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Electronic supporting information

Flexible solid-state supercapacitors based on freestanding nitrogen-doped porous carbon nanofibers derived from electrospun polyacrylonitrile@polyaniline nanofibers

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Calculations

Calculation of specific capacitances in three-electrode configuration:

Specific capacitances (C_s) calculated from the CV curves used the following equation:

$$C_s = (\int Idt)/(mV)$$

'I' was the oxidation or reduction current. 'dt' was time differential. 'm' indicated the mass of the whole electrode material and 'V' indicated the voltage range of one sweep segment.

Specific capacitance could also be calculated from the GCD curves, using the following equation:

$$C_s = (I\Delta t)/(m\Delta V)$$

'I' was charge and discharge current. 'Δt' was the time for a full discharge. 'm' indicated the mass of the whole electrode materials. 'ΔV' represented the voltage within the discharge time.

Calculation of specific electrode capacitance, cell capacitance and power density, energy density of the as-synthesized symmetric supercapacitors:

Cell capacitances (C_{cell}) and ***specific electrode capacitances (C_{sp})*** were calculated as follows:

$$C_{cell} = (I\Delta t)/(m\Delta V)$$

'I' was the applied current, 'Δt' was the discharged time, 'ΔV' was the discharge potential except voltage drop, 'm' was the mass (~8 mg) of two electrodes.

$$C_{sp} = 4*C_{cell} = (4I\Delta t)/(m\Delta V)$$

Specific energy density (E_s) and ***power density (P_s)*** of the symmetric supercapacitor was calculated as follows:

$$E_s = 0.5*(C_{cell}\Delta V^2)$$

$$P_s = Es/\Delta t$$

'ΔV' was the device potential.'Δt' was the discharge time.

Areal capacitance (C_a) and ***Volume capacitance (C_v)*** of the device were also calculated according to the following formulae:

$$C_a = (I\Delta t)/(S*\Delta V)$$

$$C_v = (I\Delta t)/(V*\Delta V)$$

'I' was the discharge current. 'Δt' was the discharged time.'ΔV' was the discharge potential except voltage drop. 'S' is the geometrical area (1 cm*1.5 cm) of the device. 'V' was volume (1 cm*1.5 cm * 0.8 mm) of the device.

Volume energy density (E_v) and ***power density (Pv)*** of the symmetric supercapacitor was calculated as follows:

$$E_v = 0.5*C_v\Delta V^2$$

$$P_v = E_v/\Delta t$$

'C_v' was the volume capacitance of the device. 'ΔV' was the device potential. 'Δt' was the discharged time.

Supplementary Figures

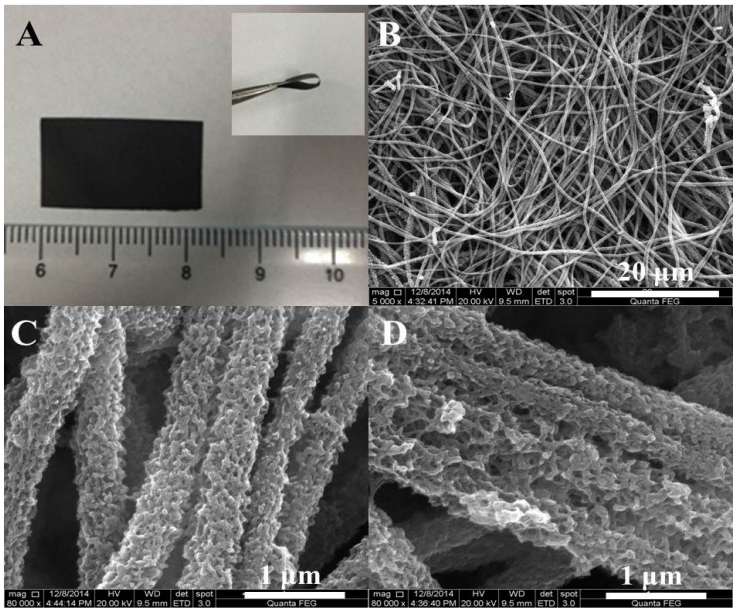

Figure S1. (A) Photograph of the NPCNFs-900. (B) SEM image of the NPCNFs-900. (C) and (D) SEM images of the NPCNFs-800 and NPCNFs-1000, respectively.

