

Supporting Information

Acid modified biomass-based N-doped O-rich hierarchical porous carbon as high-performance electrode for supercapacitors

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Experimental sections

Materials

The sawdust comes from solid wood furniture factories with containing a rich combination of various sawdust. The other chemicals were A.R. grade and can be immediate used without further purification. Sulfuric acid (H_2SO_4 , 98 wt%), nitric acid (HNO_3 , 65-67 wt%) and hydrochloric acid (HCL , 36-38 wt%) were bought from Aladdin reagent (Shanghai, China). Urea, potassium hydroxide (KOH), poly (vinyl difluoride) (PVDF) and N-methyl-2pyrrolide (NMP) were supplied by Tianjin Chemical Reagent Co., Kay Tong. Deionized (DI) water was used for cleaning up the surface residue of samples and preparing aqueous solutions throughout.

Synthesis of the CW materials

In a typical synthesis process of carbonized wood (CW), 1 g of the sawdust was ground it into finer powders and dried. Then, the dried powder was transferred to the tubular furnace, heated at 700 °C for 2 h at a rate of 5°C min⁻¹ in a continuous N₂ atmosphere. After cooling down, the sawdust powder with deionized water three times and dried at 60°C.

Synthesis of the ACW materials

To obtain the activated carbonized wood (ACW), the sawdust was added into a 16% (w/v) KOH aqueous solution at room temperature (while keeping a 2:1 mass ratio of KOH to sawdust) and stirring 2 h. After the centrifuge separation, dry the mixture overnight in a 60 °C oven to ensure sufficient drying. Then, the dried mixture was heated to 700°C in N₂ atmosphere at a heating rate of 5°C min⁻¹, and was heated at 700°C for 2 h. Finally, the carbonized material was added in 1 M HCl for stirring 2 h to ensure remove the impurities and salts such as K₂CO₃ generated due to activation reaction completely. Then, washed with deionized water to PH=7 and dried at 60°C for 24 h.

Synthesis of the UACW materials

Like ACW, preparation urea doped activated carbonized wood (UACW) had a similar process. The only difference was that urea needed to be added when adding sawdust into

KOH aqueous solution to stir, and the mass ratio of sawdust, KOH and urea must meet 1:2:1.

Synthesis of the AUACW materials

The acid modified urea doped activated carbonized wood (AUACW) materials were prepared by a physical and chemical activation and high temperature activation. 0.1 g of the UACW powder were added into the 4 mL of mixed acid solution (concentrated H₂SO₄ and concentrated HNO₃ in a 3:1 (v:v) ratio) and ultrasonic treatment 30 min. Then centrifuged, and washed with deionized water for many times until PH = 7, dried at 60°C for 24 h, and finally obtained AUACW materials.

Physical characterization

The surface morphology of the material was observed by scanning electron microscope (SEM, JSM-7500F). The crystal structure of the samples was obtained by transmission electron microscope (TEM, JEM-2100) at 20.00 KV. The pore structure of carbon materials was analyzed by the adsorption and desorption isothermal curve using a high-speed automatic surface area and pore analyzer (Autosorb-iQ3). Brunauer-Emmett-Teller (BET) method and Barrent-Joyner-Halenda model were used to calculate the specific surface area and pore size distribution curves. The crystal phase composition of the prepared material was studied by X-ray diffraction (XRD, TD-3500) test in the diffraction angle range of 5°-80°. The degree of graphitization of samples was detected by laser Raman spectrometer (Raman, DXR220192805). Fourier transform infrared (FTIR, Nicolet iS10) spectral data were collected to obtain information on relevant functional groups. The composition and content of chemical elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermofisher Escalab Xi+) and energy dispersion spectrometry (EDS).

Electrochemical measurement

In this experiment, the CHI660E electrochemical workstation was used to evaluate the electrochemistry performance of as-prepared biomass porous carbon materials in 1 M KOH solution. The AUACW electrode was used as working electrode (WE), the platinum electrode as counter electrode (CE) and Hg/HgO as reference electrode (RE). The electrochemical

characteristics of electrodes were measured by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements.

