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1 Supporting Information

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3 Dual-Functional Hard Template Directed One-step Formation of Hierarchical

4 Porous Carbon–Carbon Nanotube Hybrid for Lithium –Sulfur Batteries

5 Chong Luo ^{a,b}, Shuzhang Niu ^{a,b}, Guangmin Zhou ^c, Wei Lv ^{a,*}, Baohua Li ^a, Feiyu

Kang ^{a,b} and Q	Juan-Hong	Yang a,d,*
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- 7 ^a Engineering Laboratory for Functionalized Carbon Materials and Shenzhen Key
- 8 Laboratory for Graphene-based Materials, Graduate School at Shenzhen, Tsinghua
- 9 University, Shenzhen 518055, China.
- 10 ^b Laboratory of Advanced Materials, School of Materials Science and Engineering,
- 11 Tsinghua University, Beijing 100084, China
- 12 ^c Shenyang National Laboratory for Materials Science, Institute of Metal Research,
- 13 Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, P. R. China
- 14 ^d School of Chemical Engineering and Technology, Tianjin University, Tianjin

15 300072, China.

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17	Corresponding	author
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- 18 * E-mail: lv.wei@sz.tsinghua.edu.cn, yang.quanhong@sz.tsinghua.edu.cn,
- 19 qhyangcn@tju.edu.cn;
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1 Experimental Section

2 Materials preparation

Preparation of HPCC: In a typical experiment, 25 g Ni(NO₃)₂·6H₂O solution (20 wt 3 %) was added into 50 g NaOH solution (10 wt %), and then suffered a continuously 4 stirring for 4 h for the uniformly formation of Ni(OH)₂ dispersion. Then, 25 g ethanol 5 solution of phenolic resin (20 wt %) was dropply added in above dispersion under 6 intense stirring. The formed uniform mixture was evaporated at 60 °C to remove 7 solvent, and then was carbonized under a mixture atmosphere (5% H₂ -95% Ar) via a 8 2 h heat treatment under 200 °C and a following 4 h pyrolysis under different 9 temperatures of 500, 600, 700 and 800 °C. Finally, the obtained products were washed 10 with 3 M HCl solution and deionized water and then dried at 80 °C. The final 11 products prepared at different pyrolysis temperature are denoted HPCC-500, HPCC-12 600, HPCC-700 and HPCC-800. For comparison, the hierarchical porous carbon with 13 few CNTs (denoted HPC) was prepared with a pyrolysis temperature of 600 °C in the 14 15 pure Ar atmosphere.

Preparation of HPCC-S hybrid: 65 wt % sulfur and 35 wt % HPCC were uniformly mixed through grinding and then this mixture was heated at 155 °C for 12 h in a sealed vessel filled with N₂ protection. Then, the temperature was increased to 250 °C and kept for 0.5 h to vaporize the superfluous sulfur on the outer surface of the HPCC. After cooling down to the room temperature, the HPCC-S hybrids were obtained.

21 Materials characterization

22 All as-prepared materials were characterized by wide angle X-ray diffraction (XRD,

1 Rigaku), scanning electron microscopy (SEM, HITACHI-4800) equipped with an energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM, 2 FEI TECNAIG2 F30) and thermogravimetric analysis (TG-DSC, Netzsch, STA449). 3 Raman spectra was recorded with a HORIBA HR800 using 532 nm incident radiation. 4 The surface area and pore volume of the samples were determined by nitrogen gas 5 adsorption at 77 K with an automated adsorption apparatus (Micrometrics, ASAP 6 2020). The surface area was determined from the Brunauer-Emmett-Teller (BET) 7 equation and pore size distribution (PSD) of HPCC was calculated based on 8 adsorption-desorption using the density functional theory (DFT). 9

10 Electrochemical measurements

The electrode was prepared by mixing the HPCC-S, carbon black, and polyvinylidene 11 difluoride (PVDF) with a weight ratio of 8:1:1 in N - methyl pyrrolidone (NMP) 12 solvent to form a slurry. Then the slurry was coated onto a carbon-coated aluminum 13 foil using a doctor blade and dried at 60 °C under vacuum for 10 h. The mass loading 14 15 of sulfur in the obtained cathode is $\sim 1.0 \text{ mg cm}^{-2}$. The coin cell (CR2032) with a metallic lithium anode was assembled in an Ar-filled glove box (Mbraun) to evaluate 16 the electrochemical performance of the as-obtained sample. The microporous 17 polypropylene sheet (Celgard 2500) was used as the separator. The electrolyte was 18 1M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) dissolved in a mixture of 19 1,2-dioxolane(DOL) and dimethoxymethane(DME) (1:1 by volume) with adding 1 wt % 20 LiNO₃. The electrolyte added in each coin cell was about 40 µL. Cyclic voltammetry 21 (CV) experiment and electrochemical impedance spectroscopy (EIS) were carried out 22

using electrochemical workstation (PRASTAT P4000). The galvanostatic
 charge/discharge performance test and the rate capability at different C-rates were
 performed using a Land 2001A cell test system (Wuhan, China) at 298K. The EIS
 spectra were obtained in the frequency range of 100 kHz to 10 MHz with an AC
 voltage amplitude of 5 mV at the open-circuit potential.

7 Supplementary Figures



Fig. S1 XRD patterns of the uncarbonized phenolic resin/ Ni(OH)₂ precursor, HPCC before and after washing. Na₂CO₃ was formed by the CO₂ from the decomposition of phenolic resin with Na⁺ ions. Besides, Ni(OH)₂ was decomposed into NiO and then reduced into Ni by the formed carbon and H₂ under high temperature.



Fig. S2 SEM image of HPCC particles with the size of about 1-3 µm.



9 Fig. S3 HRTEM images of HPCC obtained at different temperature. With the
10 increasing temperature, the thickness of CNTs wall decreases and the graphitic degree
11 of CNT wall increases.



10 a heating rate of 5 °C min⁻¹.





Fig. S7 Rate performance of HPCC-S under different current densities.



Fig. S8 CV profiles of HPC-S with a scan rate of 0.1 mV s^{-1}



Fig. S9 Charge-discharge profiles of HPC-S at different rates

Table S1 EDS analysis of HPCC-600

Element	С	0	Ni	Na
Weight Ratio (%)	87.6	11.6	0.6	0.2

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