Electronic Supplementary Information

Hierarchical porous graphitic carbon for high-performance supercapacitors at high temperature†

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Electrochemical measurement

Carbon product (80 wt%), acetylene black (15 wt%) and polytetrafluoroethylene (PTFE) binder (5 wt%) were mixed in ethanol, then coated onto nickel-foam current collectors (1×1 cm^2), and dried at 120 °C for 12 h. The mass loading of the active materials in each working electrode was ~1.5 mg cm^{-2}. For the three-electrode system, Pt foil and Hg/HgO electrode were used as the counter and reference electrodes, respectively. The electrochemical performance was tested in 6 mol L^{-1} KOH electrolyte. For the two-electrode system (2032 stainless steel coin cell, PTFE as insulation), both 6 mol L^{-1} KOH and $EMIMBF_4$ were used as the electrolyte, respectively. The dried electrodes (~1.5 mg cm^{-2}, 0.2 mm in thickness) were symmetrically assembled with glassy paper as the separator in a glove box filled with argon. The cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) measurements were carried out using an electrochemical workstation (CHI660E, ChenHua Instruments Co. Ltd., Shanghai).

For the three-electrode system, the specific capacitance derived from galvanostatic tests were calculated by the following equations:

$$C_{sp} = \frac{\mathrm{I}\Delta t}{m\Delta V} \qquad (1)$$

in which C (F g^{-1}) is the specific capacitance; I (A) is the discharge current; Δt (s) is the discharge time; ΔV (V) is the potential window; and m (g) is the mass of the active materials.

$$\rho = \frac{1}{V_{total} + \frac{1}{\rho_{carbon}}} \qquad (2)$$

in which ρ (g cm^{-3}) is the density of electrode materials; V_{total} (cm^3 g^{-1}) is the total pore volume of active material measured by nitrogen isotherm; and ρ_{carbon} is the density of carbon (2 g cm^{-3}).

$$C_v = C\rho \qquad (3)$$

in which C_v (F cm^{-3}) is the volumetric capacitance; C (F g^{-1}) is the specific capacitance; and ρ (g cm^{-3}) is the density of electrode materials.

For the two-electrode system, the specific (or gravimetric) capacitances (C, F g^{-1}) were calculated using equation 4 for galvanostatic charge-discharge method and equation 5 for cyclic voltammetry data:

$$C_{sp} = \frac{4\mathrm{I}\Delta t}{m\Delta V} \qquad (4)$$

$$C = \frac{2}{mv(V_b - V_a)}\int_{V_a}^{V_b} \mathrm{I}dV \qquad (5)$$

in which I (A) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential window, v (V s^{-1}) is the scan rate, V_b and V_a (V) are the high and low potential limit of the CV tests; and m (g) is the total mass of the active materials.

To construct the Ragone plot, the energy density E (Wh kg^{-1}) and P (W kg^{-1}) based on the electrode were calculated by the following equations:

$$\mathrm{E} = \frac{1}{8}C_{sp}(\Delta V)^2\left(\frac{1000}{3600}\right) \qquad (6)$$

$$\mathrm{P} = 3600\frac{E}{\Delta t} \qquad (7)$$

in which C (F g^{-1}) is the specific capacitance, and ΔV (V) is the potential window, and Δt (s) is the discharge time.

