SUPPLEMENTARY INFORMATION

Boric acid-mediated B,N-codoped chitosan-derived porous carbons with high surface area and greatly improved supercapacitor performance

Zheng Ling, Gang Wang, Mengdi Zhang, Xiaoming Fan, Chang Yu, Juan Yang, Nan Xiao, and Jieshan Qiu*

Preparation of Samples

Chitosan (viscosity, 50-800 mPa·s; degree of deacetylation, 80-95%) was purchased from Sinopharm Chemical Reagent Co. Ltd. The boric acid was purchased from Shenyang Xinxing Chemical Reagent Co. Ltd. All chemicals were used as received.

For a typical run, two grams of chitosan powder was wetted using 4 mL deionized water and then protonated by 1 mL 1 M hydrochloric acid. After addition of water and acid, the wet powder was mixed in a mortar for 10 minutes by hand, and then 0.1 g g^{-1} of boric acid aqueous solution at 80 °C was poured into the treated chitosan. The mixture was grinded in the agate mortar for 30 minutes forming a thick paste. The paste was heated to 800 °C at a heating rate of 5 °C min^{-1} in flowing nitrogen (99.999%, 100 mL min^{-1}) and kept for 1 h at this temperature, then naturally cooled to room temperature. The as-made sample was grinded into fine powder and labeled as 1B-2CHI-N, here the number refers to a 1:2 mass ratio of boric acid to chitosan. The as-made 1B-2CHI-N was refluxed for 1.5 h in deionized water to remove as-produced B_2O_3, leading to a product named as 1B-2CHI-WT. For comparison, the sample was also made in the absence of boric acid by the same approach and named as 2CHI-WT, revealing the positive effect of boric acid.

Characterization methods

Nitrogen adsorption/desorption was performed at -196 °C on a physical adsorption instrument (ASAP2020, Micromeritics, USA). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The total pore volumes (V_{total}) were calculated from the adsorbed N_2 amount at $P/P_0 \approx 1$. The micropore volumes were calculated from the Dubinin-Astakhov (DA) equation. The pore size distribution was calculated by the density functional theory (DFT) using carbon slit pores as equilibrium model.

The as-prepared samples were analyzed by a powder X-ray diffractometer (D/MAX-2400, Japan) using Cu-Kα radiation generated at 40 kV and 100 mA.

The morphology was studied by a field emission scanning electron microscopy (FE-SEM, NOVA NanoSEM 450, FEI, USA).

The boron content was detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 2000DV, PerkinElmer Inc., USA). The nitrogen content was detected by combustion method (Vario EL III, Elementar, Germany). The atomic concentrations of boron, nitrogen, and oxygen at the surface of the 1B-2CHI-WT were determined by the X-ray photoelectron spectrometer (ESCALAB 250, Thermo VG, USA) with Al Kα radiation (15 kV, 150 W).

* Corresponding author. Fax: +86 411 84986024. E-mail address: jqiu@dlut.edu.cn (J. S. Qiu)

The thermal gravimetric (TG) analysis was conducted on a Mettler Toledo TGA/SDTA851^e TGA. Samples were placed in a ceramic crucible and heated up to 850 °C at a heating rate of 10 °C/min in N_2. The paste formed by boric acid and chitosan with a mass ratio of 1:2 was freeze dried before conducting TG analysis in order to confirm the effect of boric acid on the pyrolysis of chitosan and eliminate the effect of the water contained in the paste.

The performance of the as-prepared materials as the electrode of supercapacitors was evaluated using a CHI 660D electrochemical workstation (Shanghai Chenhua, China). The cyclic voltammertry (CV) and galvanostatic charge/discharge were employed. All the tests were firstly conducted in a three-electrode system with a Pt foil (20 mm* 20 mm) as the counter electrode, a Hg/Hg_2SO_4 electrode as the reference electrode, and 1 M sulfuric acid as electrolyte. The electrode sheets for working electrodes were prepared by mixing the as-prepared carbon with carbon black and poly(tetrafluoroethylene) (PTFE) at a weight ratio of 85:10:5. The paste was rolled into a uniform sheet with thickness of about 108 μm and punched into 1 cm^2 discs. The disc weight ranges from 6 to 8 mg after vacuum drying for 12 h at 100°C. The electrode sheet was sandwiched by Ti meshes, and they were pressed at 2 MPa for 20 seconds. The electrodes were impregnated in 1 M sulfuric acid for 24 hours under vacuum before conducting tests.

