Electronic Supplementary Information

Nanoporous Carbon through Direct Carbonization of Zeolitic Imidazolate Framework for Supercapacitor Electrodes

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Experimental Section

Synthesis of nanoporous carbon: Nanoporous carbons were synthesized by carbonization of commercially available zeolitic imidazolate framework ZIF-8 (Basolite Z1200, purchased from Aldrich) under a flow of nitrogen gas at different temperature ranging from 600 to 1000 °C. Typically, about 500 mg of well ground ZIF-8 was homogeneously dispersed in a ceramic boat. The ceramic boat was then put into a tube furnace. The sample was exposed to a flow of nitrogen (~45 mL·min⁻¹) at room temperature for an hour and afterward the furnace was heated to the targeted carbonization temperature with a heating rate of 5 °C·min⁻¹. After reaching the targeted temperature, it was held for 5 h and then cooled down to room temperature. The resultant black powder was collected and then washed with a 10 wt% HF aqueous solution. The sample was stirred in the HF solution for 24 h and then collected by centrifugation. The washing process was repeated twice. Finally, the carbon sample was rinsed with a copious amount of distilled water and then dried at 60 °C overnight. The obtained nanoporous carbons are denoted as Z-*n*, where *n* is the carbonization temperature.

Characterization: Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 instrument. Raman spectra were recorded on a Photon Design spectrometer using an argon ion laser with an excitation wavelength of 514 nm. Pore characteristics of the materials were assessed from nitrogen adsorption–desorption isotherms measured at -196 °C on a Micromeritics TriStar II 3020. Before the measurement, the samples were degassed at 180 °C under vacuum for 12 h. Thermogravimetric and differential thermal analysis (TG-DTA) was performed on an SII NanoTechnology TG/DTA 6200 instrument using pure nitrogen as a carrier gas with a heating rate of 5 °C·min⁻¹.

Electrochemical test: Cyclic voltammograms (CVs) were obtained from an ALS/CH Instruments electrochemical analyzer (model 611B) using a standard three-electrode cell at ambient temperature. The working electrodes were fabricated as follow. First, 2.0 mg of the

carbon sample was added to 1000 μ L of water and then subjected to ultrasonication for an hour. The suspension was dropped onto a glassy carbon electrode. After drying, a 0.5 wt% Nafion solution was coated on the sample. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. For all electrochemical measurements, 0.5 M H₂SO₄ was used as the electrolyte and the experiments were done within a potential range of -0.2 to 1.0 V (vs. Ag/AgCl) at different scan rates.

Fig. S1



Fig. S1 SEM images of (a, b) ZIF-8, (c, d) Z-700, (e, f) Z-800, (g, h) Z-900, and (i, j) Z-1000.

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Fig. S2 Raman spectra of the obtained nanoporous carbon samples.

Fig. S3



Fig. S3 Nitrogen adsorption-desorption isotherms (solid and open symbols represent adsorption and desorption isotherms respectively) of the carbon samples *before acid washing*. The isotherms of Z-700, Z-800, Z-900, and Z-1000 are shifted vertically by 300, 500, 800, and 1200 cm³ g⁻¹ STP, respectively.





Fig. S4 TG-DTA curves of ZIF-8 under nitrogen with a heating rate of 5 °C·min⁻¹.