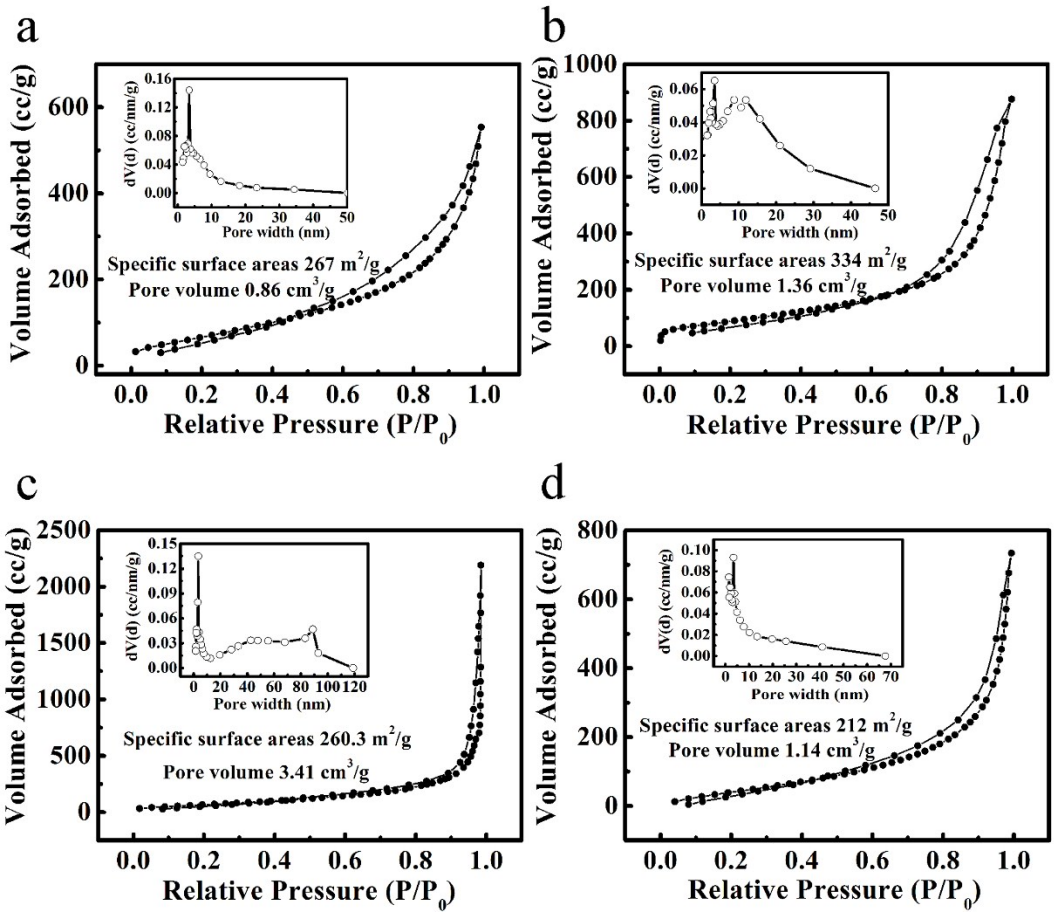

Fig. S1 The SSA was measured by nitrogen adsorption-desorption isotherms (BeiShiDe Instrument-S&T 3H-2000PS1) after vacuum drying at 120 °C for 1 h. The Brunauer-Emmett-Teller (BET) method was used for calculating the specific surface area, and the Barrett-Joyner-Halenda (BJH) model was used for estimating the pore size distribution. Nitrogen adsorption–desorption isotherm (with the pore size distribution in the inset) of (a) *'GC-Mg/ZA'*, (b) *'GC-1Mg/U'*, (c) *'GC-3Mg/U'*, and (d) *'GC-5Mg/U'*.

