Supporting Information

Facile synthesis of nitrogen-doped carbon nanosheets with developed hierarchical porosity for high performance supercapacitors and lithium-sulfur batteries

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Experimental Section

Synthesis of Electrode material

a. Synthesis of porous carbon materials

Magnesium citrate and potassium citrate were used as received (Beijing Xiandai Reagent Co., China). In order to get stablized porous structures, the heat treatment procedures of four porous carbons were set up according to the thermogravimetric analysis (TGA) curve of magnesium citrate (as shown in Fig. S1a), and isothermal treatment at three knee points were conducted (as shown in Fig. S1b). To be specific, the pyrolysis process was carried out in a tubular furnace at 220, 350, 435 °C for 1 h and then 850 °C for 2 h with a ramp rate of 2 °C min^{-1} under N_2 atmosphere. The product was thoroughly washed with diluted HCl solution and deionized water, and then dried at 120 °C to get the porous carbon samples. Following NH_3 treatment was performed under NH_3 atmosphere at 800 °C for 1 h to achieve the nitrogen-doped porous carbon samples.

b. Synthesis of N-HPCNS/S and N-MPCNS/S cathodes

N-HPCNS/S and N-HMCNS/S composites were prepared by melt diffusion method. N-HPC was mixed with the sublimed sulfur (99.99% Aladdin) with weight ratios of 1:3, and ground into uniformity. Then, the composite was heated at 155 °C for 10 h and further treated in a tubular furnace at 300 °C under N_2 atmosphere for 0.5 h to remove the sulfur on the outer surface.

Material Characterization

The morphology and microstructure were examined with a scanning electron microscopy (SEM, LEO-1530) and transmission electron microscopy (TEM, Tecnai G20, 200 kV). N_2 adsorption isotherms were measured by using a volume adsorption apparatus (autosorb-1) at 77 K. The total pore volumes were estimated from single point adsorption (P/P$_0$= 0.99), the specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, the micropore surface area and micropore volume were determined by t-plot method, and pore size distributions (PSD) were derived from density functional theory (DFT). The weight percentages of sulfur in the carbon/sulfur (C/S) composites were measured by TGA measurement on a TA 2950 instrument. The samples were tested under N_2 atmosphere from 30 °C to 700 °C at a heating rate of 10 °C min^{-1}. PHI Quantera Imaging X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemistry. X-ray diffraction (XRD) patterns were obtained from a D8 Advance Diffractometer (Bruker AXS) with a Cu Kα source.

Electrochemical test

For supercapacitor electrodes, the porous carbons (N-HPCNS and N-MPCNS) were mixed with 15% PVDF, 10% carbon black (Super P) and plenty of NMP as solvent to get a homogeneous slurry. Then the slurry was coated onto a copper foil and

subsequently dried at 80 °C for 4 h and at 120 °C in vacuum for 12 h. While the working electrode of Li-S batteries were prepared by mixing C/S composite (N-HPCNS/S and N-MPCNS/S) with 10% PVDF and 10% carbon black. The slurry was coated onto an aluminum foil and then dried at 60 °C for 24 h. The electrodes were punched into a disk with a diameter of 12 mm for electrochemical tests. The mass loading of porous carbon electrodes were ~ 1.2 mg, while the mass loading of C/S composite electrodes were ~ 1.5 mg.

For symmetric supercapacitors, cyclic voltammetry (CV) tests were performed in VSP-300 electrochemical interface with a voltage window of 0-2.7 V. The electrolyte is 1 M $LiPF_6$ in EC/DEC (1:1 by volume). The specific capacitance of single electrode was calculated through the following equations: $C = 4 (\int idV)/(vm\Delta V)$, where i is the current (A), v is the potential scan rate (mV s^{-1}), m is the total mass of the electroactive materials (g), ΔV is the potential change (V). Galvanostatic charge/discharge cycling (GC) measurements were performed in Arbin-BT2000 test station. The specific capacitance of single electrode was calculated according to the formula: $C = 4I\Delta t/(m\Delta V)$, where I is the constant current (A), ΔV is the potential change (V) within the discharge time Δt (s).

The power and energy density were calculated based on the total mass of electrode materials. The energy density was calculated using the following formula: $E = 1/8 C(\Delta V)^2$. The power density is calculated by $P = E/\Delta t$. A LAND battery tester (Jinnuo Electronics Co., Wuhan, China) was used to perform the GC tests of the Li-S batteries with a voltage window of 1.7-2.8 V. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at 1:1 volume ratio with 1 wt% $LiNO_3$ added as an additive. The rate set for Li-S cell tests was referenced to the mass of sulfur active material in the cathode, and 1 C equaled to 1675 mA g^{-1}. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed in VSP-300

electrochemical interface.

