Supporting Information:

Scalable One-Step Synthesis of N,S Co-Doped Graphene-Enhanced Hierarchical Porous Carbon Foam for High-Performance Solid-State Supercapacitors

Liya Ma,^{*a*} Jin Liu,^{*b*} Song Lv,^{*a*} Qin Zhou,^{*a*} Xinyu Shen,^{*a*} Shaobo Mo,^{*a*} and Hua Tong^{*a*,*c*,*} ^{*a*} Key Laboratory of Analytical Chemistry for Biology and Medicine, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

^b State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

^c Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

* Corresponding author: Hua Tong (E-mail address: sem@whu.edu.cn;

Tel: +8602768764510; Fax: +8602768752136)

1. Experimental Materials

Chitosan (degree of deacetylation $\geq 95\%$, viscosity 100-200 mpa.s) and Polytetrafluoroethylene (PTFE, 60 wt% suspension in water) were obtained from Aladdin Industrial Co., Ltd (Shanghai, China). Glutaraldehyde solution (25 wt%), potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), potassium bicarbonate (KHCO₃), potassium hydroxide (KOH) and thiourea were analytical reagents and purchased Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without further treatment, and ultrapure water was used throughout the experiments.

2. Synthesis of several typical HPCF samples

To confirm that the K₂CO₃ was the optimized activating agent, several typical HPCF samples were prepared by the same procedures and conditions as that of the HPCF but adding the KHCO₃, KOH and Na₂CO₃ solution instead of the K₂CO₃ solution, which were denoted as the HPCF-KH, HPCF-KO and HPCF-Na respectively. Moreover, the other two specimens, denominated as HPCF-K4 and HPCF-K5, were made by the identical processes and conditions as that of the HPCF but adding the 4 mL and 6 mL instead of the 5 mL of K₂CO₃ solution for comparison.

3. Fabrication of the solid-state symmetric supercapacitor device

A solid-state symmetric supercapacitor (SSC) was assembled by using two N,S-GHPCF electrodes with exactly the same mass, where polyvinyl alcohol (PVA)/KOH as the gel electrolyte were employed. The PVA/KOH gel electrolyte was prepared as follows: 3 g of KOH and 3 g of PVA powder were dissolved in 30 ml DI water with

vigorously stirring at 85 °C until the mixture turned clear. The N,S-GHPCF electrode was prepared by mixing the active materials, acetylene black and PTFE together in weight ratio of 8:1:1, followed by coating the mixture onto Ni foams. Then, the electrode was dried at 80 °C under vacuum. Finally, the two pieces of electrodes were immersed into the PVA/KOH gel electrolyte for 10 min. The SSC was successfully constructed by pressing these two electrolyte-pregnant electrodes until the electrolyte was solidified and excess water evaporated.



Figure S1 SEM images of the HPCF (a-c), HPCF-KH (d-f), HPCF-KO (g-i) and

HPCF-Na (j-l) with different magnifications.

SEM images collected for the four typical HPCFs show several structural differences among them, although they all had a 3D porous structure (Figure S1). First, the HPCF and the HPCF-Na feature a network of interconnected sheets (Figure S1a and j), while the HPCF-KH and the HPCF-KO are characteristic of random interconnected macropores (Figure S1d and g). Second, the HPCF and the HPCF-KH specimens both have more obvious dispersed pores (Figure S1b and e) compared to the HPCF-KO and the HPCF-Na samples (Figure S1h and k). Moreover, only the HPCF possesses appropriate pores with homogenously distribution (Figure S1c), while the HPCF-KH is covered with pore of random sizes (Figure S1f), the HPCF-KO is merely full of pits by erosion (Figure S1i) and the HPCF-Na is decorated with cracks without obvious pores. Therefore, the K₂CO₃ is considered as the optimized activating agent for the HPCFs as the HPCF has the 3D interconnected structure with superior porosity.



Figure S2 (a) Nitrogen adsorption/desorption isotherm and (b) pore size distributions of the HPCF, HPCF-KH, HPCF-Na, HPCF-KO, HPCF-K4 and HPCF-K6

The nitrogen adsorption and desorption isotherm curves (Figure S2a) of all the samples with various activators showed an IUPAC type-I microporous structure. From the pore size distribution curves (Figure S2b), the size of nanopores is less than 2 nm. In more detail, the characteristics of the obtained various HPCF-X are listed in Table S1, which clearly shows that the HPCF had the largest specific surface area and pore volume among all as-prepared carbons.



Figure S3 (a) CV curves at a scan rate of 20 mV s⁻¹ and (b) GCD curves at a current density of 1A g⁻¹ of the HPCF, HPCF-KH, HPCF-Na, HPCF-KO, HPCF-K4 and

HPCF-K6 electrodes.

The electrochemical properties of the as-obtained samples were assessed in a three-electrode cell. For comparison, the CV tests at 20 mV s⁻¹ and GCD measurements at 1 A g⁻¹ were conducted on several typical HPCF-X as shown in Figure S3a and b. The CV and GCD curves of the HPCF exhibit the largest CV-circulated area and the longest discharge time, revealing the highest capacitance among that of all samples as is shown in Table S1, which is in excellent accord with the nitrogen adsorption and desorption results.

