Supporting Information

Individual Nanoporous Carbon Spheres with High Nitrogen Content from Polyacrylonitrile

Nanoparticles with Sacrificial Protective Layers

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N₂ adsorption and desorption isotherms and pore size distributions of the as-prepared NPC-S, NPC-P, and NPC-M



Figure S1. (a) N_2 adsorption and desorption isotherms and (b) pore size distribution of the as-prepared nanoporous carbon sphere (NPC-S) and nanoporous carbon monolith (NPC-M) prepared with $ZnCl_2$ impregnation, and porous carbons (NPC-P) prepared from pure PAN without $ZnCl_2$ impregnation.

Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) were determined from N₂ adsorption isotherms at 77 K. Nitrogen sorption isotherms of the as-prepared nanoporous carbon spheres (NPC-S), porous carbons prepared from pure PAN homopolymer (NPC-P), and ZnCl₂ activated PAN NPs (NPC-M) were shown in Figure S1a. Nitrogen sorption isotherms show a hysteresis loop, indicating the existence of mesopores. The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. Without the addition of ZnCl₂, the total SSA of NPC-P was only ~191 m²/g with a much narrower pore size distribution mainly located around 2 nm. After the impregnation of ZnCl₂, the SSA of NPC-M increased up to about 1212 m²/g. Therefore, ZnCl₂ obviously plays a key role in the formation of the highly porous microstructure of porous carbon during the carbonization process. The pore size distribution showed that the size of the majority of the pores falls in the range of 2–10 nm (Figure S1b). XPS results showed that the residual zinc content in NPC-S is negligible (0.0054 wt%), which means that all the salt is essentially evaporated away after the carbonization process.

XPS survey spectra of porous carbons



Figure S2. XPS survey spectrum of NPC-S (a) and NPC-M (b).

As shown in Figure S2a, XPS of the NPC-S and NPC-M samples showed the presence of the C 1s peak at ~284.8 eV, the N 1s peak at ~398.8 eV, and the O 1s peak at ~531.8 eV. Therefore the surfaces of NPC-S and NPC-M were dominated by carbon, nitrogen, and oxygen. The surface N contents were comparable with the results of elemental analysis, indicating the uniformity of nitrogen distribution throughout the entire nanoporous carbons.



Figure S3. The decomposed Raman spectra of the as-prepared NPC-M (a) and NPC-S (b).

Electrochemical measurements of NPC-S and NPC-M



Figure S4. CV curves for (a) NPC-S and (b) NPC-M in O₂-saturated 0.1 M aqueous KOH solutions recorded at a scan rate 100 mV/s.



Figure S5. (Left) Rotating disk electrode study of NPC-M in O₂-saturated 0.1 M KOH electrolyte at a scan rate 10 mV/s and (right) Koutecky-Levich analysis of LSV curves presented in (left).

Polarization curves of NPC-M at different rotating speeds recorded at a scan rate 10 mV/s and Koutecky-Levich plots derived from the polarization curves.

Performance of NPC-M as electrode in supercapacitor



Figure S6. Electrochemical capacitive behavior of NPC-M measured in a two-electrode system by using 1 M Na₂SO₄ aqueous solution as electrolyte within the potential range of 0 to 0.8 V. (a) cyclic voltammetry (CV) curves at various scan rates, (b) galvanostatic charge-discharge curves at different current densities, (c) specific capacitance as a function of scan rate ranging from 2 to 2000 mV/s, (d) specific capacitance as a function of current density ranging from 0.1 to 20 A/g, (e) the Nyquist plot, and (f) cycle durability at a current load of 2 A/g.

Figure S6 shows the electrochemical capacitive behavior of NPC-M measured in a two-electrode system by using 1 M Na₂SO₄ aqueous solution as electrolyte within the potential range of 0 to 0.8 V. Figure S6a showed the GCD curves of the device at various current densities ranging from 0.1 to 20 A/g. The specific capacitance dropped quickly as the current density increased. The discharge curves of the carbon capacitors are not symmetrical with the corresponding charge curves. The specific capacitance was ~175 F/g at a current density of 100 mA/g.

Table S1 XPS data for NPC-S and NPC-M.