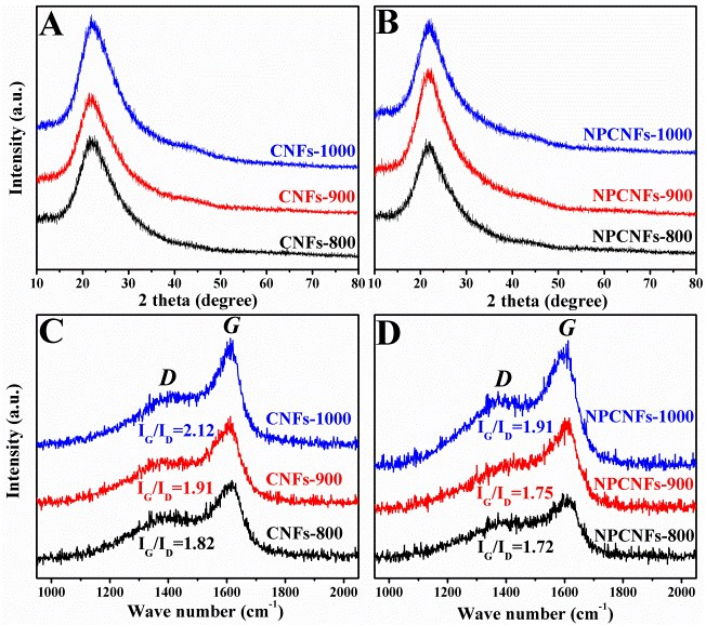

Figure S2. (A) and (B) XRD patterns of CNFs and NPCNFs, respectively. (C) and (D) Raman spectra of CNFs and NPCNFs, respectively.

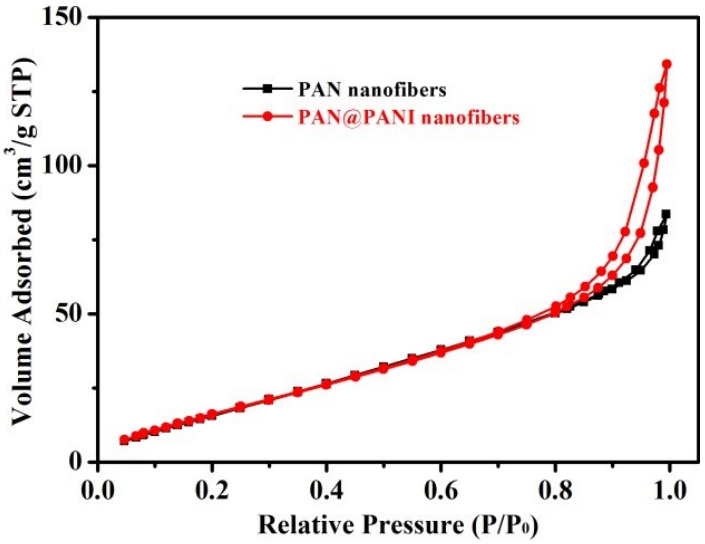

Figure S3. N_2-adsorption isotherms of PAN nanofibers and PAN@PANI nanofibers

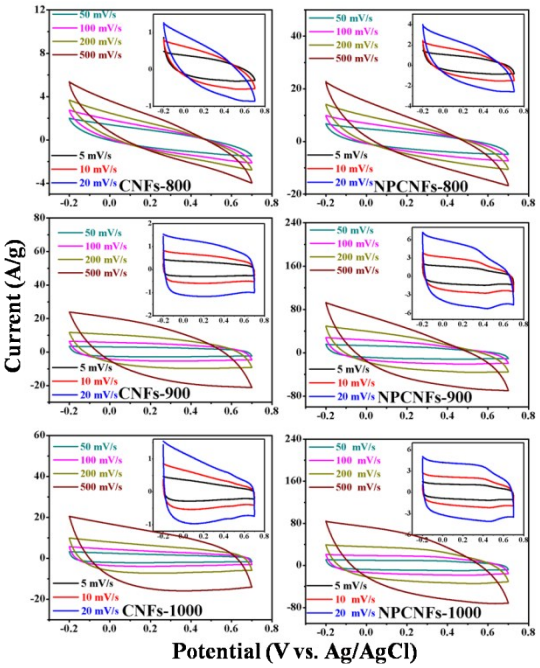

Figure S4. CV curves at the scan rates from 5 to 500 mV/s of CNFs and NPCNFs by different carbonized temperature from 800 to 1000 °C, respectively.