The specific capacitance (C, F g^{-1}) of the as-made carbon can be calculated through the following equations using the data from cyclic voltammetry.

$$C = \frac{\int IdV}{vm\Delta V} \quad (1)$$

where I is the response current (A), V is the potential (V), v is the scan rate of potential (V s^{-1}), m is the mass of the as-made carbon (g) and ΔV is the potential window (V).

The performance is also studied by galvanostatic charge/discharge, and the specific capacitance (C, F g^{-1}) is calculated via equation (2).

$$C = \frac{I\Delta t}{m\Delta V} \quad (2)$$

where I is the constant discharge current (A), Δt is the discharge time (s), m is the mass of the as-made carbon (g) and ΔV is the potential window (V).

Supercapacitors were assembled using two electrodes of 1B-2CHI-WT with identical mass. The non-woven fabric was used as separator and 1 M H_2SO_4 as electrolyte. The energy density and power density can be calculated through the following equations:

$$E = \frac{1}{2}CV^2 \quad (3), \qquad P = \frac{E}{t} \quad (4)$$

Where E stands for the energy density and P for power density, C denotes the specific capacitance, V is the voltage (V) across the two electrodes, and t stands for the discharge time.

Supplementary data

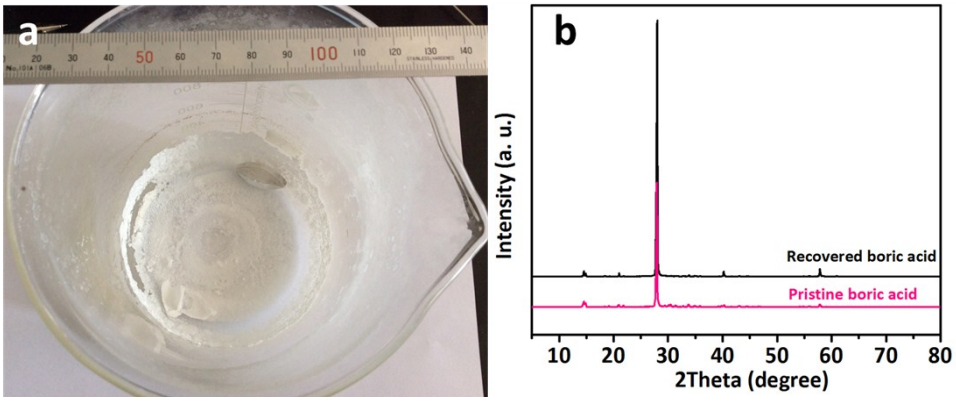

Figure S1 (a) Digital image of recovered boric acid, (b) XRD profiles of recovered and pristine boric acid.

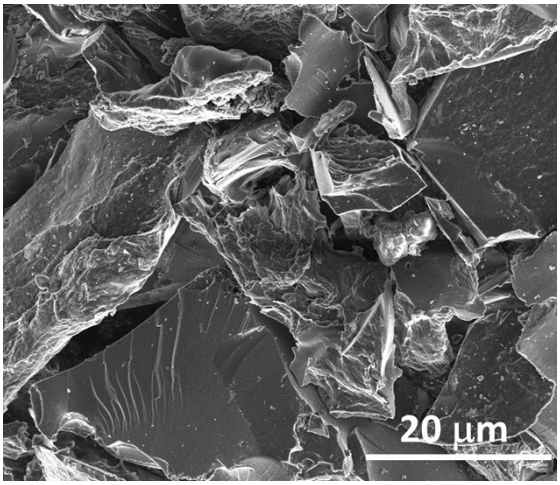

Figure S2 FE-SEM image of 2CHI-WT.