		Potential range/	Scan rate/	Particle density ^a /	Capacitance ^b			
Material	Electrolyte	V	$mV \cdot s^{-1}$	g·cm ⁻³	F·g ⁻¹	µF·cm ⁻²	F·cm ⁻³	Ref.
MOF-derived	carbon							
Z-900	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	-0.2 to 1.0	5	0.93	214	20	200	This work
NPC	$1 \text{ M H}_2\text{SO}_4$	-0.5 to 0.5	5	0.39	204	7	80	S1
NPC ₆₅₀	$1 \text{ M H}_2\text{SO}_4$	-0.5 to 0.5	5	0.51	167	11	84	S2
C800	$1 \text{ M H}_2\text{SO}_4$	-0.5 to 0.5	5	0.50	188	9	94	S3
C1000	$1 \text{ M H}_2\text{SO}_4$	-0.5 to 0.5	5	0.32	161	5	52	S3
MC-A	6 M KOH	-1.0 to 0	2	0.55	208	12	114	S4
MPC-A	6 M KOH	-1.0 to 0	2	0.41	196	15	81	S4
MAC-A	6 M KOH	-1.0 to 0	2	0.61	271	12	165	S4
Templated porous carbon by nanocasting								
Y-AN	$1 \text{ M H}_2\text{SO}_4$	0 to 0.6	2	0.74	340	20	250	S5
BMC-I	$1 \text{ M H}_2\text{SO}_4$	0 to 0.8	2	0.96	112	17	108	S6
BMC-II	$1 \text{ M H}_2\text{SO}_4$	0 to 0.8	2	1.01	99	21	100	S6
Carbon aerogel-derived carbon								
CA1-800	$2 \text{ M H}_2 \text{SO}_4$	0 to 1.2	2	0.50	225	31	111	S7
COU-2	$1 \text{ M H}_2\text{SO}_4$	-0.2 to 0.8	2	0.86	184	27	159	S8
K-COU-2	$1 \text{ M H}_2\text{SO}_4$	-0.2 to 0.8	2	0.57	244	14	139	S8
AMC-6	0.1 M NaCl	-0.4 to 0.6	1	0.48	188	10	91	S9
Carbide-deriv	ved carbon							
TiC-CDC	$1 \text{ M H}_2\text{SO}_4$	-0.5 to 0.5	5		190	12 °	140 ^c	S10
Carbon fiber-based material								
ACF4	6 M KOH	0 to 1.0	1	0.38	371	11	139	S11

 Table S1
 Capacitances in aqueous electrolytes of various porous carbons reported in the
representative literatures.

^{*a*} Particle density = [Total pore volume + $1/\rho_{carbon}$]⁻¹, where ρ_{carbon} is the true density of carbon (2 g·cm⁻³)^{S12}. ^{*b*} Gravimetric capacitances in F·g⁻¹ were taken from the references; interfacial capacitances in μ F·cm⁻² were normalized to the BET surface area; volumetric capacitances in F·cm⁻³ were calculated from the particle density of carbon materials. ^{*c*} Taken from the reference.

References

- S1 B. Liu, H. Shioyama, T. Akita and Q. Xu, J. Am. Chem. Soc., 2008, 130, 5390.
- S2 B. Liu, H. Shioyama, H. Jiang, X. Zhang and Q. Xu, Carbon, 2010, 48, 456.
- S3 H.-L. Jiang, B. Liu, Y.-Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong and Q. Xu, J. Am. Chem. Soc., 2011, 133, 11854.
- S4 J. Hu, H. Wang, Q. Gao and H. Guo, *Carbon*, 2010, 48, 3599.
- S5 C. O. Ania, V. Khomenko, E. Raymundo-Piñero, J. B. Parra and F. Béguin, Adv. Funct. Mater., 2007, 17, 1828.
- S6 D.-W. Wang, F. Li, Z.-G. Chen, G. Q. Lu and H.-M. Cheng, *Chem. Mater.*, 2008, **20**, 7195.
- S7 M. C. Gutiérrez, F. Picó, F. Rubio, J. M. Amarilla, F. J. Palomares, M. L. Ferrer, F. del Monte and J. M. Rojo, J. Mater. Chem., 2009, 19, 1236.
- S8 J. Jin, S. Tanaka, Y. Egashira and N, Nishiyama, Carbon, 2010, 48, 1985.
- S9 X. Wang, J. S. Lee, C. Tsouris, D. W. DePaolib and S. Dai, J. Mater. Chem., 2010, 20, 4602.
- S10 J. Chmiola, G. Yushin, R. Dash and Y. Gogotsi, J. Power Sources, 2006, 158, 765.
- S11 B. Xu, F. Wu, R. Chen, G. Cao, S. Chen, Z. Zhou and Y. Yang, Electrochem. Commu., 2008, 10, 795.
- S12 H. Itoi, H. Nishihara, T. Kogure and T. Kyotani, J. Am. Chem. Soc., 2011, 133, 1165.