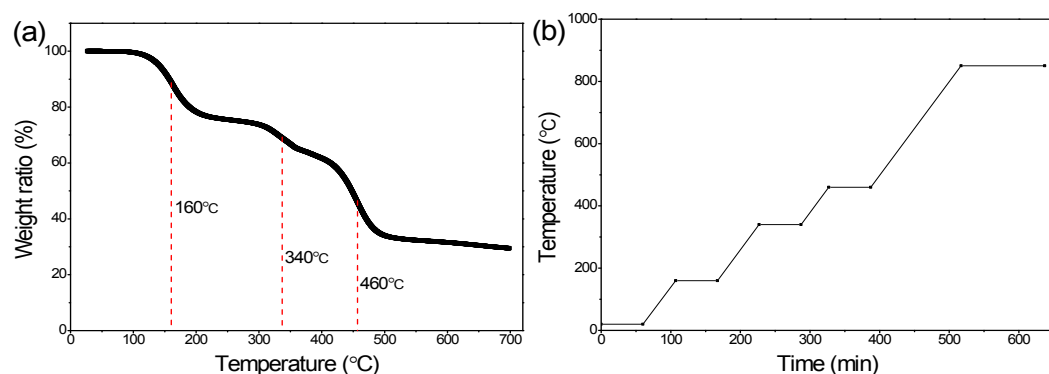**Supplementary Figures and Tables**

Fig. S1 (a) Thermogravimetric analysis (TGA) curve of magnesium citrate, and (b) the heat treatment procedures.
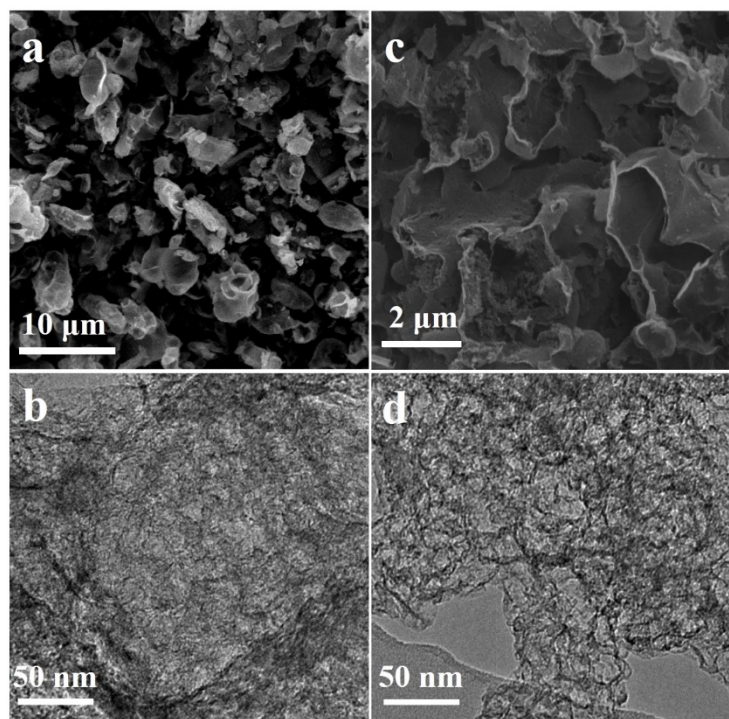

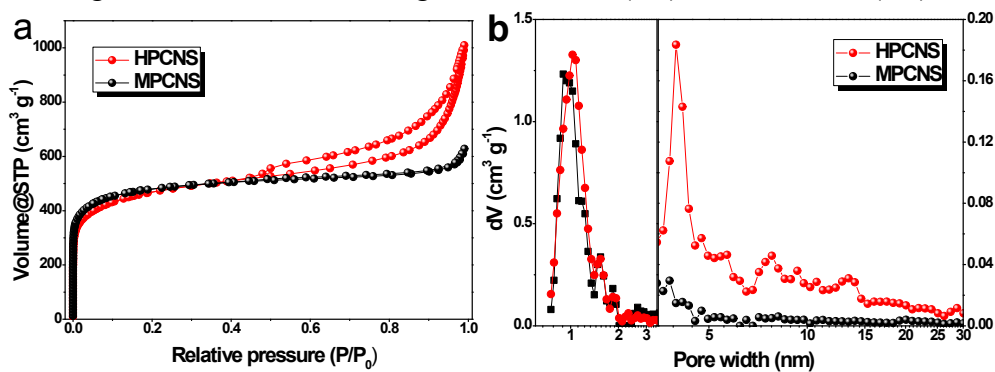Fig. S2 SEM and TEM images of N-HPC1 (a,b), and N-HPC2 (c,d).

