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Modification of Ultra-microporous Dominated Carbon by O/N-containing Functional Groups Grafted for Enhanced Supercapacitor Performances

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Experimental Section

1. Materials

Melamine (Chemically Pure), formaldehyde (37 wt.%), sodium hydrate (NaOH) and analytically pure potassium hydrate (KOH) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium polyacrylate (PAAS, the main ingredient of super absorbent polymer) was supplied by ANJUHUANBAO Co. Ltd., China. All the chemical reagents were used as received without further purification procedures. Distilled deionized water was employed for all the experiments.

2. Synthesis of MF/PAAS IPNs

In a typical experimental procedure, 1g of melamine was added to 40ml of deionized water and stirred, and the pH value was adjusted to 8-9 with NaOH aqueous solution, and then 1.63ml of 37% formaldehyde solution was added. Water bath at 80℃, the solution turns from turbid to clear, which means that the prepolymer of methylol melamine is formed. Then add 1g of PAAS under vigorous stirring conditions, until the PAAS network is completely swelled and all the prepolymer aqueous solution is fully absorbed, and then heated to 95 ℃ and maintained for 6 hours to obtain MF/PAAS IPNs. Dry it at 60℃ for 24 hours.

3. Preparation of Ultra-microporous carbon.

The obtained IPNs was ground to a fine powder. Then, porous carbon was produced by carbonizing the IPNs powder under an N_2 atmosphere for 2 hours. The final temperature and heating rate of the furnace were 900°C and 2°C/min, respectively. The product is expressed as UPC.

4. Heteroatom functional groups grafted onto the surface of ultramicroporous carbon.

The hydrothermal conditions are carried out according to the orthogonal experiment shown below. And In a typical experimental procedure, add 300 mg UPC to 14M HNO_3 solution and stir for half an hour, then transfer it to a 100 ml PTFE autoclave and hydrothermally heat at 60°C for 8 hours, cool naturally and wash it until the solution is neutral. Dry it at 60°C. and the sample is recorded as 60°C-14M-8h. The other samples are named according to x °C-y M-z h in turn, as shown in Table S1 and S2. For example, the corresponding test number 1 is named 60°C-6M-6h.

Table S1. Table of factors and levels in ours experiment.

Levels \ Factors	Temperature (A)/ °C	Concentration of HNO_3 (B)/M	Reaction time (C) /h
1	60	6	6
2	80	10	4
3	100	14	8

Table S2. Experimental scheme.

Test number	A	B	Empty list	C	Experimental program
1	1	1	1	1	A1B1C1
2	1	2	2	2	A1B2C2
3	1	3	3	3	A1B3C3
4	2	1	2	3	A2B1C3
5	2	2	3	1	A2B2C1
6	2	3	1	2	A2B3C2
7	3	1	3	2	A3B1C2
8	3	2	1	3	A3B2C3
9	3	3	2	1	A3B3C1

5. Structural characterization

X-ray diffraction (XRD) patterns were measured on the Bruker Focus D8 diffractometer with Cu Kα radiation (40 kV, λ=0.15418 nm) between 10° and 80°. Raman spectras were obtained by a Renishaw invia spectrometer with 520 nm Ar-ion laser. The morphologies and structures of the samples were obtained using scanning electron microscopy (SEM) and transmission electron microscopy (TEM, 200 kV). Pore structure was researched using the JWGB surface area and porosity analyzer. Specific surface areas were analyzed by Brunauer–Emmett–Teller (BET) theory. The pore size distribution (PSD) was calculated according to the Horvath-Kawazoe (H-K) model (for microporous) and Barret-Joyner-Halenda (BJH) model (for mesopores and macropores). The total pore volumes were calculated from the amount adsorbed at a relative pressure P/P_0 of 0.99.

6. Electrochemical characterization

All the electrode was obtained by mixing electroactive material powder (80 wt %), conductive graphite (7.5 wt %), acetylene black (7.5 wt %) and polytetrafluorethylene (PTFE, 5 wt % dispersed in water) in ethanol. The mixture was pressed into a foamed nickel current collector (surface area: 1 cm * 1 cm). The mass of the electroactive material powder in each electrode was about 4 mg. The foamed nickel was pressed at 10 MPa after which was dried in a vacuum oven at 60 °C for 12 hours. The electrochemical properties (cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy) of the EDLC were measured using an electrochemical workstation (CHI660E, Shanghai, China). The specific capacitance (C_g) is calculated according to the equation $C_g = I \times \Delta t /(m \times \Delta V)$, where $C_g(F\ g^{-1})$, m(g), I(A), Δt(s) and ΔV(V) represent specific capacitance, working electrode mass, constant current density, discharge time and discharge potential, respectively.