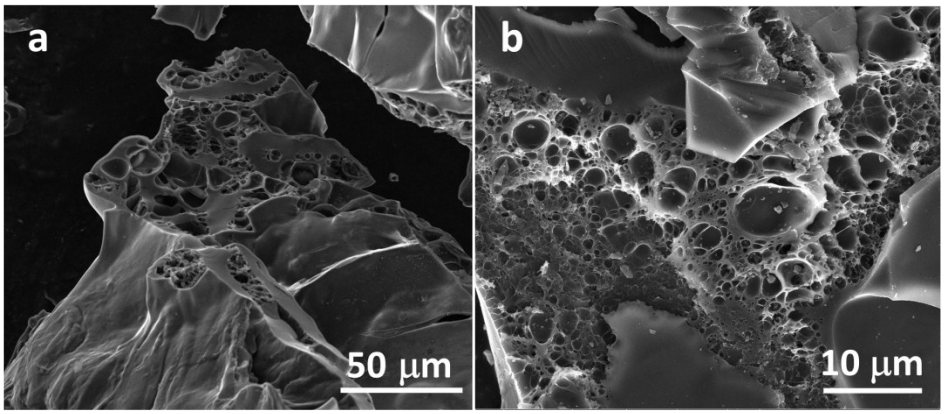

Figure S3 FE-SEM images of (a) 1B-CHI-N and (b) 1B-2CHI-WT.

Table S1 Boron species and binding energy obtained by XPS

Element	Content (wt%)	Component	Binding energy (eV)	Relative content （%）
B 1s	0.96	B-sub-C	189.27	4.04
		BC_2O	190.09	32.46
		BN	191.01	25.98
		BCO_2	191.83	26.62
		B_2O_3	192.81	10.90

Table S2 Nitrogen species and binding energy obtained by XPS

Element	Content (wt%)	Component	Binding energy (eV)	Relative content （%）
N 1s	4.63	B-N	398.24	25.75
		N-6	399.38	27.06
		N-5	400.51	26.13
		N-Q	401.48	21.06

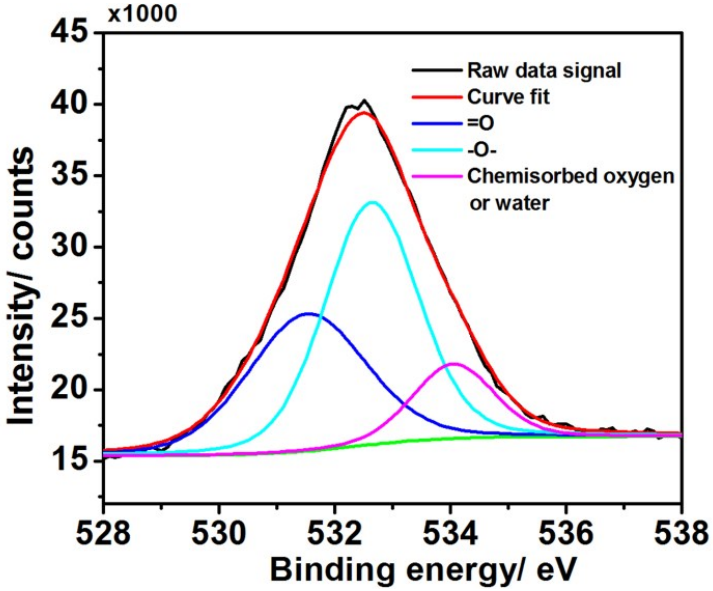

Figure S4 O 1s XPS spectra of 1B-2CHI-WT

Table S3 Oxygen species and binding energy obtained by XPS

Element	Content (wt%)	Component	Binding energy (eV)	Relative content （%）
O 1s	12.20	=O	531.52	35.99
		-O-	532.63	50.54
		Chemisorbed oxygen or water	534.04	13.47

