# **Supporting Information**

# Novel Approach for Sulfur-doped Hierarchically Porous Carbon with an Excellent Capacitance for Electrochemical Energy Storage

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## **Content:**

Materials preparation and characterization

Fig. S1 (a) XRD, (b) EDX spectra and (c) mapping images of SnS@carbon.

Fig. S2 HRTEM of the SnO<sub>2</sub>@carbon.

Fig. S3 (a) SEM and (b) TEM of carbon, (c) SEM, (d) mapping images and (e) EDX spectra of S-doped carbon, (f)  $N_2$  adsorption-desorption isotherms of carbon (inset is the corresponding pore size distribution curve).

Table S1 A summary of the specific surface area, pore volume and pore-size distribution data for carbon and S-doped carbon samples.

Table S2 XPS peak assignments of C 1s, O 1s and S 2p for carbon and S-doped carbon samples.

Fig. S4 A proposed electrochemical energy-storage mechanism on S-doped carbon with a hierarchical porous structure.

Fig. S5 Cyclic voltammogram curves of S-doped carbon electrode at different scan rates.

Fig. S6 Cycling performance of S-doped carbon electrodes at a current density of 10 A·g<sup>-1</sup>.

Table S3 A comparison of specific capacitances, doping agents, cycling performance, and pore-creating methods of the reported heteroatom-doped carbon electrodes.

## Materials preparation and characterization

Materials Preparation: 2 mmol  $SnCl_4 \cdot 5H_2O$  was mixed with 18 mmol glucose and 30 mL distilled H<sub>2</sub>O at room temperature, in which 8 mmol NH<sub>2</sub>CSNH<sub>2</sub> was added. After stirring, the mixed solution was then heated in a microwave hydrothermal oven at 200 °C for 40 min. Thereafter, the system was permitted to cool down to the room temperature. The brown precipitate called  $SnO_2$ @carbon was finally collected by filtration and washed several times with absolute ethanol and dried in vacuum at 60 °C for 10 h. The obtained intermediate sample was then calcined in N<sub>2</sub> (g) at 700 °C, 800 °C for 4 h, and the resulted product was correspondingly denoted as SnS@carbon and S-doped carbon, respectively. Pure carbon sample was also prepared by using the above procedure except that only glucose (18 mmol) was mixed with water (30 mL) in the reaction system. The resulted carbon product after microwave-hydrothermal process was defined as carbon-MH and the carbon-MH after calcination at 800 °C was denoted as carbon.

Microwave-assisted hydrothermal treatment was performed using WX-600 (Preekem, Shanghai) microwave digestion reaction system. The time, pressure/temperature, and power were automatically program-controlled by software. The wattage used in our experiment was dependent on both pressure as well as temperature to a maximum of 30 MPa and 250 °C, respectively.

Structural and Morphology Characterization: The structure and phase purity of the products were examined by XRD on a Philip-X'Pert X-ray diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda$ =1.5418 Å). The general morphologies of the as-synthesized samples were characterized by scanning electron microscopy (SEM, JEOL JEM-6300F). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by using a JEOL JEM-200CX microscope operating at an accelerating voltage of 200 kV. N<sub>2</sub> adsorption/desorption isotherms were measured by Gold APP V-Sorb 2800 with N<sub>2</sub> as an adsorbate at 77 K. Before measurements, all samples were degassed at 300 °C for 6 h. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) equation and the pore size distribution was estimated from the desorption branch of N<sub>2</sub> isotherms by the Barret-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an UIVAC-PHI PHI 5000 VersaProbe spectrometer. The amounts of C, H, O and N elements were measured with a Vario EL III elemental analyser (Elementar, Germany).

