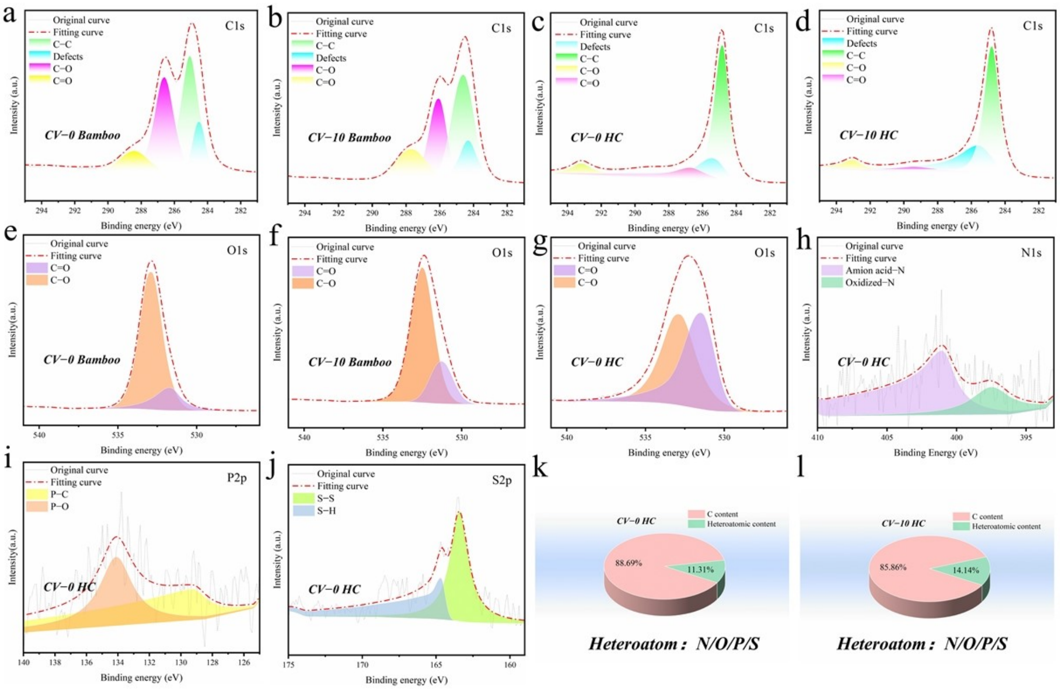

**Fig. S6** (a–j) XPS high–resolution spectra of C1s, O1s, N1s, P2p and S2p for various samples, and the heteratom content of (k) CV–0 HC and (l) CV–10 HC determined by XPS.