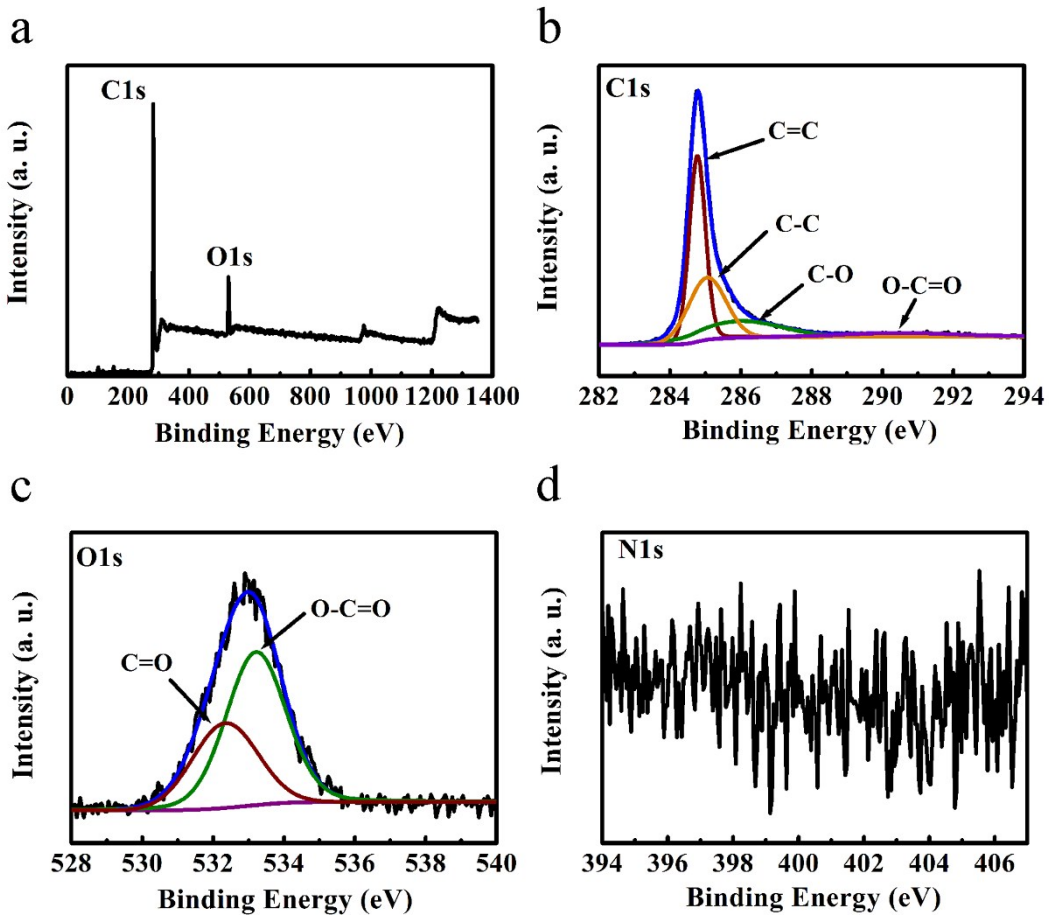

Fig. S2 (a) XPS survey, (b) C1s, (c) O1s and (d) N1s spectra of the *'GC-3Mg/U'* sample.

Fig. S3 The urea and zinc acetate dehydrate mixture at the same conditions.