Electrochemical Measurements: The working electrode was a mixture of 80 wt% assynthesized sample, 10 wt% acetylene black and 10 wt% polyvinylidene difluoride (PVDF) in the presence of N-methyl pyrrolidinone (NMP). After being stirred overnight, the slurry was pasted onto a graphite sheet. The working area of the electrode was set as  $1 \times 1 \text{ cm}^2$  and the mass loading of the electrode materials was controlled around 1.2 mg. The thickness of the electrode materials was around 25 µm and made by a doctor blade. The electrode was dried at 120 °C under vacuum for 10 hours. The test of symmetric supercapacitors based on two electrodes separated by a porous nonwoven cloth were performed at 25 °C in a two-electrode cell in the 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The supercapacitor performance was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge techniques within the voltage range of -0.1 V to 1.1 V. Different scan rates (5, 10, 20, 50, 100 mV·s<sup>-1</sup>) and constant current densities  $(0.5~20 \text{ A} \cdot \text{g}^{-1})$  were employed. Cyclic voltammetry (CV) was conducted using a RST3100 electrochemical workstation (Suzhou, China). The galvanostatic charge and discharge experiments were carried out at room temperature using a LAND CT2001A battery testing system (Wuhan, China). Electrochemical impedance spectroscopy (EIS) measurements were also conducted using a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA), where the amplitude of the input ac signal was kept at 5 mV and the frequency range was set between  $1 \times 10^{-2}$  Hz and  $1 \times 10^{5}$  Hz.

The specific capacitance of the electrode material ( $C_s$ , F·g<sup>-1</sup>) was calculated from the

$$2 \times I_{cons} \times \Delta t$$

discharge curve through the equation  $C_s = \overline{m \times \Delta V}$ , where  $I_{cons}$  is the constant current in discharging, *m* the mass of active material on one electrode,  $\Delta t$  the discharge time, and  $\Delta V$ the voltage change during discharge.

The energy density (*E*, Wh·kg<sup>-1</sup>) of the cell was calculated according to the equation  $E=C_s \times \Delta V^2$ 

 $\overline{2 \times 4 \times 3.6}$ . Note: with the factor 4, the specific capacitance of electrode material ( $C_s$ ) is converted to the capacitance of the cell based on the total mass of active material; with the factor 3.6, the units of energy density (*E*) is converted from J· g<sup>-1</sup> to Wh· kg<sup>-1</sup>. The average

power density (P, W· kg<sup>-1</sup>) of the cell was obtained by  $P = \frac{E \times 3600}{\Delta t}$ .



Fig. S1 (a) XRD, (b) EDX spectrum and (c) mapping images of SnS@carbon.



Fig. S2 HRTEM of the SnO<sub>2</sub>@carbon.



Fig. S3 (a) SEM and (b) TEM of carbon, (c) SEM, (d) mapping images and (e) EDX spectrum of S-doped carbon, (f)  $N_2$  adsorption-desorption isotherms of carbon (inset is the corresponding pore size distribution curve).

Table S1 A summary of the specific surface area, pore volume and pore-size distribution data for carbon and S-doped carbon samples.

Sample	$S_{\rm BET}{}^{\rm a}$	$V_{\rm total}^{\rm b}$	Pore size distribution			_
	$(m^2 \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$	$V_{\rm micro}$ (%)	) <sup>c</sup> $V_{\text{meso}}$ (%	) <sup>c</sup> $V_{\text{macro}}$ (%) <sup>c</sup>	
carbon	534	0.29	85.0	15.0	0	_
S-doped carbon	735	0.84	55.8	38.9	5.3	

a) specific surface area based on Brunauer-Emmett-Teller equation;

b) total pore volume at  $p/p_0 = 0.990$ ;

 c) volume percentages of micro-(pore width <2 nm), meso-(pore width within 2-50 nm) and macropores (pore width >50 nm, IUPAC classification), respectively.