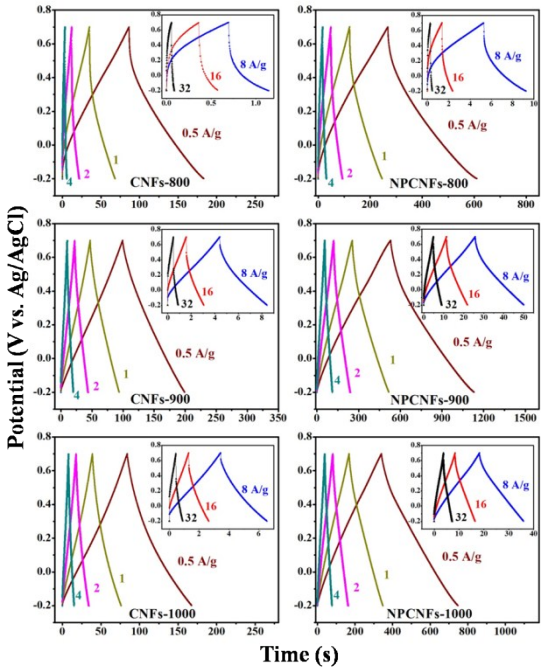

Figure S5. GCD curves at the current densities from 0.5 to 32 A/g of CNFs and NPCNFs by different carbonized temperature from 800 to 1000 °C, respectively.

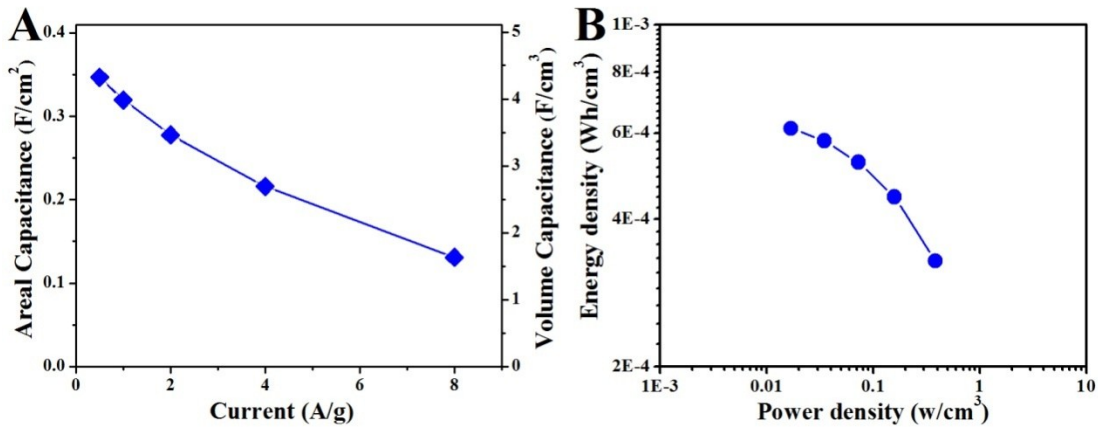

Figure S6. (A) Areal capacitance and volume capacitance; (B) Volume energy density and power densityof the device.