Sample	$S_{BET}\left(m^2g^{1}\right)$	D (nm)	$V_t (cm^3 g^{-1})$	$V_{mi} (cm^3 g^{-1})$	C_{KOH} (F g ⁻¹)
HPCF	1916.6	2.07	0.93	0.81	304
HPCF -KH	1634.4	1.96	0.81	0.74	282
HPCF -Na	1268.3	2.61	0.67	0.50	223
HPCF -KO	1448.0	2.40	0.74	0.62	253
HPCF -K4	1772.7	2.15	0.88	0.74	292
HPCF-K6	1737.4	2.60	0.88	0.74	287

Table S1 Pore structure parameters and electrochemical properties of HPCF, HPCF-KH, HPCF-Na, HPCF-KO, HPCF-K4 and HPCF-K6 a

^a Notation: S_{BET}: total BET surface area; D: BJH desorption average pore diameter; V_t: total pore volume; V_{mi}: micropore volume; C_{KOH}: specific capacitance obtained at current density of 1 A g⁻¹ in 6 M KOH.



Figure S4 FTIR spectra of the GO and the N,S-GHPCF.

To further confirm the GO was reduced into rGO during the thermal annealing process, FTIR measurements were performed as shown in Figure S4. Apparently, the peak representing carboxylic C=O (1716 cm⁻¹) totally disappears, and the peak for C-OH stretching vibrations (1388 cm⁻¹) dramatically weakens, indicating the oxygen-containing groups decrease on the carbon plane.^{1, 2}



Figure S5 High-resolution O 1s XPS spectrum of the N,S-GHPCF.



Figure S6 Images of the wetting process. N,S-GHPCF was used as the substrate and 6 M aqueous KOH was used as the liquid.

Figure S6 shows three pictures taken in sequence during one measurement. It is clear to conclude that N,S-GHPCF can be completely wetted by the aqueous KOH electrolyte, suggesting its superior wettability contributed by the surface heteroatom functionalities.



Figure S7 (a-b) CV curves at various scan rates and (c-d) GCD curves at different



current densities of the HPCF electrode.



current densities of the N,S-HPCF electrode.



Figure S9 (a-b) CV curves at various scan rates and (c-d) GCD curves at different



current densities of the N-GHPCF electrode.

Figure S10 (a) GCD curves and (b) Nyquist plots of the N,S-GHPCF electrode at a current density of 10 A g⁻¹ before and after 10000 charge-discharge cycles.



Figure S11 (a) CV curves at large scan rates and (b) GCD curves at high current

densities of the as-assembled symmetric supercapacitor device.

Table S2 Comparison of the electrochemical properties of the reported carbon-based

Samples	Specific surface area (m ² g ⁻¹)	Electrolyte	Specific capacitance	Rate capability
N-self-doped CS/PANI composites ³	45	1 M H ₂ SO ₄	373 F g^{-1} (1 A g $^{-1}$)	73.7% (1 to 10 A g ⁻¹)
N-self-doped carbon materials with hierarchical porosity ⁴	1011	6 M KOH	250.5 F g ⁻¹ (0.5 A g ⁻¹)	65.5% (1 to 100 A g ⁻¹)
3D interconnected sheet-like porous carbons ⁵	1593	6 M KOH	314 F g ⁻¹ (0.05 A g ⁻¹)	62.1% (0.05 to 100 A g ⁻¹)
N,S co-doped hierarchical porous carbon nanorods ⁶	1543	6 M KOH	282 F g ⁻¹ (1 A g ⁻¹)	71.6% (1 to 20 A g ⁻¹)
N-self-doped hierarchically porous carbon foam ⁷	1013	6 M KOH	246.5 F g ⁻¹ (0.5 A g ⁻¹)	$67.5\% (0.5 \text{ to } 100 \text{ A g}^{-1})$
N/S co-doped hierarchical porous carbons ⁸	1093.5	6 M KOH	272 F g ⁻¹ (1 A g ⁻¹)	63% (1 to 100 A g ⁻¹)
N/S codoped hierarchical porous carbon materials ⁹	575	6 M KOH	302 F g ⁻¹ (1 A g ⁻¹)	56% (1 to 10 A g^{-1})
N,S co-doped activated corncob sponge ¹⁰	1873.6	6 M KOH	404.2 F g ⁻¹ (0.1 A g ⁻¹)	62.6% (0.1 to 10 A g ⁻¹)

electrodes in a three-electrode configuration

N,S co-doped porous carbon nanosheets ¹¹	1533	6 M KOH	298 F g ⁻¹ (0.5 A g ⁻¹)	78.2% (0.5 to 50 A g ⁻¹)
N,S co-doped carbon microsphere ¹²	773.1	6 M KOH	277.1 F g ⁻¹ (0.3 A g ⁻¹)	63% (0.3 to 5 A g ⁻¹)
Nitrogen-rich porous carbon–graphene aerogels ¹³	814	$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	421 F g ⁻¹ (1 A g ⁻¹)	72.5% (1 to 50 A g^{-1})
N, S-codoped ultramicroporous carbon nanoparticles ¹⁴	695	6 М КОН	225 F g ⁻¹ (2 A g ⁻¹)	71% (2 to 20 A g ⁻¹)
N,S co-doped hierarchical porous graphene hydrogels ¹⁵	252	6 M KOH	251 F g ⁻¹ (0.5 A g ⁻¹)	54.4% (0.5 to 100 A g ⁻¹)
3D N-doped mesoporous graphene ¹⁶	627	1 M H ₂ SO ₄	408 F g ⁻¹ (1 A g ⁻¹)	62.5% (1 to 10 A g ⁻¹)
3D hierarchical porous N,S			405 F g ⁻¹ (1 A g ⁻¹)	72 8% (1 to 100 Å g ⁻¹)
co-doped carbon foam	2279.2	6 M KOH	410 F g ⁻¹ (1 mV s ⁻	$72.0\% (1 to 100 A g^{-1})$
(This work)			1)	72.770 (1 to 200 m v S)

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