Peak	Binding energy (eV)		Assignment	Relative peak area (%)	
	carbon	S-doped carbon		carbon	S-doped carbon
C 1s	284.6	284.6	C-C/C=C	26.8	23.8
	285.0	285.0	C-H	41.5	42.2
	286.2	286.2	C-O/C-S	23.4	19.5
	288.5	288.5	C=O	8.3	7.0
	/	290.7	$\pi$ - $\pi$ * transition in	/	7.5
			aromatic rings		
	/	531.4	O=S	/	32.6
O 1s	532.5	532.5	O-C-O	69.4	30.6
	533.8	533.7	O=C-O	39.6	27.8
	/	164.0	C-S-C	/	41.2
S 2p	/	165.2	C-SO-C	/	38.2
-	/	168.4	C-SO <sub>2</sub> -C	/	20.6

Table S2 XPS peak assignments of C 1s, O 1s and S 2p for carbon and S-doped carbon samples.



Fig. S4 A proposed electrochemical energy-storage mechanism on S-doped carbon with a hierarchical porous structure.

An electrochemical energy-storage mechanism of S-doped carbon is schematically illustrated in Fig. S4. S-doped carbon has a large specific surface area and pore volume, and its meso-/macropores can behave as an "ion-buffering reservoir",<sup>1</sup> which can shorten the diffusion distance of H<sup>+</sup> and make a better penetration of H<sup>+</sup> into the S-doped carbon cluster.

Meanwhile, the size of S-doped carbon cluster is only tens of nanometers, being much smaller than that of the pure carbon sphere. Thus, the diffusion distance of charges into the interiors of S-doped carbon cluster is greatly reduced. Furthermore, the introduction of electron-rich sulfur dopant would modify the environment of carbon surface and enlarge the total polarization and electronic conductivity of the medium. The existed aromatic sulfide, sulfoxide and sulfone are believable to play a positive role in the whole capacitance as the sulfone and sulfoxide species would undergo redox faradic reactions, resulting in a stable good performance even at a relative high current density.



Fig. S5 Cyclic voltammogram curves of S-doped carbon electrode at different scan rates.



Fig. S6 Cycling performance of S-doped carbon electrodes at a current density of 10 A·g<sup>-1</sup>.

Table S3 A comparison of specific capacitances, doping agents and pore-creating methods of

Material	Capacitance	Cycling performance	Doping agents/ method for creating pores	Ref
S-doped carbon				
S-doped carbon monoliths	$\begin{array}{c} 206 \ F \cdot g^{-1} \\ (0.5 \ A \cdot g^{-1}) \end{array}$	/	sulfonated poly(divinylbenzene) networks/CO <sub>2</sub> activation	2
S-doped carbon monoliths	191 F·g <sup>-1</sup> (2 mV·s <sup>-1</sup> )	/	4,4'-thioldiphenol/none	3
S-doped activated carbons	$200 \text{ F} \cdot \text{g}^{-1}$ (1 mV·s <sup>-1</sup> )	/	2-thiophenemethanol/ KOH activation	4
S-doped carbon/graphene composites	$\frac{155 \text{ F} \cdot \text{g}^{-1}}{(1 \text{ A} \cdot \text{g}^{-1})}$	$\frac{140 \text{ F} \cdot \text{g}^{-1} @1 \text{ A} \cdot \text{g}^{-1}}{8000 \text{ cycles}}$	poly(sodium 4-styrene sulfonate)/none	5
N,S-co-doped carbon	139 F·g <sup>-1</sup> (50 mA·g <sup>-1</sup> )	/	thiourea, urea, sulphuric acid/none	6
N,S-co-doped carbon	$\frac{180 \text{ F} \cdot \text{g}^{-1}}{(1 \text{ A} \cdot \text{g}^{-1})}$	/	pyrrole, sulphuric acid/ SBA-15 template	7
N,S-co-doped carbon	264 F·g <sup>-1</sup> (0.25 A·g <sup>-1</sup> )	154 F·g <sup>-1</sup> @1 A·g <sup>-1</sup> 1000 cycles	hair/KOH activation	8

the reported heteroatom-doped carbon electrodes.