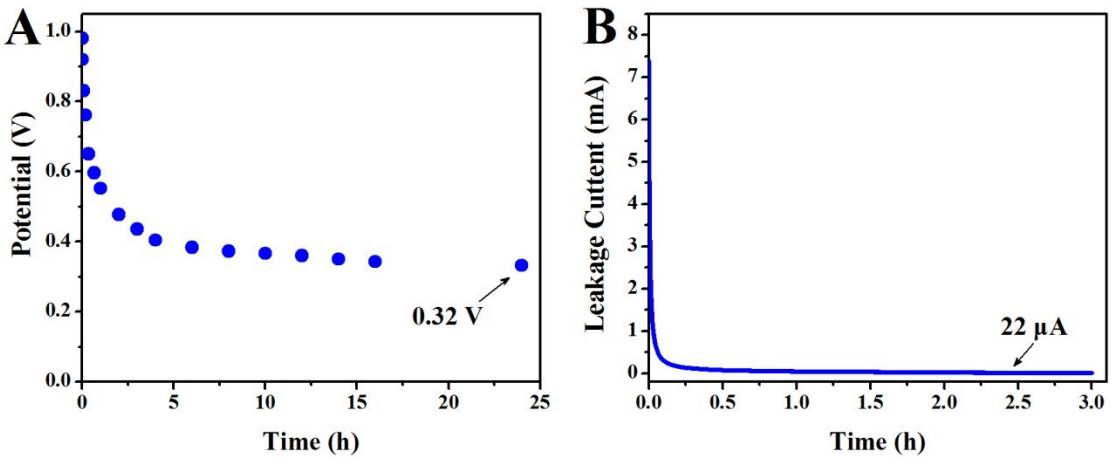

Figure S7. (A) self-discharge curve of the device after charged at 1V for 10 minnutes; (B) Leakage current curve of the device charged at 2 mA to the potential of 1 V and kept for nearly 3 hours.

Reference	Freestanding	N Content [a]	S_{BET} (m^2/g)	Capacitance (F/g)	Rate capability (F/g)	Cycling stability
1	No	3.3 wt.% [b]	1463	363 at 0.1 A/g	182 at 20 A/g	97% at 1 A/g after 5000
2	No	10 wt.% [b]	1330	211 at 1 A/g	200 at 20 A/g	--
3	No	--	1626	354 at 0.2 A/g	160 at 10 A/g	85% at 5 A/g after 10,000
4	No	15 wt.% [b]	1741	230 at 0.5 A/g	175 at 20 A/g	--
5	No	6.02 wt.% [b]	753	260 at 1 A/g	215 at 4 A/g	100% at 1 A/g after 1000
6	No	1.6 wt.%	2118	408 at 1 mV/s	251at 200 mV/s	99% at 10 A/g after 6000
7	No	2.2 wt.% [b]	1080	238 at 100 mV/s	238 at 400 mV/s	99% at 100 mV/s after 3000
8	No	--	400	208 at 0.02A/g	--	--
9	No	--	2633	257 at 0.5 A/g	184 at 100 A/g	--
10	No	3.8 at.%	1184	388 at 1 A/g	232 at 100 A/g	98% at 10 A/g after 8000
11	No	--	1466	314 at 0.5 A/g	254 at 1 A/g	94% at 10 A/g after 10,000
12	No	--	677	234 at 5 mV/s	193 at 200 mV/s	--
13	No	7.34 wt.% [b]	--	197 at 0.5 A/g	138 at 40 A/g	98% at 0.5 A/g after 5000
14	No	0.88 at.%	3012	385 at 0.05 A/g	235 at 50 A/g	94% at 0.45 A/g after 2500
15	No	2.85 at.%	2725	342 at 0.2 A/g	212 at 20 A/g	98% at 10 A/g after 1000
16	No	2.35 at.%	2397	365 at 0.5 A/g	289 at 20 A/g	99% at 1 A/g after 10,000
17	No	8.2 at.%	701	197 at 0.2 A/g	143 at 20 A/g	99% at 5 A/g after 1000
18	No	12.7 wt.% [b]	393	167 at 0.05 A/g	126 at 5 A/g	--
19	No	4 at.%	445	184 at 0.05 A/g	172 at 2A/g	--
20	No	--	1014	217 at 0.5 A/g	88 at 40 A/g	--
This Work	Yes	8.96 at.%	410	335 at 0.5 A/g	175 at 32 A/g	--

[a] Based on XPS unless noted;
[b] Based on Element analysis.

Table S1. Comparison of the electrochemical performance of the reported nitrogen-doped porousbased electrodes and the similar works in three-electrode configuration test.