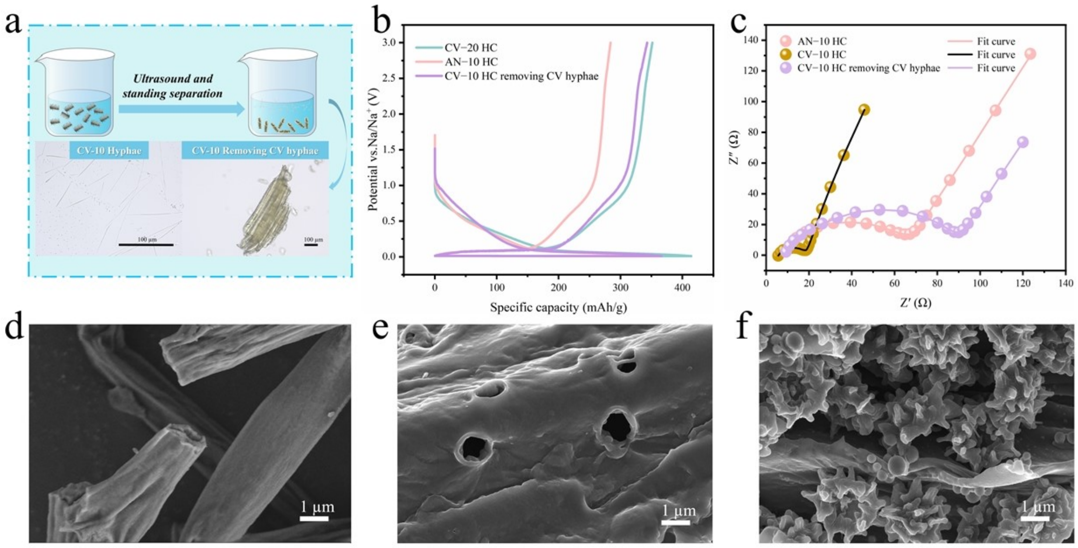

**Fig. S7** (a) Schematic diagram of CV hyphae and bamboo substrate separation by ultrasonic and standing method for CV–10 Bamboo sample, and their stereo microscope photographs; (b) Initial charge–discharge curves of CV–20 HC, AN–10 HC and CV–10 HC removing CV hyphae; (c) EIS of AN–10 HC, CV–10 HC and CV–10 HC removing CV hyphae samples; SEM images of (d) CV hyphae derived carbon, (e) CV–10 HC removing CV hyphae, (f) AN–10 HC.

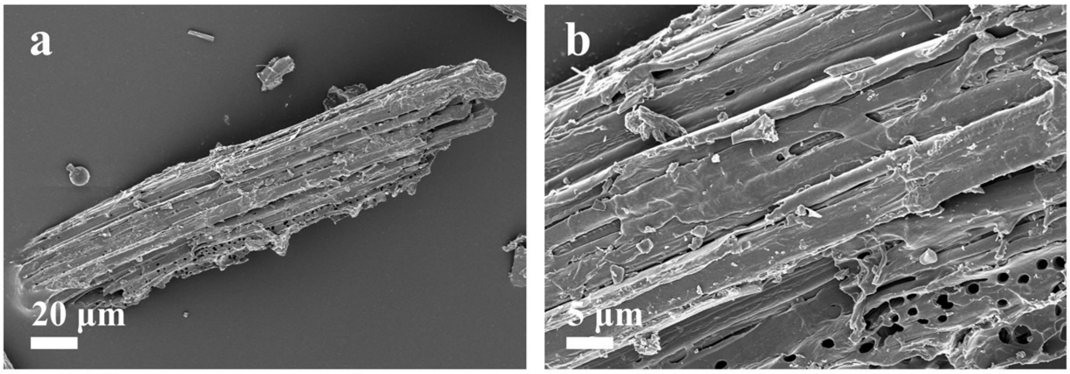

**Fig. S8** (a, b) SEM images of CV–20 HC at different magnifications.

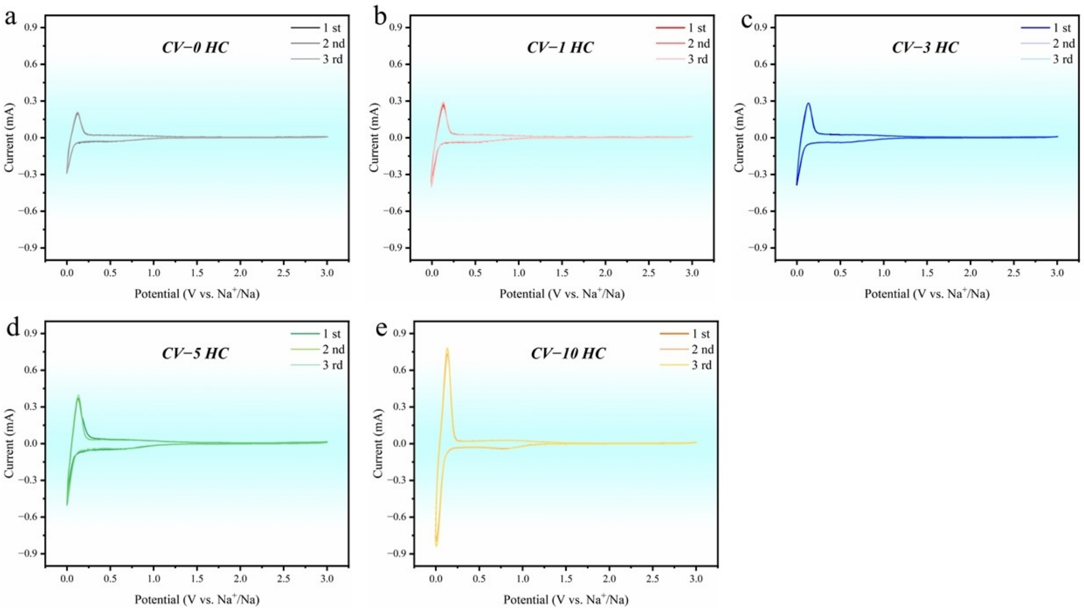

**Fig. S9** Cyclic voltammetry curves of (a) CV–0 HC, (b) CV–1 HC, (c) CV–3 HC, (d) CV–5 HC (e) CV–10 HC at a scanning rate of 0.1 mV/s, respectively.