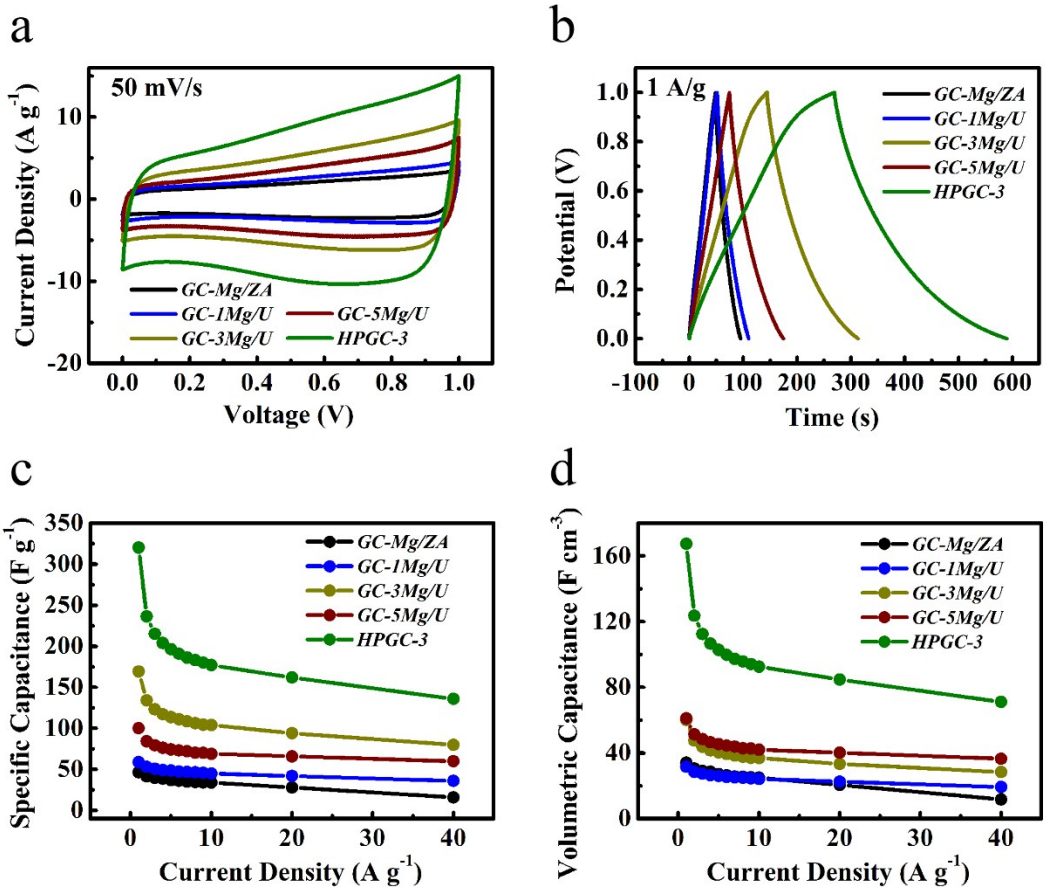

Fig. S4 Electrochemical performance of all samples measured in a three-electrode system using 6 mol L^{-1} KOH electrolyte. (a) CV curves at a scan rate of 50 mV s^{-1}. (b) Charge–discharge curves at a current density of 1 A g^{-1}. (c) Gravimetric capacitances at different current densities from 1 to 40 A·g^{-1}. (d) Volumetric capacitances at different current densities

Table S1 Comparison of the specific capacitances of previously fabricated hierarchical porous carbons using three-electrode systems.

Materials	Electrolyte	Current Density	Specific Capacitance (F·g^{-1})	Ref. No.
Hierarchical porous graphitic carbon	**6 M KOH**	**1 A·g^{-1}**	**320**	**This work**
Hierarchical porous carbon fibers	3 M KOH	1 A·g^{-1}	189.7	[1]
Three-dimensional beehive-like hierarchical porous carbons	6 M KOH	1 A·g^{-1}	287	[2]
Hierarchical hollow porous carbon spheres	6 M KOH	1 A·g^{-1}	303.9	[3]
Hierarchical porous carbons	6 M KOH	0.2·A g^{-1}	283.4	[4]
Porous carbon through hard–soft dual templates	6 M KOH	1 A·g^{-1}	153	[5]
Hierarchical porous carbons	6 M KOH	1 A·g^{-1}	190	[6]
Nitrogen-doped porous carbon nanofibers	6 M KOH	1 A·g^{-1}	202	[7]
Nitrogen and sulfur codoped porous carbon microsphere	6 M KOH	0.1 A·g^{-1}	295	[8]
Chlorine-doped ordered mesoporous carbon	6 M KOH	0.5 A g^{-1}	220	[9]