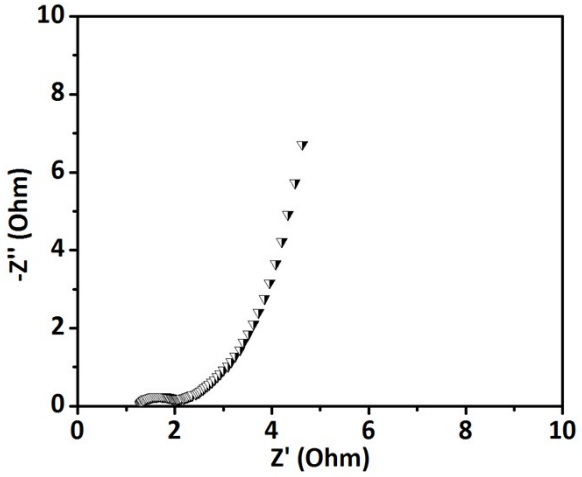

Figure S5 Nyquist plot of 1B-2CHI-WT in the frequency range of 10 mHz to 100 kHz.

Table S4 Results of boron- and nitrogen-co-doped and boron-doped carbons for supercapacitors in literatures

Sample	Gravimetric capacitance ($F\ g^{-1}$)	S_{BET} ($m^2\ g^{-1}$)	B content Wt%	N content Wt%	System voltage (V)	Scan rate	Electrolyte	System	Ref.
1B-2CHI-WT	306 227	710	2.06	8.19	-0.7-0.3 V vs Hg/Hg_2SO_4	0.1 A g^{-1} 2 mV s^{-1}	1 M H_2SO_4	3E/GC	This work
CNB-3	247	376	0.66	0.53	-1 – 0 V vs Hg/HgO	0.5 A g^{-1}	6 M KOH	3E/GC	[1]
BN-GAs	239 132	249	~3.0 at%	~0.6 at%	0-0.8V vs SCE	1 mV s^{-1} 100 mV s^{-1}	1 M H_2SO_4	3E/CV	[2]
B0.12-OMC	196	1392	0.30	-	-1 – 0 V vs Hg/HgO	50 mA g^{-1}	6 M KOH	3E/GC	[3]
BCN	30	50	14.24 at%	10.46 at%	-1.4-1 V vs Ag/AgCl	10 mV s^{-1}	2 M $CaCl_2$	3E/CV	[4]
P3-900	146	598	0.3 wt%	-	-0.3-0.6V vs Ag/AgCl	0.5 mV s^{-1}	1 M H_2SO_4	3E/CV	[5]
PAAB-900	>300	410	~8 wt%	-	-0.2-0.8 V vs SCE	2 mV s^{-1}	1 M H_2SO_4	3E/CV	[6]
BNC-9	268 247	894	8.4 at%	7.1 at%	-0.1- -0.9 V vs Ag/AgCl	0.1 A g^{-1} 2 mV s^{-1}	6 M KOH	3E/GC 3E/CV	[7]
BNCC		621	2.2 wt%	~0.1 at%	0-2 V	-	Organic	2E	[8]

References

1. D. C. Guo, J. Mi, G. P. Hao, W. Dong, G. Xiong, W. C. Li and A. H. Lu, *Energy Environ. Sci.*, 2013, **6**, 652-659.
2. Z. S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. Feng and K. Müllen, *Adv. Mater.*, 2012, **24**, 5130-5135.
3. X. Zhai, Y. Song, J. Liu, P. Li, M. Zhong, C. Ma, H. Wang, Q. Guo and L. Zhi, *J. Electrochem. Soc.*, 2012, **159**, E177-E182.
4. T. Tomko, R. Rajagopalan, P. Aksoy and H. C. Foley, *Electrochim. Acta*, 2011, **56**, 5369-5375.
5. C. Moreno-Castilla, M. B. Dawidziuk, F. Carrasco-Marín and Z. Zapata-Benabithe, *Carbon*, 2011, **49**, 3808-3819.
6. H. Konno, T. Ito, M. Ushiro, K. Fushimi and K. Azumi, *J. Power Sources*, 2010, **195**, 1739-1746.
7. H. Guo and Q. Gao, *J. Power Sources*, 2009, **186**, 551-556.
8. S. Sepehri, B. B. García, Q. Zhang and G. Cao, *Carbon*, 2009, **47**, 1436-1443.