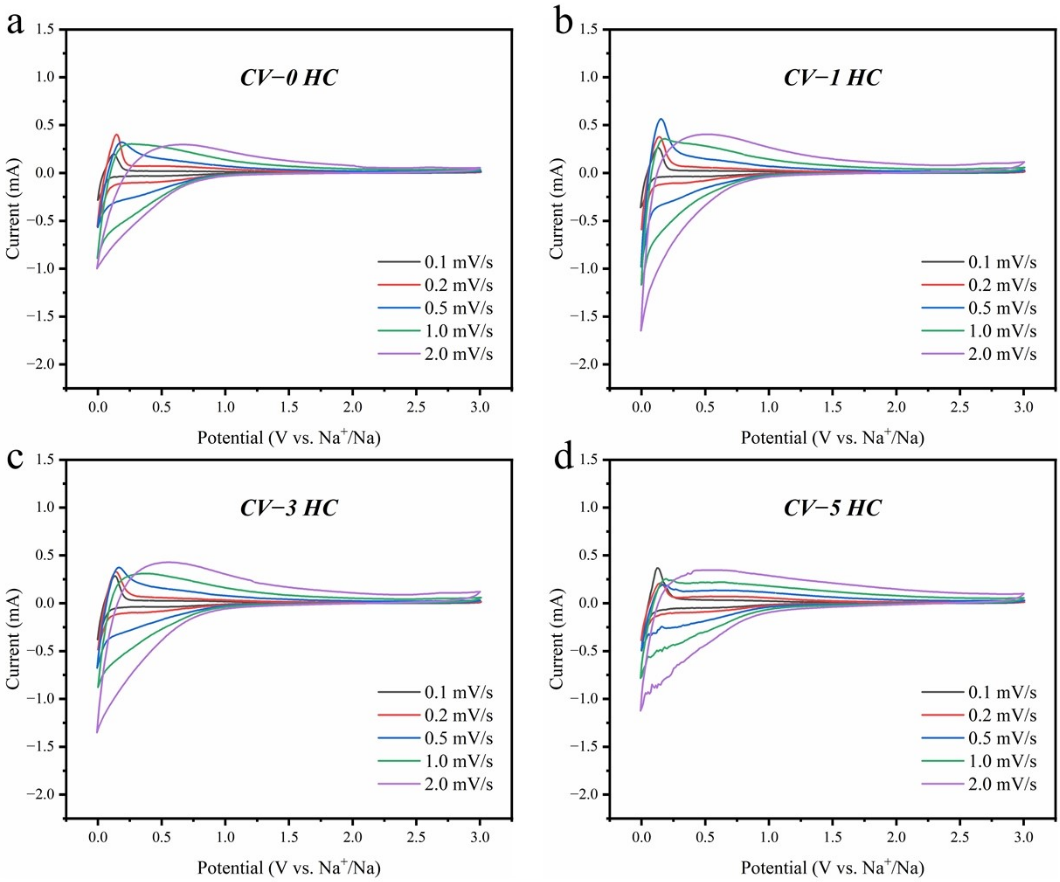

**Fig. S10** Cyclic voltammetry curves at varied scanning rates ranging from 0.1 to 2.0 mV/s for (a) CV–0 HC, (b) CV–1 HC, (c) CV–3 HC, and (d) CV–5 HC, respectively.

