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Porous carbon derived from a biomass with unique honeycomb-like microstructure for high-performance supercapacitors

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Experimental

Synthesis of electrode materials: Fig. 1 illustrates the synthetic process for the new AC. The detailed procedures are as follows: 6 g of the collected ailanthus altissima stems were immersed into 20 mL aqueous solution of KOH (1 M) and agitated at 60 °C for 24 h. Subsequently, the resulting mixture was filtered and freeze-dried at -53 °C for 24 h in order to maintain their inherent structure. The dried ailanthus altissima stems were further carbonized under an argon atmosphere by heating at 600 °C, 700 °C, 800 °C for 2 h, respectively, with a ramp rate of 3 °C min⁻¹. After thermal treatment, the product was washed with diluted hydrochloric acid and distilled water, and dried at 120 °C for 12 h. The obtained samples were designated as CK-X, where X represented the activation temperature, including CK-700, CK-800, and CK-900. Furthermore, the CKU-800 samples were prepared in presence of KOH and urea mixtures (1:4) at an activation temperature of 800 °C through the same process described above.

Materials characterization: The morphology of the samples was investigated by using a field emission scanning electron microscope at an accelerating voltage of 20.0 kv (FE-SEM, Supra55, Carl Zeiss) and a high resolution transmission electron microscope (HR-TEM, Tecnai G2 F30 S-TWIN). The structural analysis of the samples was performed on a wide angle X-ray diffractometer (WAXD, 2500VB2+PC, Japan). Raman spectroscopy was performed using a Senterra R200-L (Bruker Optics, Germany) with an excitation wavelength of 514 nm. Ten percent of the maximum power of the laser was employed during general scanning. Nitrogen adsorption and desorption isotherms were measured at 77 K after the samples were degassed at 473 K for 4 h using a Brunauer-Emmett-Teller (BET) surface area measurement system (JW-BK200C, China). The specific surface area (SSA) was determined through BET method and the micropore surface area was obtained by using the t-plot method. The total pore volume was calculated based on the nitrogen adsorption volume at the maximum relative pressure. The micropore volumes and pore size distribution were calculated according to Horvath-Kawazoe (HK) and Barrett-Joyner -Halenda (BJH) methods. To investigate the surface chemistry characteristic and elemental composition of the AC samples, X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) using a monochromatic Al Ka X-ray (1486.6 eV) source.

Electrochemical measurements: The CK-X sample was mixed with poly(vinylidene difluoride) (PVDF) binder in a 1-methyl-2-pyrrolidone (NMP) solution to form a slurry at a weight ratio of 90:10. The working electrode was prepared by casting the slurry onto the platinum current collectors and then dried in a vacuum oven at 120 °C overnight. The loading mass of active materials on each platinum plate was about 2.0 mg cm⁻². The electrochemical measurements were carried out in a three-electrode system with 1 M H_2SO_4 as an electrolyte, an Ag/AgCl electrode (3.5 M KCl, 0.2046 V vs. standard hydrogen electrode at 25 °C) as a reference electrode and a slice of platinum plate as a counter electrode. Before testing, the working electrodes were immersed in the electrolyte for 24 h. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Autolab PGSTAT 302N, Metrohm). CV curves were recorded between -0.1 and 0.9 V at various scanning rates (10-400 mV s⁻¹). EIS was carried out in the frequency range from 0.01Hz to 10 KHz. The galvanostatic charge/discharge processes were conducted on a battery tester (LAND CT2001A, China) over a voltage range of -0.1 to 0.9 V at different current densities (0.5-20 A g⁻¹). The specific capacitance was calculated based on the mass of the samples within the electrodes.

Supporting results

The microstructural parameters of these samples are summarized in Table S1 in detail. The CKU-800 exhibited a SSA of 1776.9 m² g⁻¹ (Table S1), which was much higher than that of CK–700 (847.9 m² g⁻¹), CK-800 (891.8 m² g⁻¹) and CK-900 (878.2 m² g⁻¹). The highest pore volume of 0.99 m³ g⁻¹ was also obtained for CKU-800.