#### N/P/B-doped carbon

N-doped graphene	$\begin{array}{c} 245 \ F{\cdot}g^{-1} \\ (0.25 \ A{\cdot}g^{-1}) \end{array}$	214 F·g <sup>-1</sup> @0.25 A·g <sup>-1</sup> 2000 cycles	melamine-resorcinol- formaldehyde/ none	9
N-doped mesoporous carbons	$\begin{array}{c} 230 \ \mathrm{F} \cdot \mathrm{g}^{-1} \\ (0.5 \ \mathrm{A} \cdot \mathrm{g}^{-1}) \end{array}$	/	cyanamide/ hard template	10
N-enriched carbon nanofibers	$220 \text{ F} \cdot \text{g}^{-1} \\ (0.2 \text{ A} \cdot \text{g}^{-1})$	162 F·g <sup>-1</sup> @5 A·g <sup>-1</sup> 1000 cycles	g-C <sub>3</sub> N <sub>4</sub> /none	11
N-doped carbon nanotube	$\begin{array}{c} 215 \ \mathrm{F} \cdot \mathrm{g}^{-1} \\ (0.2 \ \mathrm{A} \cdot \mathrm{g}^{-1}) \end{array}$	/	1,3,5-triazine-2,4,6- triamine/none	12
P-enriched carbons	220 F·g <sup>-1</sup> (1 A·g <sup>-1</sup> )	180 F·g <sup>-1</sup> @5 A·g <sup>-1</sup> 15000 cycles	H <sub>3</sub> PO <sub>4</sub> /H <sub>3</sub> PO <sub>4</sub> activation	13
P-doped graphene	115 F·g <sup>-1</sup> (50 mA·g <sup>-1</sup> )	98 F·g <sup>-1</sup> @5 A·g <sup>-1</sup> 5000 cycles	H <sub>3</sub> PO <sub>4</sub> /H <sub>3</sub> PO <sub>4</sub> activation	14
B-doped graphene	369 F·g <sup>-1</sup> (5 mV·s <sup>-1</sup> )	171 F·g <sup>-1</sup> @10 A·g <sup>-1</sup> 10000 cycles	H <sub>3</sub> BO <sub>3</sub> /none	15
N, B-co-doped graphene	239 F·g <sup>-1</sup> (5 mV·s <sup>-1</sup> )	$\begin{array}{c} 230 \ \text{F} \cdot \text{g}^{-1} @ 2 \ \text{A} \cdot \text{g}^{-1} \\ 1000 \ \text{cycles} \end{array}$	NH <sub>3</sub> BF <sub>3</sub> /none	16
N, P-co-doped mesoporous carbons	210 F·g <sup>-1</sup> (1 A·g <sup>-1</sup> )	$\frac{200 \text{ F} \cdot \text{g}^{-1} @1 \text{ A} \cdot \text{g}^{-1}}{3000 \text{ cycles}}$	urea and phytic acid/ hard template	17
N, P-co-doped porous carbons	260 F·g <sup>-1</sup> (50 mA·g <sup>-1</sup> )	$\frac{150 \text{ F} \cdot \text{g}^{-1} @1 \text{ A} \cdot \text{g}^{-1}}{1000 \text{ cycles}}$	shrimp shell and H <sub>3</sub> PO <sub>4</sub> / H <sub>3</sub> PO <sub>4</sub> activation	18
This work	443 F·g <sup>-1</sup> (0.5 A·g <sup>-1</sup> )	$\begin{array}{c} 252 \ \mathrm{F} \cdot \mathrm{g}^{-1} @ 4 \ \mathrm{A} \cdot \mathrm{g}^{-1} \\ 2000 \ \mathrm{cycles} \\ 170 \ \mathrm{F} \cdot \mathrm{g}^{-1} @ 10 \ \mathrm{A} \cdot \mathrm{g}^{-1} \\ 8000 \ \mathrm{cycles} \end{array}$	thiourea/none	

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