The blank nickel foam (9 cm×1 cm) was treated by 1 M HCl, acetone, ethanol and deionized water under ultrasonic for 15 min to remove impurities such as oxidation layer, grease and dust on the surface, and then dried at 60 °C for using. For porous carbon electrodes, grind them thoroughly with acetylene black in a mass ratio of 7:2 and added an appropriate amount of PVDF-NMP mixture by ultrasonic for 5 min. Then, the mixture was transferred to a blank foam nickel with an area of 1cm × 1cm. At last, dried the electrode at 60 °C for about 4 h, and the mass of material loaded on the electrode is about 1-2 mg.

For three-electrode system, the specific capacitance of the working electrode (C_1 , F g⁻¹) can be calculated from the GCD measurement according to the following formula:¹

$$C_1 = \frac{I * \Delta t}{m * \Delta V} \quad (\text{S1})$$

where I represents the discharge current (A), Δt represents the discharge time (s), m represents the sample load on the working electrode (mg), and ΔV represents the voltage difference at discharge (excluding ohmic drop) (V).

The electrodes of the same size and load mass were assembled into symmetrical supercapacitors. Based on the GCD results, the relevant electrochemical parameters can be calculated as follows:²

Specific capacitance of a single electrode (F g⁻¹):

$$C_2 = \frac{4 * I * \Delta t}{m * \Delta V} \quad (\text{S2})$$

Specific capacitance of a supercapacitor (F g⁻¹):

$$C_3 = \frac{I * \Delta t}{m * \Delta V} \quad (\text{S3})$$

Energy density (Wh kg⁻¹):

$$E = \frac{C_3 * \Delta V^2}{2 * 3.6} \quad (\text{S4})$$

Power density (W kg⁻¹):

$$P = \frac{3600 * E}{\Delta t} \quad (\text{S5})$$

where I represents the discharge current (A), Δt represents the discharge time (s), m represents the sample load and (mg) of the load on the two electrodes and ΔV represents the voltage difference at discharge (excluding ohmic drop) (V).

In the two-electrode system, the current law of parallel devices is as follows:³

$$q_1 = C_1 U, q_2 = C_2 U \quad (\text{S6})$$

$$q = q_1 + q_2 \quad (\text{S7})$$

$$C = \frac{q}{U} = C_1 + C_2 \quad (\text{S8})$$

The voltage law for series devices is as follows: ³

$$U_1 = \frac{q}{C_1}, U_2 = \frac{q}{C_2} \quad (\text{S9})$$

$$U = U_1 + U_2 \quad (\text{S10})$$

$$\frac{1}{C} = \frac{U}{q} = \frac{1}{C_1} + \frac{1}{C_2} \quad (\text{S11})$$

where U , q and C in the above formula represent the voltage (V), electric charge (C) and equivalent capacitance (F) in the system, respectively.

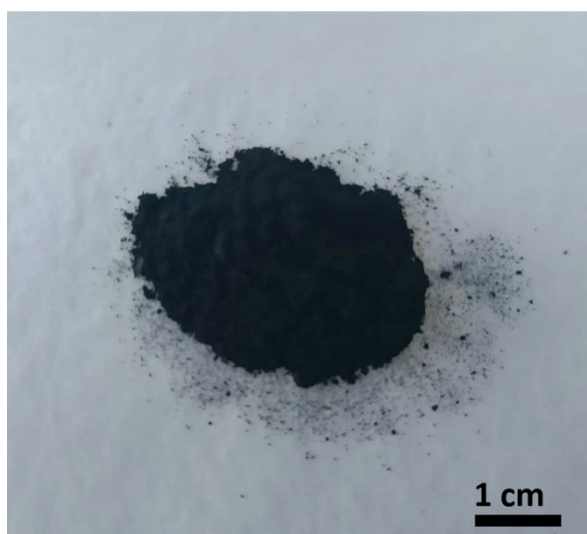


Fig. S1 Optical photos of AUACW samples.