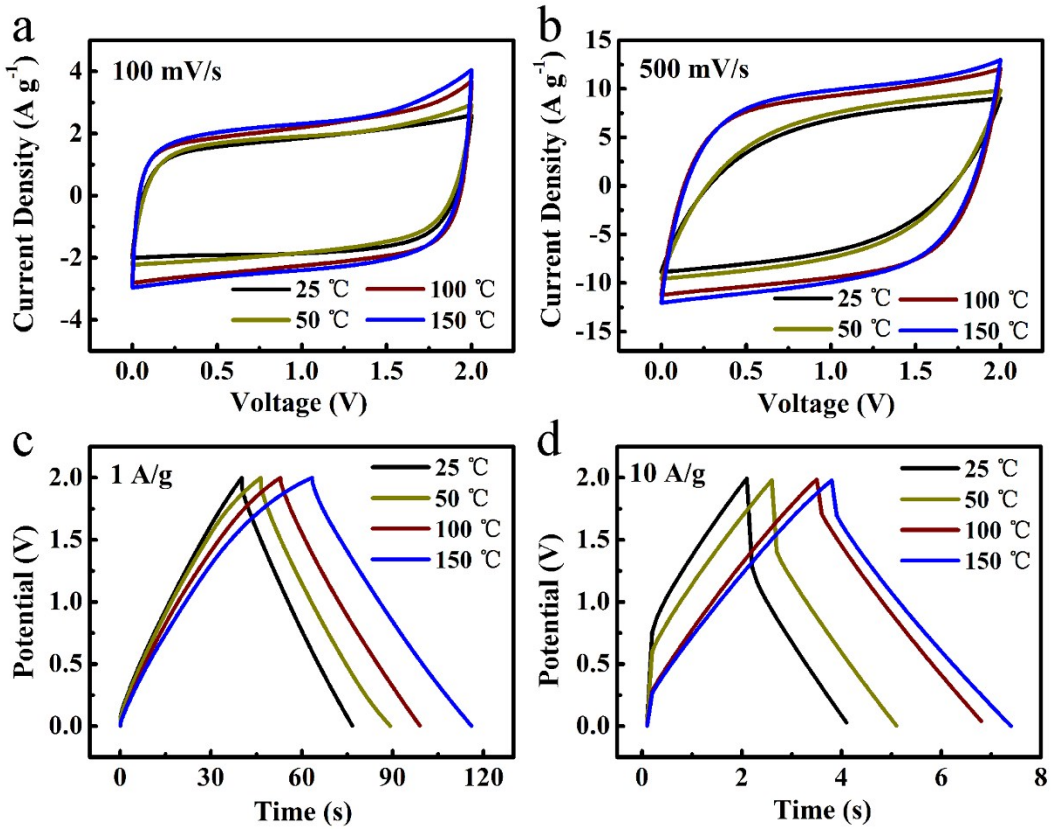

Fig. S5 Electrochemical performance characteristics of *'HPGC-3'* measured in a two-electrode system using $EMIMBF_4$ electrolyte operating at 25 °C, 50 °C, 100 °C and 150 °C, respectively. CV curves at a scan rate of (a) 100 mV s^{-1}; (b) 500 mV s^{-1}. Charge–discharge curves at a current density of (c) 1 A g^{-1}; (d) 10 A g^{-1}.

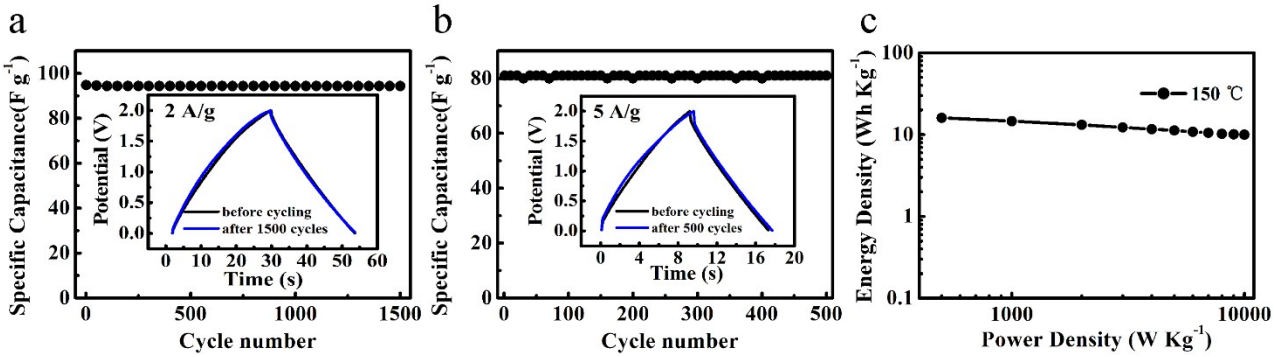

Fig. S6 (c) Cycling stabilities measured at 2 A g^{-1} operating at 150 °C, with the magnified galvanostatic charge-discharge curves before and after 1500 cycles in the inset. (b) Long-term stability of *HPGC-3'*-based supercapacitors under dynamic thermal stresses, with the magnified galvanostatic charge-discharge curves before and after 500 cycles in the inset. (c) Ragone plot of *'HPGC-3'*.