7. Assembly of the symmetrical supercapacitor

The specific assembly process is as follows: The electrode preparation process is as described above. Repeat this process to get two electrodes with the same composition and content. Connect the two electrodes to the positive and negative electrodes of the electrolytic cell and ensure that the two electrode sheets are parallel to each other, and then add electrolyte (6M KOH or 1M Na_2SO_4) to flood the electrodes. In this way, the symmetrical supercapacitor is assembled.

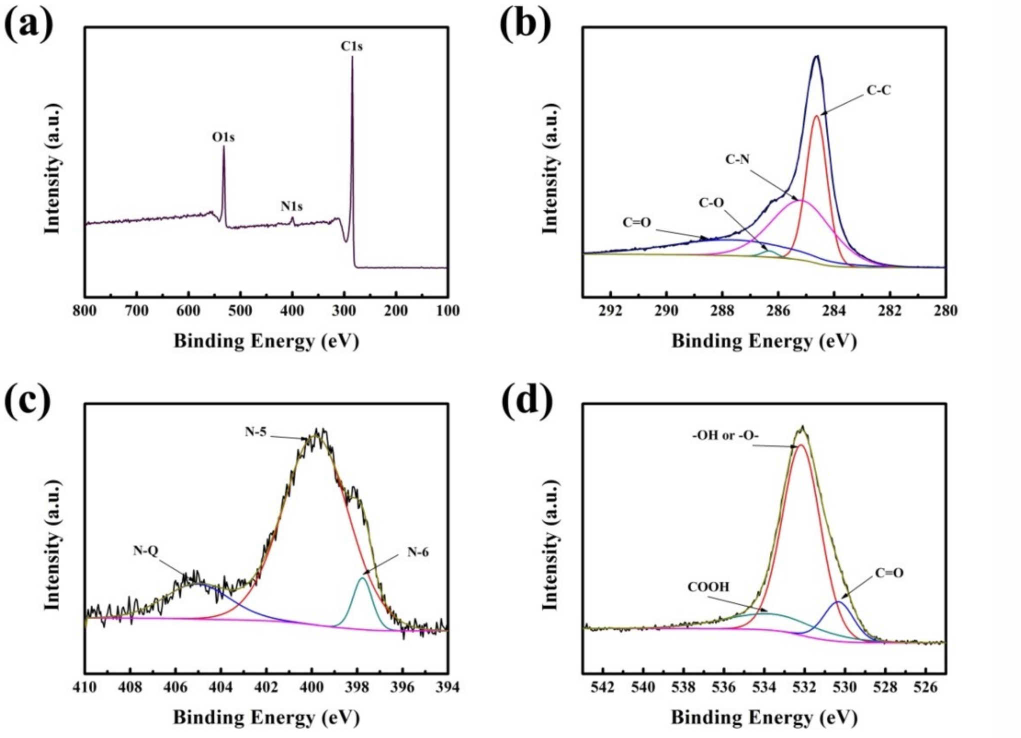

Figure S1. (a) XPS survey spectra and high-resolution XPS spectra of (b) C 1s, (c) N 1s and (d) O 1s of the sample 80℃-10M-6h.

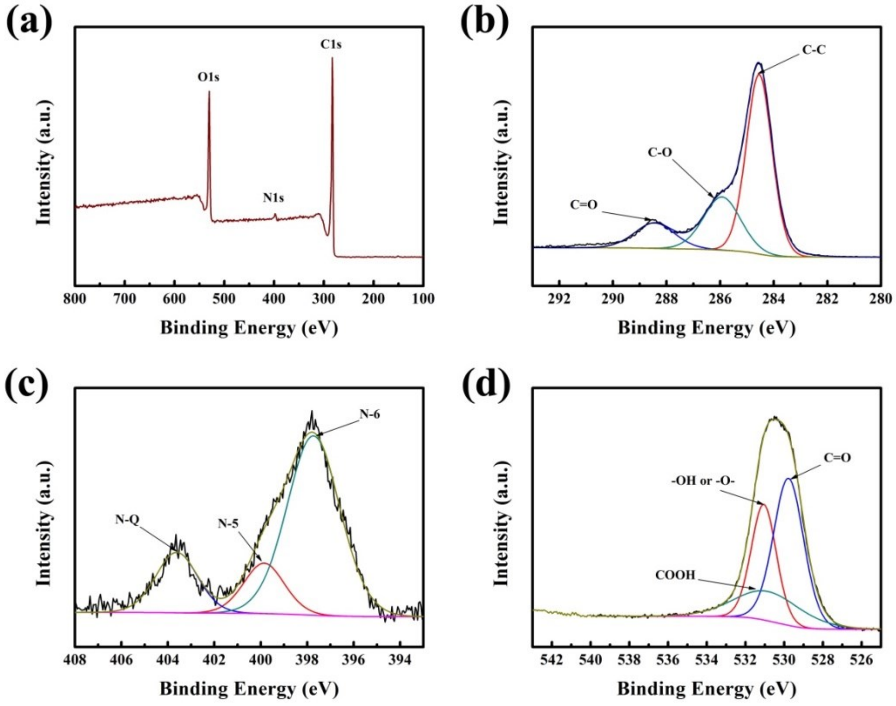

Figure S2. (a) XPS survey spectra and high-resolution XPS spectra of (b) C 1s, (c) N 1s and (d) O 1s of the sample 100℃-10M-8h.