Items	СК-700	CK-800	СК-900	CKU-800
BET surface area (m ² g ⁻¹)	847.9	891.8	878.2	1776.9
Total pore volumes (cm ³ g ⁻¹)	0.440	0.613	0.537	0.993
Micropore volumes (cm ³ g ⁻¹)	0.371	0.366	0.370	0.763
Average pore diameter (nm)	5.181	4.017	3.981	4.441

Table S1. Microstructural parameters of the porous carbon samples.

X-ray photoelectron spectroscopy (XPS) measurements were used to carry out the chemical identification of the heteroatoms in all the samples. The XPS survey spectra is shown in Fig. S1a. The C1s XPS spectra obtained for CK-700 CK-800 and CK-900 samples showed rather complex deconvoluted patterns (Fig. S2a-c). All these samples exhibited a broad peak at 284.6 eV and this peak could be deconvoluted into three distinct peaks revealing the presence of signals from C=C (284.6 eV), C-O (285.7 eV), C=O (288.2 eV). In the O1s spectrum (Figure. S2d-f), three peaks located at 531.4 eV, 532.9 eV and 534.2 eV represented the carbonyl groups (C=O), phenol-type groups (C-OH)/ether-type groups (C-O-C) and chemisorbed oxygen and/or adsorbed water (chemisorbed O), which can enhance the wettability and contribute to pseudocapacitance.¹ Moreover, the CKU-800 sample exhibited distinct characteristic peak belonging to N element deriving from the pyrolysis of urea at nitrogen atmosphere. The high resolution C1s curve showed the presence of a C-N bond (285.8 eV) in CKU-800 sample (Fig. S1b). As shown in Fig. S1c, the N1s peak in the nitrogen doped samples (CKU-800) can be divided into three different regions, representing pyridinic N (N-6 at 398.5±0.2 eV), pyrrolic or pyridonic N (N-5 at 399.9±0.2 eV) and quaternary N (N-Q at 400.8±0.2 eV).² The Ndoping was suggested to improve the wetting ability between the pore walls and electrolytes and enhance the conductivity of the carbon materials that can help to maintain the high rate performance. In addition, the atomic contents of the carbon samples with different temperature quantitatively were analyzed in the XPS test, as shown in Table S2.

Table S2. Atomic contents of the carbon samples with different temperature.

Items	C1s	O1s	N1s	Si2p
СК-700	64.22	25.07	1.45	9.27
СК-800	76.13	18.74	0.96	4.17
СК-900	79.33	15.88	1.04	3.75
CKU-800	77.17	16.34	2.65	3.84



Fig. S1 (a) The total XPS spectra of porous carbon, and (b) C 1s, (c) N 1s and (d) O1s spectra of CKU-800.



Figure S2. C1s (a, b, c) and O1s (d, e, f) XPS spectra of CK-700, CK-800, CK-900.

The Table S3 shows the comparison of specific capacitance of porous carbon supercapacitors in this study with that of reported carbon-based supercapacitors in the relevant reports.

Materials	Activating agent	SSA	Electrolyte	Cd	Sc	Reference
		(m ² g ⁻¹)		(A g ⁻¹)	(F g ⁻¹)	
Willow catkin	КОН	1533	6M KOH	0.5	298	[S1]
Bamboo byproduct	КОН	1472	6M KOH	0.1	301	[S2]
Cotton	КОН	1563	6M KOH	0.1	314	[83]
tobacco rods	КОН	2115	6M KOH	0.5	286.6	[S4]
oil palm kernel shell	КОН	727.3	1М КОН	0.5	210	[85]
waste corn cob	HNO ₃	543.68	0.5M H ₂ SO ₄	0.5	221	[S6]
shell of broad beans	КОН	655.4	1M H ₂ SO ₄	0.5	229	[S7]
cashmere	КОН	1358	6M KOH	0.5	363	[S8]
shiitake	(NH4)3PO4/KOH	2335	6M KOH	0.5	315	[89]
chicken albumen	КОН	1227	1M H ₂ SO ₄	0.5	282	[S10]
lignite	КОН	1257	1M H ₂ SO ₄	0.5	291	[S11]
Ailanthus altissima	KOH/urea	1776.9	1M H ₂ SO ₄	0.5	306	This work

Table S3. Specific capacitance of reported carbon-based supercapacitors.

* a three-electrode system test; SSA refers to the specific surface area; Cd refers to current density; Sc refers to specific capacitance

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