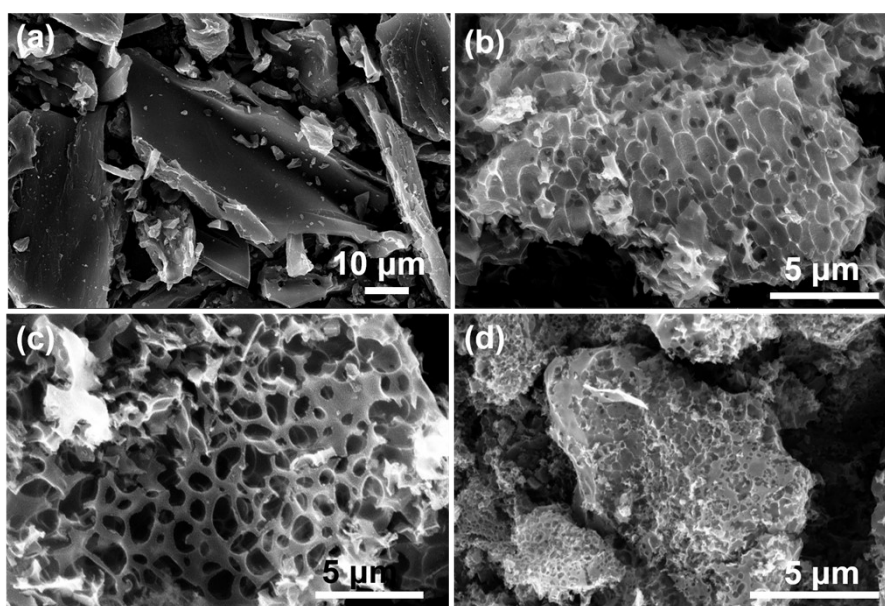


Fig. S2 SEM images of (a) CW, (b) ACW, (c) UACW and (d) AUACW materials.

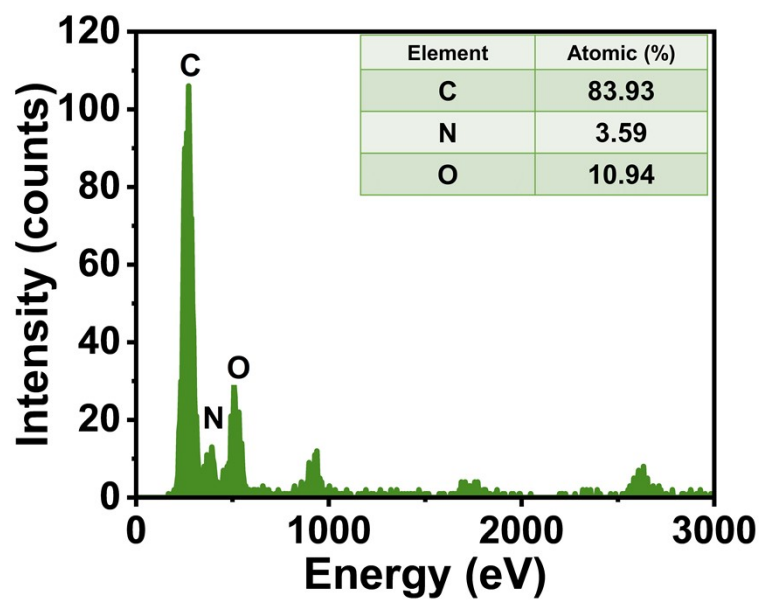


Fig. S3 EDS mapping of AUACW.