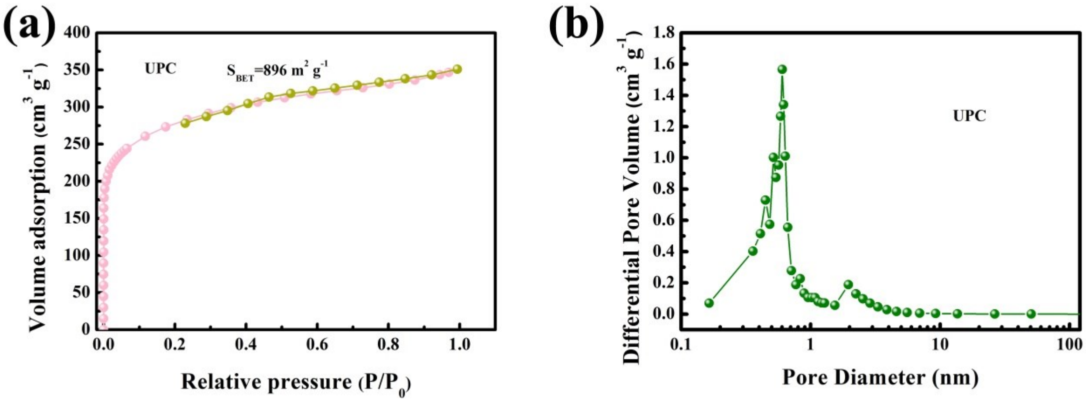

Figure S3. Nitrogen adsorption/desorption isotherms and pore size distribution of UPC.

Table S3. The porosity parameters including specific surface areas and pore volume of all the samples

Samples	S^{a}_{BET} (m^2 g^{-1})	S^{b}_{mic} (m^2 g^{-1})	V^{c}_{total} (cm^3 g^{-1})	V^{d}_{mic} (cm^3 g^{-1})
UPC	896	663	0.543	0.361
60°C-6M-6h	813	616	0.458	0.289
60°C-10M-4h	782	589	0.438	0.274
60°C-14M-8h	788	627	0.432	0.279
80°C-6M-8h	879	609	0.526	0.304
80°C-10M-6h	878	611	0.517	0.303
80°C-14M-4h	843	607	0.506	0.297
100°C-6M-4h	843	633	0.446	0.294
100°C-10M-8h	515	369	0.333	0.177
100°C-14M-6h	636	421	0.404	0.219

[a] Specific surface area, estimated using a model of Brunauer-Emmett-Teller (BET)

[b] Micropore specific surface area, calculated by t-plotting.

[c] Total pore volume, obtained by using nitrogen as the adsorbent at a maximum relative pressure of $P / P_0 = 0.99$.

[d] Micropore volume, estimated according to the DR method.

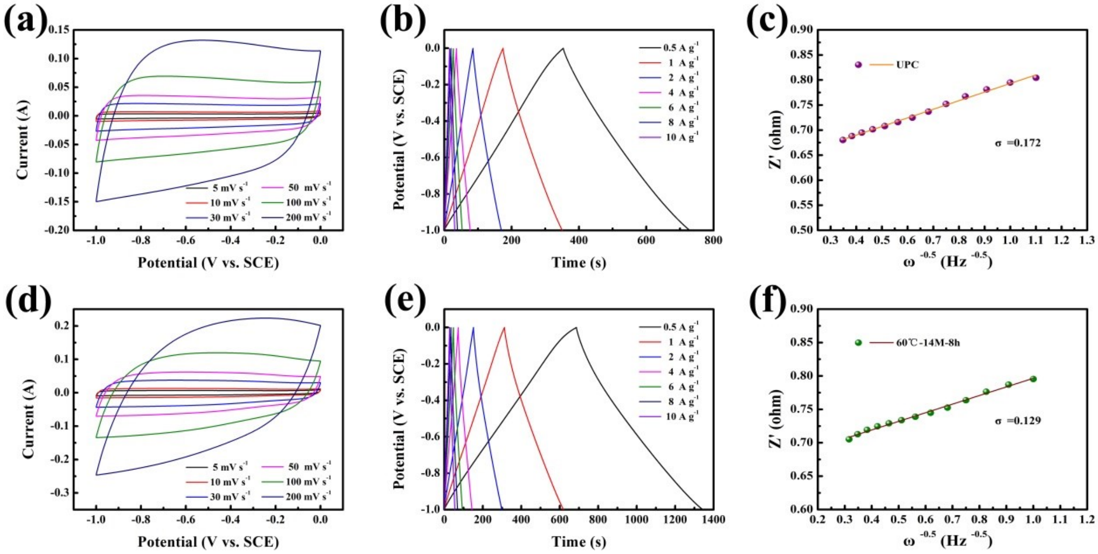

Figure S4. The comparison of electrochemical performances between UPC and 60°C-14M-8h: (a, d) CV curves; (b, e) GCD curves; and (c, f) diffusion coefficient.

