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Supporting Information for

An Unusual Low-Surface-Area Nitrogen Doped Carbon for Ultrahigh Gravimetric and Volumetric Capacitances

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Experimental

Synthesis of PS templates

Monodispersed PS microspheres were synthesized according to procedures reported previously.[1, 2] In a typical preparation, 150 mL of styrene was dispersed in 300 mL deionized water under magnetic stirring, into which 40 mL of $K_2S_2O_8$ (0.7 wt%) was slowly added. The mixture was then heated to 110 °C and held for 2 h under nitrogen protection to allow the polymerization of styrene. After that, the obtained milky solution was filtered to get monodispersed PS microsphere product.

Synthesis of resol

To achieve resol solution,[3] phenol (61 g) was firstly liquefied at 45 °C in a flask, to which 20 wt % NaOH (13 g) aqueous solution and 37 wt % formalin solution (105 g) were added continuously. Then the mixture was maintained at 70 °C for 1 h to allow the polymerization of resol and phenol, by which a low-molecular-weight resol solution can be made. After the resol solution was cooled down to room temperature, we further adjusted its pH value to neutral (7.0) using HCl solution, and placed the solution in a vacuum oven to evaporate water at a temperature below 52 °C. Finally, the product was dissolved in ethanol to give a concentration of 40 wt% resol solution, and an additional centrifugation step was conducted to remove solid NaCl.

Synthesis of NHC and the control sample HC, MacroNC, and MesoC

The sample NHC was prepared by using resol as carbon precursor, melamine foam as nitrogen source, polystyrene (PS) microspheres as macroporous hard-templates, and triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, MW_{av} =12,600) (F127) as mesoporous soft-templates. Firstly, PS microsphere solution was dropwisely infused into the framework of a piece of melamine foam (MF) till it is fully filled. After dried at 60 °C, the foam was further repeatedly infiltrated for three times to make the framework fully filled with PS microspheres. After that, a solution containing 3.2 g of F127 and 8.0 g of resol solution was also filled into the voids of the PS/MF hard-template framework. Due to relatively large resistance resulted from narrow and small voids formed by PS stacking, the PS/MF template was firstly vacuumed before infiltration to make an easy suck in of the solution. The obtained resol/F127/PS/MF composite was left at ambient temperature for 12 h to allow the evaporation of ethanol solvent, and then solidified at 100 °C for 24 h and at 130 °C for 24 h, respectively. Finally, the composite was calcined at 900 °C for 3 h under N_2 purge to remove F127 and PS microsphere templates, and simultaneously to transform the resol to N-doped carbon, which is named as NHC.

Besides, we also prepared three related samples for comparison. When no MF was used, the mixed solution of resol and F127 was infiltrated into the PS colloidal crystals and calcined, to prepare hierarchically porous carbon, labeled as HC. When no resol and F127 was added, calcinating MF/PS would produce macroporous nitrogen doped carbon, MacroNC. And the mesoporous carbon, MesoC was made via an evaporating induced self-assembly route, by using F127 as soft template and resol as carbon precursor.

Characterizations

Transmission electron microscopy (TEM) images were achieved with a Zeiss LIBRA 200 FEG TEM microscope operated at 200 kV. Scanning electron microscopy (SEM) measurements were conducted on a JEOL JSM-7800F microscope operated at 20 kV. Nitrogen sorption isotherms were measured on a Micromeritics Gemini VII 2390 analyzer. Before measurements, the samples were degassed *in vacuo* at 180 °C for 10 h. The micropore size distribution was measured on a Kubo X1000 analyzer, Beijing Builder, China. X-ray photoelectron spectra (XPS) were recorded on a Thermal ESCALAB 250 XI.

Electrochemical measurements

Electrochemical characterizations were performed on an electrochemical work station (Ametek VersaSTAT 3, USA) using a three-electrode system at room temperature. A Pt mesh was used as the counter electrode and an Ag/AgCl electrode (6.0 M KOH, -1.071 V vs. RHE at 298 K) was used as reference electrode, simultaneously. To prepare working electrode, the as-prepared porous samples were dispersed in an ethanol solution containing 5.0 wt% Nafion® binder. This mixture was ultrasonicated for one hour to form uniform ink, and then dropped onto a round glassy carbon electrode with a diameter of 5.0 mm. All measurements were performed in 6.0 M KOH electrolyte. The specific gravimetric capacitance was calculated based on constant current charge-discharge curves via the following equation:[4]

$$C_{sp} = \frac{I\Delta T}{m\Delta V} \tag{1}$$

And the specific volumetric capacitance C_{vol} of the electrode was estimated by the following equations:

$$C_{vol} = C_{sp} \times \rho \tag{2}$$

$$\rho = \frac{1}{V_{total} + 1/\rho_{carbon}} \tag{3}$$

In the two electrode configuration, the two almost identical electrodes were assembled with a separator between them. The area of the electrodes is about 1.0 cm^2 with a mass loading of 3.0 mg. Nickel foam was used as the current collector. The CV and galvanostatic charge–discharge tests were performed in the potential range from -1.0 to 1.0 V. In the two-electrode setup, the gravimetric capacitance for the single electrode (C_S, F g^{-1}) was calculated according to the equation:

$$C_s = \frac{4I\Delta t}{m\Delta V} \tag{4}$$

where I (A) is the current, ΔV (V) refers to the potential change within the discharge time Δt (s), and m is the total mass (g) of active materials in both electrodes.

Besides, the energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) were calculated by using the following formulas:

$$E = \frac{C_s \Delta V^2}{8} \tag{5}$$

$$P = \frac{E}{\Delta t} \tag{6}$$

where C_S (F g^{-1}) is the gravimetric specific capacitance of the total symmetrical system, ΔV (V) refers to the discharge voltage range, and t (h) is the discharge time, respectively.

Results and Discussion

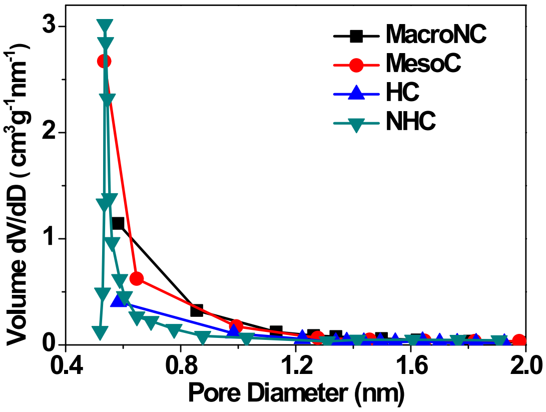

Figure S1. The size distribution of micropores for the prepared materials.

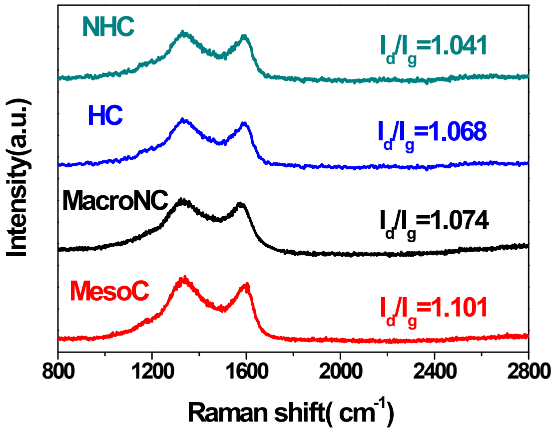

Figure S2. Raman spectra of the prepared materials.