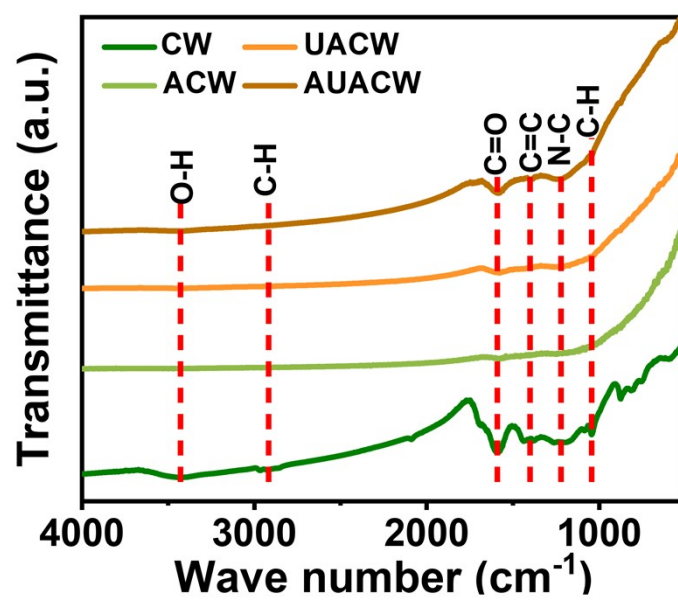


Fig. S4 FTIR spectra of CW, ACW, UACW and AUACW.

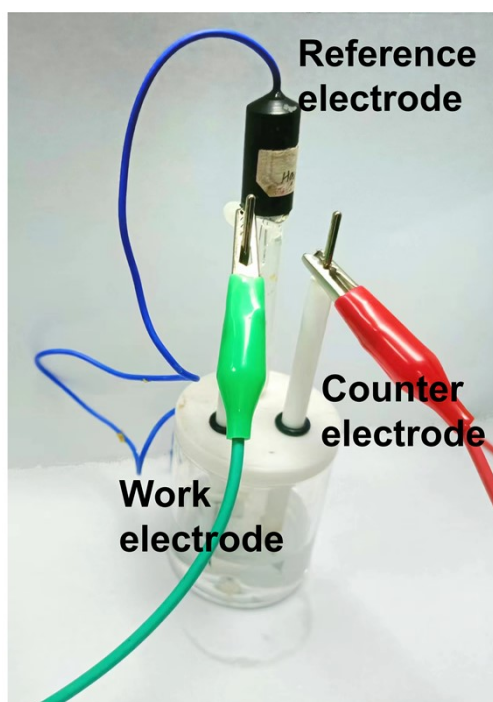


Fig. S5 Three-electrode system electrolytic cell.

