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Supporting Information for

3D hierarchical porous carbon derived from calcium lignosulfonate for high performance zinc ion hybrid capacitors

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1. Supporting Experimental Section

1.1 Materials

Calcium lignosulfonate, as the precursor of Calcium Lignosulfonate hierarchical porous carbon (denoted as LHPC), was purchased from MACKLIN (Shanghai, China). N_2 from Guangdong Yuejia gas company was used as inert protective gas.

1.2 Preparation of LHPC

Briefly, LHPCs are prepared via carbonization of CLS under a N_2 atmosphere at 700, 800 and 900 °C for 2 h at a ramp rate of 5 °C min^{-1}, separately. The carbonized materials are subsequently washed with HCL aqueous solution and deionized water and dried at 90 °C for 4 h. As prepared N-O-S codoped hierarchical porous carbons are named as LHPC-X, where X denotes the carbonization temperature.

1.3 Materials Characterization

A Merlin scanning electron microscope (SEM, Zeiss, Germany) was employed to characterize the surface morphology of LHPC. IS50R Fourier transform infrared spectroscopy (FTIR, Thermo Fisher Scientific, USA) was performed on LHPC using KBr pallet method. The degree of graphitization of LHPC was characterized by LabRAM HR Evolution micro confocal Raman spectrometer (HORIBA Jobin Yvon, France). X-ray diffraction patterns were collected on a D8 Advance X-ray diffractometer (XRD, Bruker, Germany) with a Cu Kα radiation (λ=1.5406 Å). The specific surface areas and pore diameters were measured at 77 K using ASAP 2460 N2 adsorption-desorption (Micromeritics, USA). The compositions of samples were analyzed by Escalab 250Xi X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher Scientific, USA).

1.4 Preparation of LHPC electrode and electrochemical cells for testing the LHPC based ECs (ZIC) devices

The LHPC electrodes were prepared by mixing LHPC sample with carbon black and PTFE with a weight ratio of 7:2:1 in ethanol. The mixture was stirred and dried at 60 ℃. The dried mixture was rolled into a free-standing film and dried at 90 ℃ for 5h. Then, the film was cut into electrode sheets with geometry sizes of 0.8 ×0.8 cm2. The electrode sheet was pressed onto stainless steel with a pressure of 10 MPa to fabricate the supercapacitor electrode.

Zn-ion hybrid ECs (Zn//PC ZIC): a self-made supercapacitor cells are used for assembly ZICs in air with electrode as cathode, Zn foil as anode and glass microfibre (Whatman) as the separator.

The electrolyte was 1 M ZnSO4.

1.5 Electrochemical measurements and calculations

All cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectra (EIS) measurements were conducted with Gamry interface 1010B electrochemical workstation. The EIS spectra were measured in the frequency range of 1000 kHz to 10 mHz with a voltage amplitude of 10 mV.

The specific gravimetric capacitances of electrode material (C_g, F g^{-1}) were calculated from the discharge curves of GCD in the three-electrode system:

$$C_g = \frac{I\Delta t}{Um} \tag{S1}$$

Furthermore, the C_g of electrode material in a two-electrode measurement can be calculated using equation (S2):

$$C_g = 2\frac{I\Delta t}{Um} \tag{S2}$$

where I is test current of GCD, Δt is the discharging time, U is the working voltage window and m is the mass of the electrode materials.

The capacitive contribution was calculated from CV result. The equation is described as the following:

$$i = k_1 v + k_2 v^{\frac{1}{2}} \tag{S3}$$

$$\frac{i}{v^{\frac{1}{2}}} = k_1 v^{\frac{1}{2}} + k_2 \tag{S4}$$

where $k_1 v$ and $k_2 v^{1/2}$ correspond to the current contributions from the capacitive contributions and diffusion-controlled processes.

The following equations were used to calculate the real and imaginary capacitances (C' and C'') based on EIS measurement to evaluate the capacitance response speed and the relaxation time.

$$c' = \frac{-Z''}{2\pi f A|Z|^2} \tag{S5}$$

$$c'' = \frac{-Z'}{2\pi f A|Z|^2} \tag{S6}$$

where Z'' is the imaginary impedance, Z' is the real impedance, f is frequency, A is available surface area and $|Z|$ is the magnitude of impedance.

The relaxation time was calculate using equation S7.

$$\tau = \frac{1}{f_0} \tag{S7}$$

Where f_0 is the frequency where the C'' reaches the maximum.