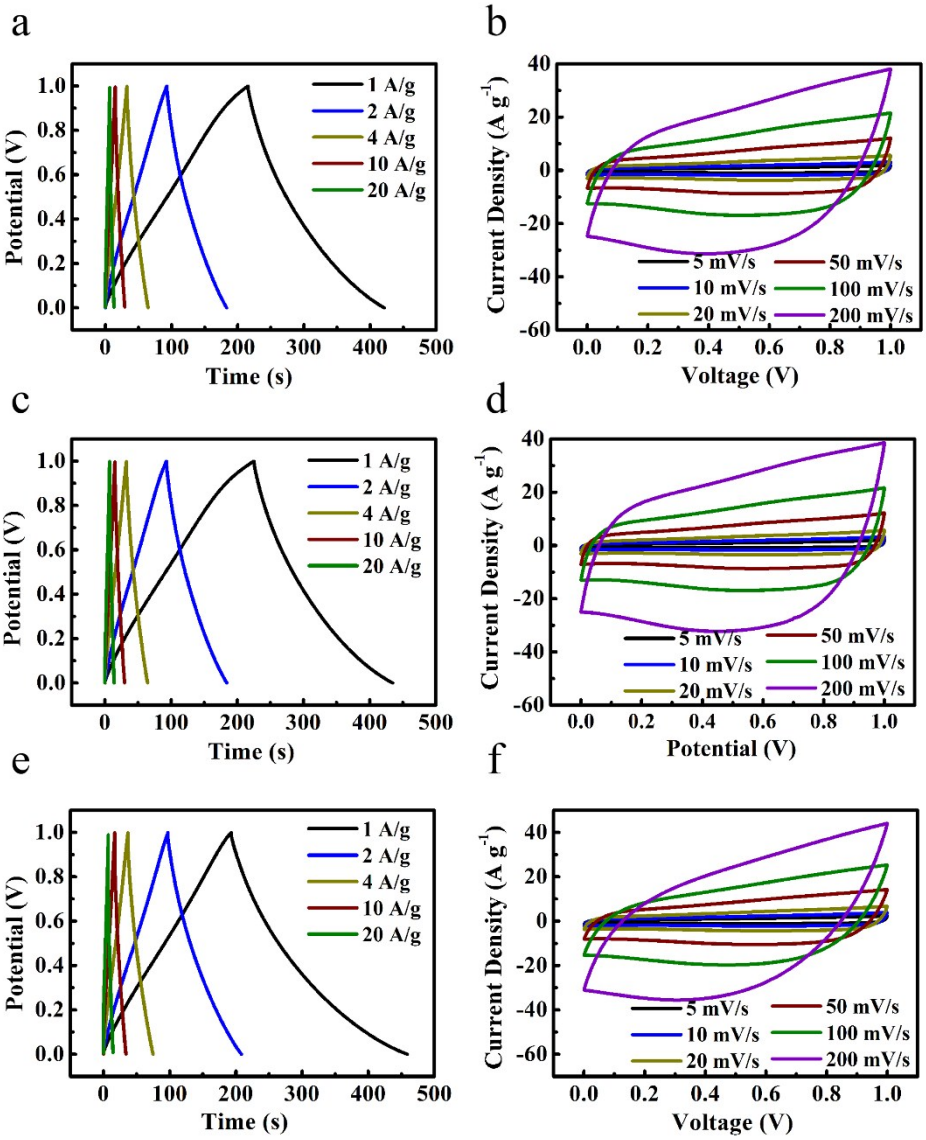

Fig. S7 Electrochemical performance of *'HPGC-3G', 'HPGC-3P'* and *'HPGC-3H'* using glycine (G), polyvinylpyrrolidone (P) and hexamethylenetetramine (H) to replace urea during the HPGC synthesis, measured in a three-electrode system in the 6 mol L^{-1} KOH electrolyte. Charge–discharge curves of (a) *'HPGC-3G'*; (c) *'HPGC-3P'*; (e) *'HPGC-3H'* at different current densities. CV curves of (b) *'HPGC-3G'*; (d) *'HPGC-3P'*; (f) *'HPGC-3H'* at different scan rates.

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