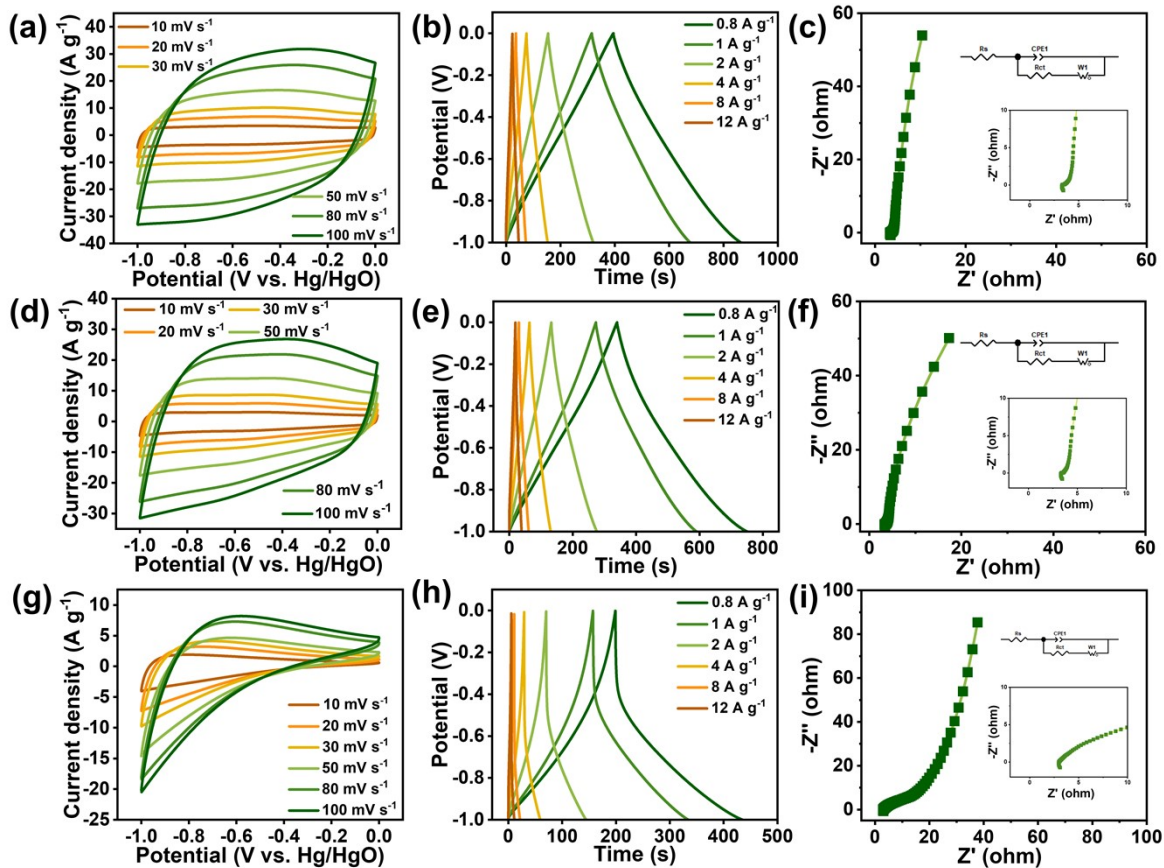


Fig. S6 Electrochemical properties of UACW, ACW and CW electrode. (a, d, g) CV curves from 10-100 $mV\ s^{-1}$. (b, e, h) GCD curves at various current density. (c, f, i) EIS curves in the frequency range from 0.01 to 100 kHz.

Table S1. Resistance values of CW, ACW, UACW and AUACW electrode.

Samples	R_s (Ω)	R_{ct} (Ω)
CW	3.107	11.123
ACW	3.461	0.136
UACW	3.435	0.109
AUACW	3.225	0.089

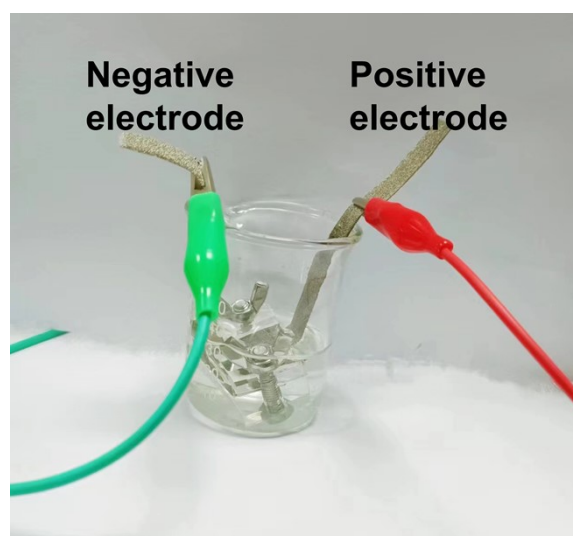


Fig. S7 Two-electrode system.

References

1. Zhao, Y.; He, X.; Chen, R.; Liu, Q.; Liu, J.; Song, D.; Zhang, H.; Dong, H.; Li, R.; Zhang, M.; Wang, J., Hierarchical NiCo₂S₄@CoMoO₄ core-shell heterostructures nanowire arrays as advanced electrodes for flexible all-solid-state asymmetric supercapacitors. *Applied Surface Science* **2018**, *453*, 73-82.
2. Bello, A.; Manyala, N.; Barzegar, F.; Khaleed, A. A.; Momodu, D. Y.; Dangbegnon, J. K., Renewable pine cone biomass derived carbon materials for supercapacitor application. *RSC Advances* **2016**, *6* (3), 1800-1809.
3. Lv, C.; Ma, X.; Guo, R.; Li, D.; Hua, X.; Jiang, T.; Li, H.; Liu, Y., Polypyrrole-decorated hierarchical carbon aerogel from liquefied wood enabling high energy density and capacitance supercapacitor. *Energy* **2023**, *270*, 126830.