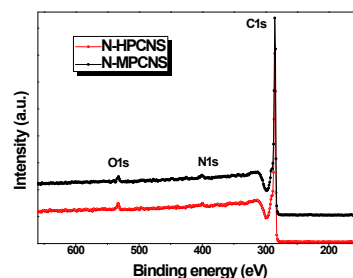Fig. S3 Nitrogen adsorption isotherms (a) and corresponding pore size distributions (b) of HPCNS and MPCNS.

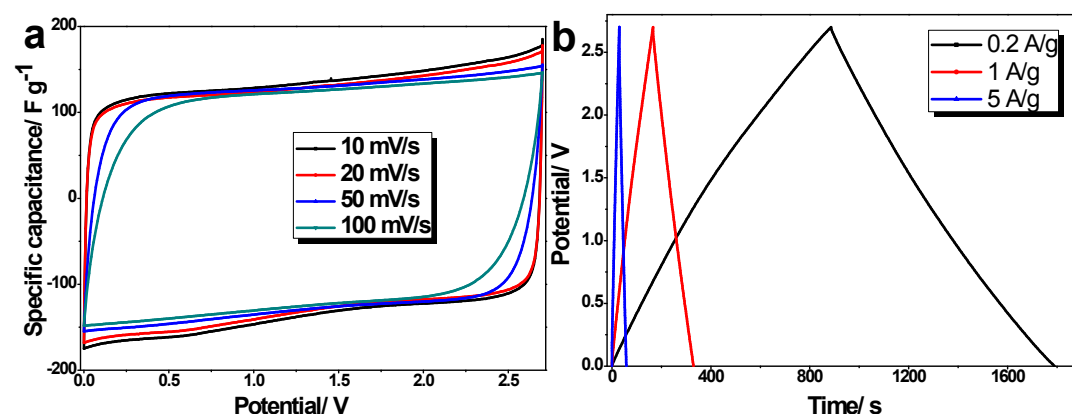Fig. S4 XPS spectra of N-HPCNS and N-MPCNS.

Fig. S5 (a) CV curves at various scan rates for N-MPCNS, (b) GC curves at various current densities for N-MPCNS.
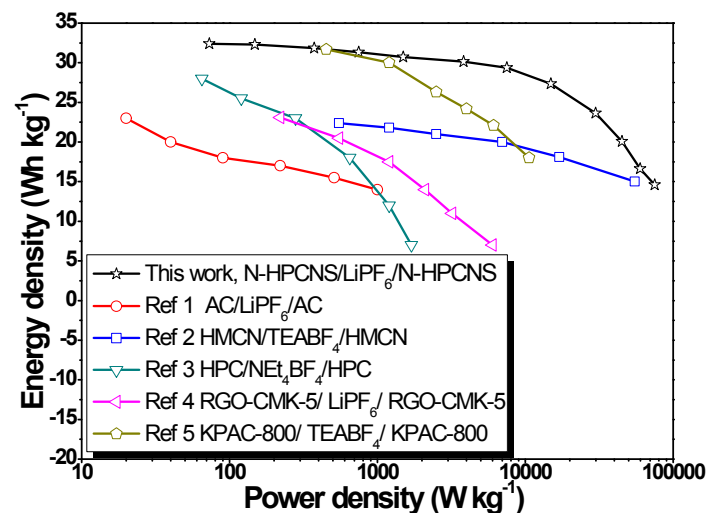

Fig. S6 Ragone plot of N-HPCNS based supercapacitor and some symmetric supercapacitors reported in the literature, namely activated carbon AC/LiPF$_6$/AC,[1] microporous carbon nanosheets HMCN/TEABF$_4$/HMCN,[2] resin-derived hierarchical porous carbon HPC/NEt$_4$BF$_4$/HPC,[3] graphene-CMK-5 composite RGO-CMK-5/ LiPF$_6$/ RGO-CMK-5,[4] and biomass-derived porous carbon KPAC-800/ TEABF$_4$/ KPAC-800.[5]
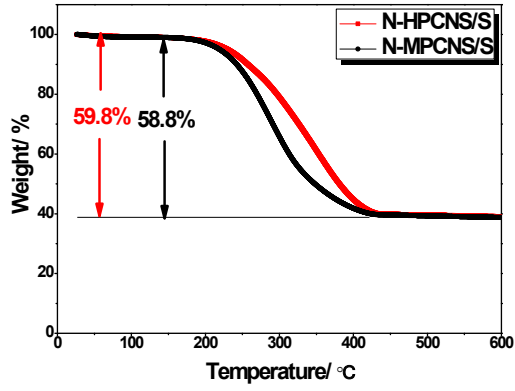
Fig. S7 TGA curve of N-HPCNS/S and N-MPCNS/S composites.
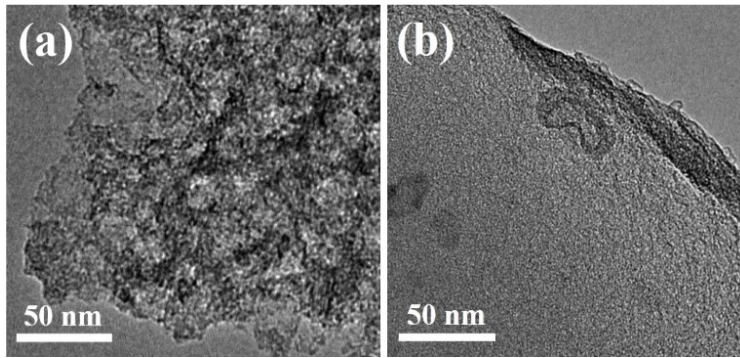