Gravimetric energy density (E) and power density (P) were calculated according to the following equation:

$$E = \frac{I\int Udt}{m} \tag{S8}$$

$$P = \frac{E}{\Delta t} \tag{S9}$$

2. Supporting Tables

Table S1 Yield rate of calcium lignosulfonate at different pyrolysis temperatures

Temperature of calcination/℃	Mass before calcination/g	Mass after calcination/g	Yield rate/%
700	5.10	2.92	57.25
800	5.04	2.95	58.53
900	5.03	2.55	50.70

Table S2 Yield rate of CCLS-700, CCLS-800 and CCLS-900 after hydrochloric acid dipping

Sample	Weight before pickling/g	Weight after pickling/g	Yield rate/%
CCLS-700	2.00	0.23	11.50
CCLS-800	2.95	0.34	11.53
CCLS-900	2.00	0.12	6.00

Table S3 Comprehensive yield rate of lignin-based porous carbon LHPC-700, LHPC-800 and LHPC-900

Sample	Combined yield rate/%
LHPC-700	6.58
LHPC-800	6.75

LHPC-900	3.04

Table S4 Characteristic pore properties of the carbon samples.

Samples	S_{BET} /m^2 g^{-1}	V_T /cm^3 g^{-1}	V_{meso} /cm^3 g^{-1}	V_{micro} /cm^3 g^{-1}	V_{meso}/V_T %	d/Å
LHPC-700	599.3	0.276	0.082	0.194	29.71	34.79
LHPC-800	542.0	0.268	0.107	0.161	39.93	32.32
LHPC-900	436.8	0.295	0.191	0.104	64.75	47.94

Notes: (1) S_{BET} represents the BET surface area; (2) V_T represents the total pore volume, measured at P/P_0 = 0.995; (3) d represents the average pore width (4V/A by BET); (4) DFT represents Density Function Theory.

Table S5 Surface chemistries of the LHPC-700 sample.

Sample	C/at%	N/at%	O/at%	S/at%
LHPC-700	85.26	2.79	11.18	0.77

Table S6 Carbon bonding environment analysis of the LHPC-700 sample.

Carbon Bonding	C-C/C=C	C-O/C-S/C-N	C=O	O-C=O/C=N
Binding Energy (eV)	284.5	285.6	286.8	288.7
Concentration (%)	71.61	16.01	8.97	3.41

Table S7 Nitrogen bonding environment analysis of the LHPC-700 sample.

Nitrogen Bonding	N-6	N-5	N-Q	N-X
Binding Energy (eV)	398.0	399.9	401.8	404.8
Concentration (%)	9.89	54.79	15.56	19.76

Table S8 Oxygen bonding environment analysis of the LHPC-700 sample.

Oxygen Bonding	C=O	C-OH/C-O-C	O=C-O
Binding	532.1	532.3	533.5

Energy (eV)			
Concentration (%)	12.29	77.92	9.79

Table S9 Sulfur bonding environment analysis of the LHPC-700 sample.

Sulfur Bonding	C-S	S-S	S=O
Binding Energy (eV)	163.8	165.0	168.6
Concentration (%)	33.68	18.03	48.29

3. Supporting Figures

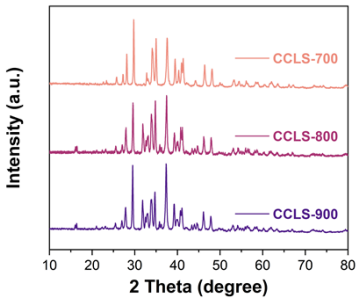

Figure S1. XRD patterns of the CCLSs by heating calcium lignosulfonate at 700, 800 and 900 °C for 2h

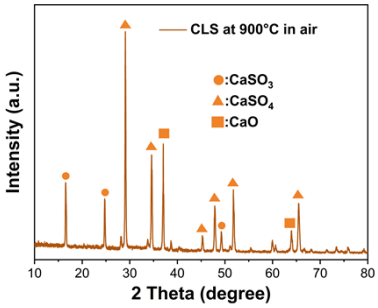

Figure S2. XRD patterns of the CLS ash

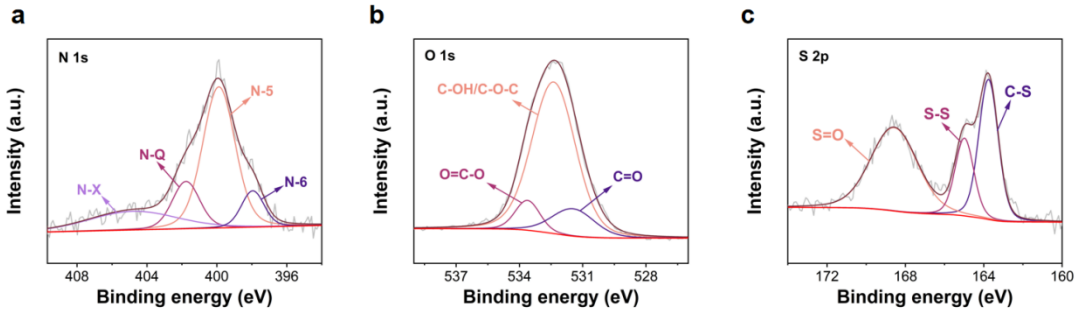

Figure S3. (a) N 1s high-resolution XPS spectrum with fitting results for LHPC-700, (b) O 1s high-resolution XPS spectrum with fitting results for LHPC-700, (c) S 2p high-resolution XPS spectrum with fitting results for LHPC-700.