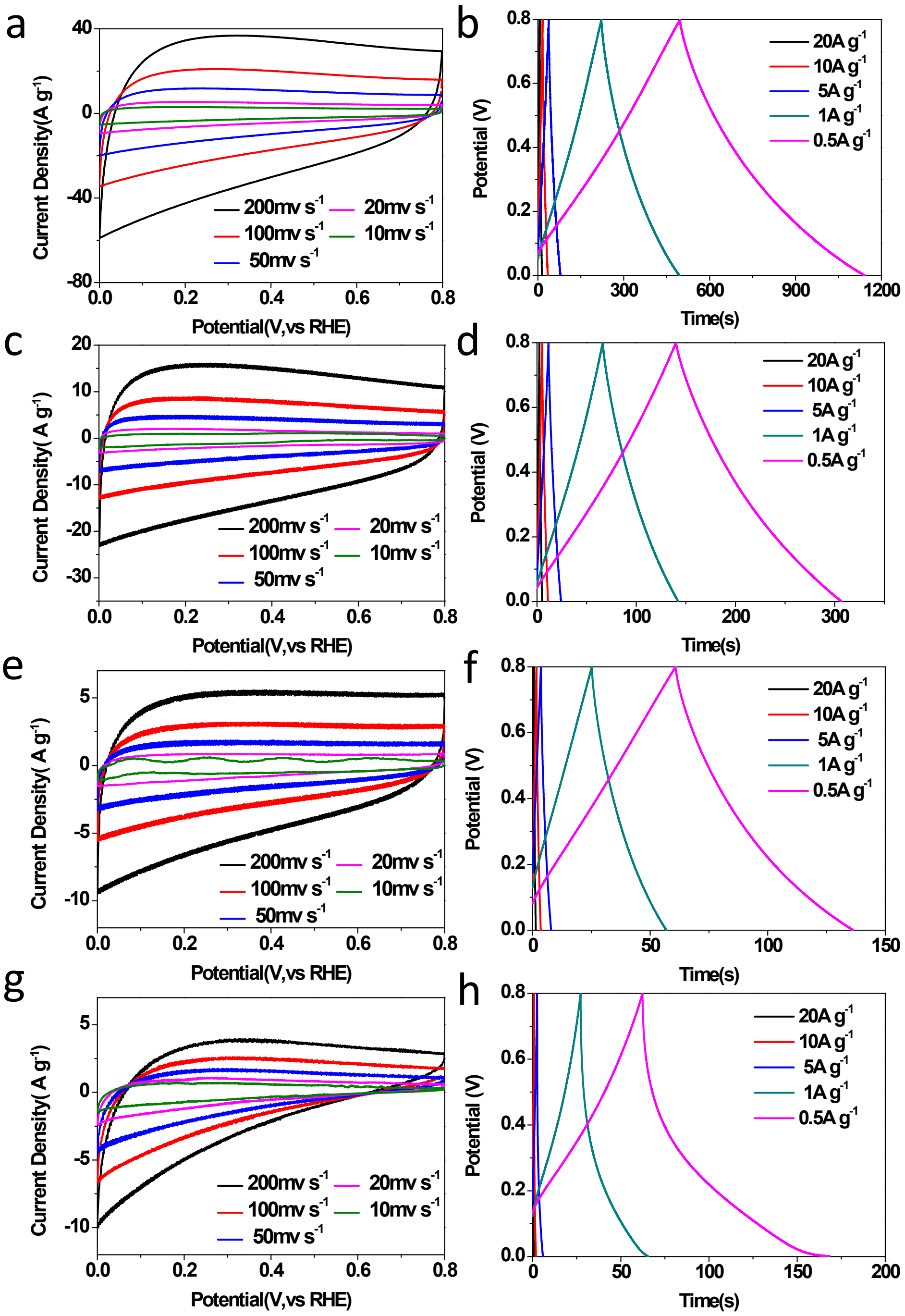

Figure S3. CV curves of NHC (a), HC (c), MacroNC (e), and MesoC (g) measured in 6.0 M KOH solution at different voltage scan rates from 10 to 200 mV s^{-1}. And galvanostatic charge-discharge curves of NHC (b), HC (d), MacroNC (f), and MesoC (h) obtained in 6.0 M KOH solution under different current densities from 0.5 A g^{-1} to 20 A g^{-1}.

Table S1. The contents of various elemental species in the prepared carbon materials obtained from XPS.

Sample	Atomic ratio (%)									
	C 1s	O 1s	O 1s (%)			N 1s	N 1s (%)			
			C=O	C-OH	C-O-C		Pyridinic N	Pyrrolic N	Quaternary N	Pyridin-N -oxide
NHC	90.73	7.90	28.10	59.77	12.13	1.37	44.5	12.0	23.9	19.6
HC	94.07	5.93	18.61	62.93	18.46	—				
MacroNC	96.39	2.89	17.57	43.77	38.66	0.72	24.1	40.5	19.2	16.2
MesoC	94.65	5.35	13.30	57.79	28.91	—				

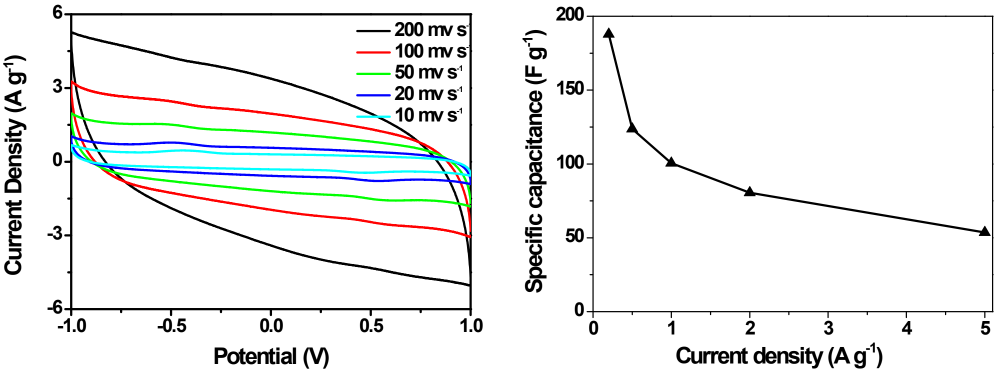

Figure S4. CV curves for NHC at different scan rates and specific capacitances at different current densities in the range of -1.0 –1.0 V based on a symmetrical two-electrode cell.