Samples	Elements	Position (eV)	FWHM	Area	Atomic%
NPC-S	C1s	284.8	3.75	267.29	84.62
	N1s	398.8	4.3	67.7	11.91
	O1s	531.8	3.92	17.38	1.88
	F1s	684.8	3.8	22.29	1.59
	Zn2p				0
NPC-M	C1s	284.8	3.74	202	92.1
	N1s	398.8	4.19	19.4	4.9
	O1s	531.8	4.64	15.8	2.4
	F1s	684.8	4.82	5.6	0.6
	Zn2p				0

Table S2 High resolution XPS data for N 1s binding energies of NPC-S and NPC-M.

Samples	Peak position		Ratio of peak area (%)			FWHM			
	N-P	N-X	N-O	N-P	N-X	N-O	N-P	N-X	N-O
NPC-S	398.9	400.7	403.5	33	46.5	20.5	1.5	2.4	5.3
NPC-M	398.6	400.5	402.5	21.5	43.2	35.3	1.5	2.6	8.3

Specific capacitance of polyacrylonitrile-based porous carbons

Table S3. Comparison of the C_s of some polyacrylonitrile-based porous materials in the literature.

Item	Materials	Method	Electrolyte	Highest Cs (F/g)	Ref.
1	web of carbon nanotube/porous	electrospinning	two-electrode system, 1 M aqueous H_2SO_4 solution	100 F/g (0.1 A/g)	1
	carbon				
2	web of porous carbon	electrospinning	two-electrode system, 6 M aqueous KOH solution	140 F/g (10 mV/s)	2
3	microporous carbon	direct pyrolysis	two-electrode system, 1 M aqueous H ₂ SO ₄ solution	258 F/g (0.5 A/g)	3
4	porous carbon nanofibers	electrospining	three-electrode system, 0.5 $M H_2SO_4$ aqueous solution	104 F/g (0.2 A/ g)	4
5	porous carbon nanospheres	emulsion polymerization and KOH activation	two-electrode system, 0.5 M aqueous H_2SO_4 solution	240 F/g (1.0 A/g)	5
6	nanofibers	electrospinning and CO_2 activation	two-electrode system, ionic liquid electrolyte	140 F/g (10 mV/s)	6
7	3D monolith of carbon nanotube/porous carbon	direct pyrolysis	three-electrode cell, 1 M aqueous H_2SO_4 solution	216 F/g (10 mV/s)	7

8	porous carbon	direct pyrolysis	two-electrode system, 1 M	244 F/g (2 mV/s)	this work
	nanospheres		Na ₂ SO ₄ aqueous solution		

Ionic liquid electrolyte: ethylmethylimidazolium bis (trifluoromethylsulfonyl) imide (EMITFSI)

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- Cs= 216 F/g, Wang Y, Fugetsu B, Wang Z, Gong W, Sakata I, Morimoto S, Hashimoto Y, Endo M, Dresselhaus M, Terrones M. Nitrogen-doped porous carbon monoliths from polyacrylonitrile (PAN) and carbon nanotubes as electrodes for supercapacitors. Scientific reports. 2017, 7: 40259.

CO2-adsorption performance of some nitrogen-containing porous carbons

Item	Carbon and nitrogen precursors	Method	CO₂ adsorption capacity (0 °C) (mmol g ⁻¹)	CO₂ adsorption capacity (25 °C) (mmol g ⁻¹)	CO ₂ /N ₂ selectivity	Ref.
1	Porous carbon from commercial PAN fibers	Electrospinning KOH activation		3.1,		1
2	Porous carbon from PAN-block-poly(n-but yl acrylate)	Pyrolysis at 700 °C	3.5	2.7	10.5	2
3	Porous carbon from N rich metal–organic framework ZIF-8	Calcined at 600, 700, 800, 900, or 1000 °C for 8 h with HF washing	5.1	3.9	59	3
4	Poly(benzoxazine-co-r esol)-Based Porous Carbon Monoliths	Pyrolysis at 800 °C	4.5	2.4	28	4
5	Ordered mesoporous carbons from phenolic resin	Pyrolysis at 600 °C		2.8	37	5
6	Porous carbons derived from metal–organic	Carbonizations at 600–1100 °C		3.31	18	6

Table S4. CO₂ adsorption capacities of some nitrogen-containing porous carbons at 25 °C and 1 atm in the literature.

	frameworks (MOFs)					
7	Porous carbon spheres	Pyrolysis at 700 °C	4.1	2.8	20	This work

- 1. Shen W, Zhang S, He Y, Li J, Fan W. Hierarchical porous polyacrylonitrile-based activated carbon fibers for CO₂ capture. Journal of Materials Chemistry. **2011**, 21(36): 14036-14040.
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