**Table S1** Cellulose, Hemicellulose, Lignin, and Starch content in CV–0 Bamboo and CV–10 Bamboo.

| | Hemicellulose (%) | Cellulose (%) | Lignin (%) | Starch (%) |
|---|---|---|---|---|
| CV−0 Bamboo | 16.80±0.29 | 39.60±0.33 | 25.50±0.86 | 2.84±0.02 |
| CV−10 Bamboo | 18.20±0.28 | 39.30±0.51 | 21.70±0.87 | 2.56±0.01 |

**Table S2** Structural parameters estimated from Nitrogen adsorption, SAXS, XRD and Raman results.

| Sample name | Nitrogen adsorption | | SAXS | XRD | | | Raman |
|---|---|---|---|---|---|---|---|
| | $S_{BET}$[a] ($m^2$/g) | $V_{pore}$[b] ($cm^3$/g) | R(nm) | $d_{002}$(nm) | $L_c$(nm) | $L_a$(nm) | $I_{D-band}/I_{G-band}$ |
| CV–0 HC | 24.526 | 0.018 | 10.390 | 0.380 | 1.417 | 0.085 | 1.823 |
| CV–1 HC | 1.855 | 0.004 | 7.340 | 0.384 | 1.518 | 0.089 | 1.864 |
| CV–3 HC | 13.969 | 0.019 | 5.170 | 0.384 | 1.590 | 0.098 | 1.912 |
| CV–5 HC | 13.244 | 0.021 | 5.840 | 0.386 | 1.622 | 0.107 | 1.917 |
| CV–10 HC | 16.118 | 0.026 | 4.110 | 0.390 | 1.586 | 0.114 | 1.968 |

[a] Surface area was calculated by Brunauer–Emmett–Teller (BET).

[b] The total pore volume was determined at a relative pressure of 0.99.

**Table S3** Assignments of the characteristic FTIR bands.

| Bands (cm$^{-1}$) | Characteristic groups |
|---|---|
| 3200−3600 | −OH [1] |
| 2900−3000 | C−H–telescopic vibration in cellulose and hemicellulose [2] |
| 1733 and 1241 | C–O stretching in O=C–H of acetyl groups and O=C–O of carboxyl groups [3] |
| 1593 | C=O asymmetric stretching vibration in lignin [4] |
| 900 and 1200 | C–O–C glycosidic bond vibration and the stretching vibrations of the C–O [5] |

**Table S4** ICP–MS test results of various bamboo samples (mg/kg) .

| Sample name | Ca | Fe | K | Si | Mg | Zn | Mn | Cu | Total content |
|---|---|---|---|---|---|---|---|---|---|
| CV–0 Bamboo | 223.19 | 98.31 | 7908.16 | 90.48 | 289.49 | 18.42 | 117.94 | 3.27 | **8749.26** |
| CV–10 Bamboo | 354.51 | 60.05 | 3869.92 | 67.36 | 130.34 | 11.41 | 40.85 | 2.04 | **4536.47** |
| CV–10 Bamboo after washing | 124.20 | 26.98 | 224.75 | 38.77 | 97.83 | 7.99 | 38.52 | 0.27 | **559.30** |
| Leaching ions | 230.31 | 33.07 | 3645.17 | 28.59 | 32.51 | 3.42 | 2.33 | 1.77 | **3977.17** |

**Table S5** The $N_2$ adsorption and desorption isotherm data from CV–20 HC.

| sample | BET Surface Area ($m^2/g$) | Pore Volume ($cm^3/g$) | Pore Size (nm) |
|---|---|---|---|
| CV–20 HC | 1.932 | 0.006 | 23.742 |

**Table S6** The first cycle electrochemical performance of HCs electrodes.

| Sample | Discharge (mAh/g) | Charge (mAh/g) | ICE (%) | Sloping (mAh/g) | Plateau (mAh/g) |
|---|---|---|---|---|---|
| CV–0 HC | 314.58 | 202.26 | 64.30 | 177.60 | 136.98 |
| CV–1 HC | 344.17 | 238.08 | 69.18 | 182.80 | 161.37 |
| CV–3 HC | 392.84 | 321.62 | 81.87 | 184.40 | 208.44 |
| CV–5 HC | 475.80 | 381.91 | 80.27 | 228.90 | 246.90 |
| **CV–10 HC** | **472.00** | **428.21** | **90.72** | **230.10** | **241.90** |
| CV–20 HC | 414.17 | 351.44 | 84.85 | 187.00 | 227.17 |
| AN–10 HC | 351.96 | 283.97 | 80.68 | 176.80 | 175.16 |
| CV–10 HC removing CV hyphae | 366.16 | 343.94 | 93.66 | 159.30 | 206.86 |

# 3. References

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