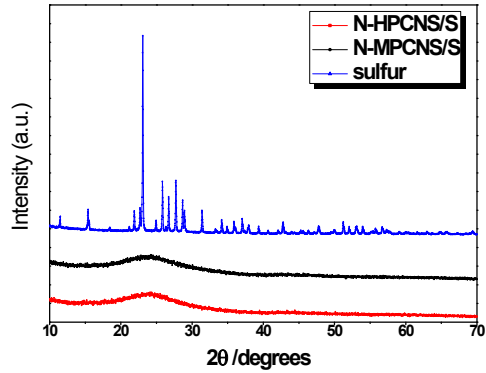Fig. S8 TEM images of N-HPCNS/S and N-MPCNS/S composites.

Fig. S9 XRD patterns of N-HPCNS/S and N-MPCNS/S composites and sublimed sulfur.
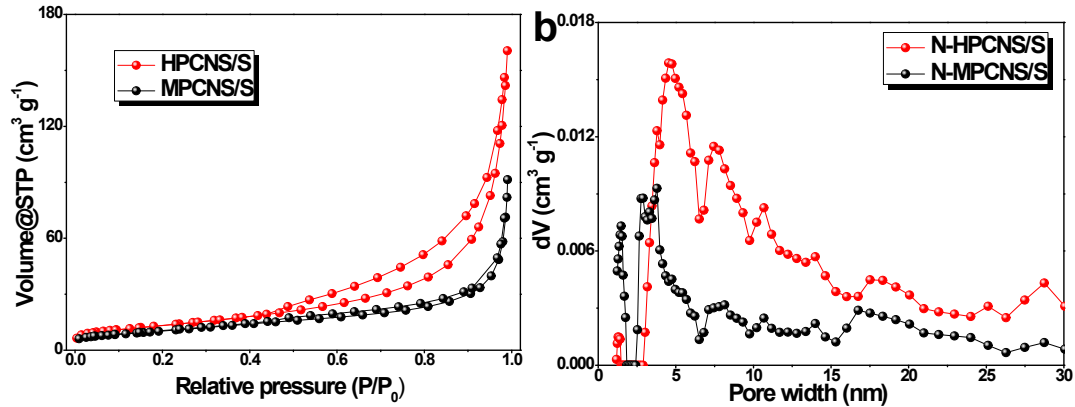

Fig. S10 Nitrogen adsorption isotherms (a) and corresponding pore size distributions (b) of HPCNS/S and MPCNS/S composites.

Table S1 Porosity parameters of porous carbon nanosheets before and after NH_3 treatment.

Porous carbons	Specific surface area/ $m^2 \, g^{-1}$	Total pore volume/ $cm^3 \, g^{-1}$	Predominant mesopore size/ nm
HPCNS	1644	1.56	2.6, 7.8, 13.4
N-HPCNS	1735	1.71	2.6, 7.8, 13.4
MPCNS	1703	0.97	2.6
N-MPCNS	1776	1.07	2.6

References

1.   H. S. Choi, J. H. Im, T. Kim, J. H. Park and C. R. Park, *J. Mater. Chem.*, 2012, **22**, 16986-16993.

2.   G. P. Hao, A. H. Lu, W. Dong, Z. Y. Jin, X. Q. Zhang, J. T. Zhang and W. C. Li, *Adv. Energy Mater.*, 2013, **3**, 1421-1427.

3.   Z. Zheng and Q. Gao, *J. Power Sources*, 2011, **196**, 1615-1619.

4.   Z. Lei, Z. Liu, H. Wang, X. Sun, L. Lu and X. Zhao, *J. Mater. Chem. A*, 2013, **1**, 2313-2321.

5.   P. Cheng, S. Gao, P. Zang, X. Yang, Y. Bai, H. Xu, Z. Liu and Z. Lei, *Carbon*, 2015, **93**, 315-324.