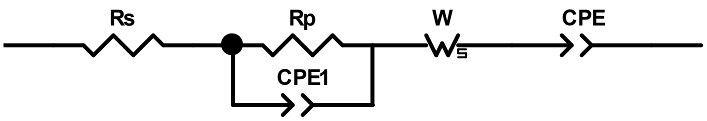

Figure S5. The fitted Randles circuit diagram

Table S4. The fitted Rs and Rp values.

Samples	UPC	60°C-6M-6h	60°C-10M-4h	60°C-14M-8h	80°C-6M-8h
Rs	0.574	0.599	0.648	0.574	0.601
Rp	0.028	0.029	0.027	0.070	0.087

Samples	80°C-10M-6h	80°C-14M-4h	100°C-6M-4h	100°C-10M-8h	100°C-14M-6h
Rs	0.612	0.558	0.579	0.588	0.610
Rp	0.059	0.031	0.059	0.097	0.086

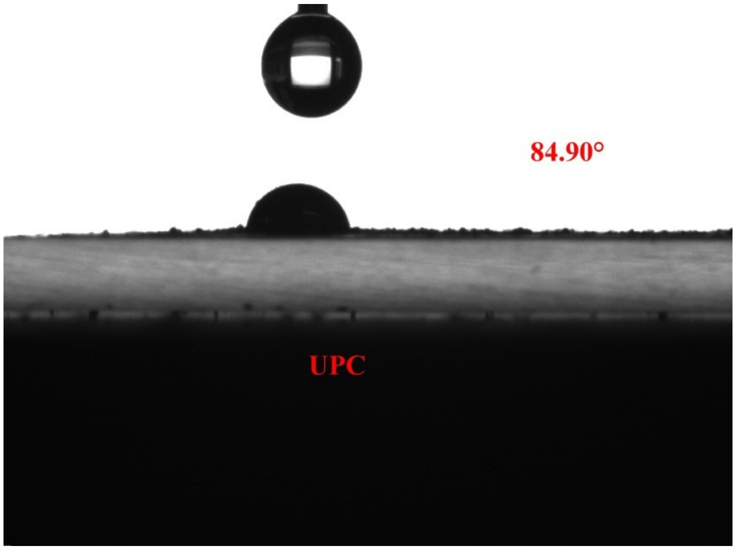

Figure S6. The water contact angle of UPC.

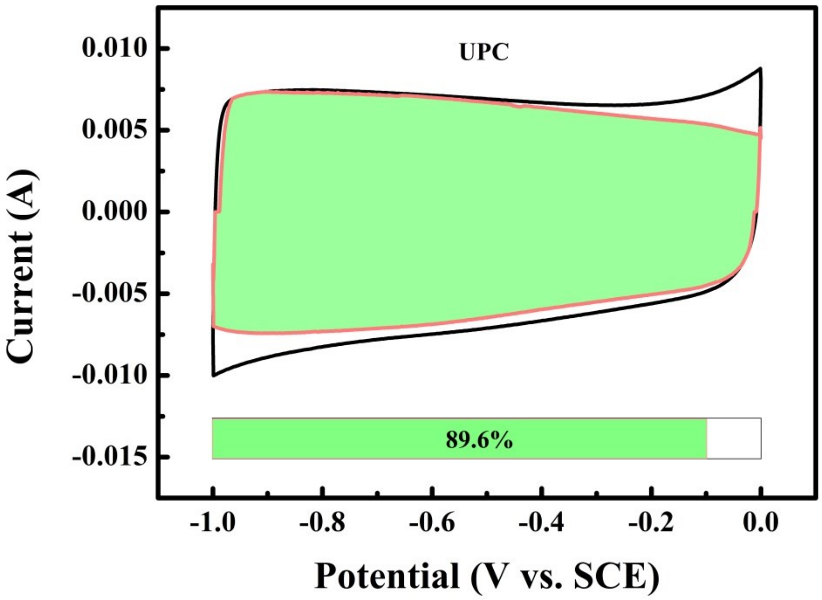

Figure S7. Distinguish the contribution of electric double layer capacitance and pseudocapacitance of UPC at 10 mV s^{-1}.