Table S2. Comparison of the structure parameters and electrochemical performances of NHC with literature results.

Materials	Test System[a]	Current Density[b] (A g^{-1})	Cs[c] (F g^{-1})	S_{BET} (m^2 g^{-1})	Cs/S_{BET} (μF cm^{-2})	Cv[d] (F cm^{-3})	Ref. No.
AC-KOH	6M KOH	0.2	297	1575	18.9	200.7	5
H-NMC-2.5	6M KOH	0.2	227	537	42.3	234.0	6
OMCNW-c	6M KOH	0.5	215	574.9	37.4	244.3	7
HPC	6M KOH	0.5	473	1313	35.8	389.0	8
MUFC-750	6M KOH	0.5	375	2553	14.7	185.6	9
OMCC-3-1	6M KOH	1	200	761	26.3	177.0	10
PCNS-6	6M KOH	1	470	1947	24.1	257.0	11
OMC/G-K	6M KOH	0.5	329.5	2109	15.6	189.4	12
HPC3-600	1M H_2SO_4	0.2	377	1203.4	31.3	330.3	4
N-CNFs-900-6h	6M KOH	1	250	1324	18.9	215.5	13
pCA-KOH-700	1M H_2SO_4	1	467	2016	23.2	278.1	14
PEA-Zn-700-40	1M H_2SO_4	0.5	370	877	42.2	397.5	15
NHC	6M KOH	0.5	**400.0**	**403**	**99.3**	**507.6**	This work

[a] All tests were conducted in three electrode systems. [b] The current density at which the maximal capacitance Cs and Cv was obtained. [c] The maximal specific gravimetric capacitance. [d] The maximal specific volumetric capacitance.

Notes and references

1. L. J. Fu, T. Zhang, Q. Cao, H. P. Zhang and Y. P. Wu, *Electrochemistry Communications*, 2007, **9**, 2140-2144.
2. Z. Liu, J. Mi, Y. Yang, X. Tan and C. Lv, *Electrochimica Acta*, 2014, **115**, 206-215.
3. C. Xue, B. Tu and D. Zhao, *Nano Research*, 2009, **2**, 242-253.
4. J. S. Wei, H. Ding, Y. G. Wang and H. M. Xiong, *ACS Applied Materials & Interfaces*, 2015, **7**, 5811-5819.
5. Z. Li, L. Zhang, B. S. Amirkhiz, X. Tan, Z. Xu, H. Wang, B. C. Olsen, C. M. B. Holt and D. Mitlin, *Advanced Energy Materials*, 2012, **2**, 431-437.
6. Y. Wang and Y. Xia, *Advanced Materials*, 2013, **25**, 5336-5342.
7. K. Wang, J. Zhang, W. Xia, R. Zou, J. Guo, Z. Gao, W. Yan, S. Guo and Q. Xu, *Journal of Materials Chemistry A*, 2015, **3**, 18867-18873.
8. X. Wu, L. Jiang, C. Long and Z. Fan, *Nano Energy*, 2015, **13**, 527-536.
9. G. Sun, L. Ma, J. Ran, B. Li, X. Shen and H. Tong, *Electrochimica Acta*, 2016, **194**, 168-178.
10. S. Wang, C. Han, J. Wang, J. Deng, M. Zhu, J. Yao, H. Li and Y. Wang, *Chemistry of Materials*, 2014, **26**, 6872-6877.
11. C. Chen, D. Yu, G. Zhao, B. Du, W. Tang, L. Sun, Y. Sun, F. Besenbacher and M. Yu, *Nano Energy*, 2016, **27**, 377-389.
12. Y. Song, Z. Li, K. Guo and T. Shao, *Nanoscale*, 2016, **8**, 15671-15680.

13. L.-T. Song, Z.-Y. Wu, H.-W. Liang, F. Zhou, Z.-Y. Yu, L. Xu, Z. Pan and S.-H. Yu, *Nano Energy*, 2016, **19**, 117-127.
14. X. Wei, S. Wan and S. Gao, *Nano Energy*, 2016, **28**, 206-215.
15. X. Wei, X. Jiang, J. Wei and S. Gao, *Chemistry of Materials*, 2016, **28**, 445-458.