Reference	Flexibility	N content [a]	S_{BET} (m^2/g)	Capacitance (F/g) [c]	Rate capability (F/g)	Cycling stability
9	No	--	2633	240 at 0.5 A/g	130 At 100 A/g	98% at 1 A/g after 2000
21	No	2.2 at.%	1646	300 at 0.1 A/g	228 at 8 A/g	90% at 1 A/g after 1000
22	No	3.3 at.%	553	239 at 5 mV/s	166 at 100 mV/s	100% at 50 mV/s after 10,000
23	No	--	2972	251 at 0.25 A/g	204 at 50 A/g	100% at 5 A/g after 2000
24	No	--	1533	280 at 1 A/g	203 at 8 A/g	99% at 1 A/g after 5000
25	No	--	1705	237 at 0.1 A/g	178 at 50 A/g	92% at 1 A/g after 20,000
26	No	4.7 wt.% [b]	2494	242 at 0.1 A/g [d]	155 at 10 A/g	92% at 2 A/g after 10,000
27	No	2.8 at.%	4279	271 at 0.1 A/g	228 at 5 A/g	96% at 0.1 A/g after 10,000
28	No	--	2340	280 at 0.1 A/g	207 at 10 A/g	100% at 10 A/g after 10,000
29	No	2.6 wt.% [b]	1420	187 at 1 mV/s	167 at 20 mV/s	98% at 0.5 A/g after 3000
30	Yes	3.62 at.% [b]	804	215 at 0.2 A/g	113 at 100 A/g	92% at 1 A/g after 1000
This Work	Yes	8.96 at.%	410	260 at 0.5 A/g [e]	98 at 8 A/g	86% at 5 A/g after 10,000

[a] Based on XPS unless noted;
[b] Based on Element analysis;
[c] Tested in aqueous electrolyte unless noted;
[d] Tested in ion liquid or organic electrolyte;
[e] Tested in solid-state electrolyte.

Table S2. Comparison of the electrochemical performance of the reported nitrogen-doped porousbased electrodes and the similar works in two-electrode configuration test.

Notes and Reference

1 M. Zhou, F. Pu, Z. Wang, S.Y. Guan, Carbon, 2014, 68, 185-194.

2 W.R. Li, D.H. Chen, Z. Li, Y.F. Shi, Y. Wan, J.J. Huang, J.J. Yang, D.Y. Zhao, Z.Y. Jiang, Electrochem. Commun.,2007, 9, 569-573.

3 J.L. Zhang, G.L. Chen, Q. Zhang, F. Kang, B. You, ACS Appl. Mater.Interf.,2015,7,12760-12766.

4 Q. Shi, R.Y. Zhang, Y.Y. Lv, Y.H. Deng, A.A. Elzatahry, D.Y. Zhao, Carbon,2015,84,335-346.

5 F.W. Ma, H. Zhao, L.P. Sun, Q. Li, L.H. Huo, T. Xia, S. Gao, G.S. Pang, Z. Shi, S.H. Feng, J. Mater. Chem.,2012,22, 13464-13468.

6 S.P. Wang, J.N. Zhang, P. Shang, Y.Y. Li, Z.M. Chen, Q. Xu, Chem. Commoun.,2014, 50,12091-12094.

7 F.B. Su, C.K. Poh, J.S. Chen, G.W. Xu, D. Wang, Q.Li, J.Y. Lin, X.W. Lou, Energy Environ. Sci., 2011, 4, 717-724.

8D. Hulicova, M. Kodama, H. Hatori, Chem. Mater.,2006,18, 2318-2326.

9 X.Y. Zheng, W. Lv, Y. Tao, J.J. Shao, C. Zhang, D.H. Liu, J.Y. Luo, D.W. Wang, Q.H. Yang, Chem. Mater.,2014, 26, 6896-6903.

10 N.P. Wickramaratne, J.T. Xu, M. Wang, L. Zhu, L.M. Dai, M. Jaroniec, Chem.

Mater.,2014,26, 2820-2828.

11X.Y. Chen, Y.Y. He, H. Song, Z.J. Zhang, Carbon, 2014, 72, 410-420.

12S.M. Li, S.Y. Yang, Y.S. Wang, H.P. Tsai, H.W. Tien, S.T. Hsiao, W.H. Liao, C.L. Chang, C.C.M. Ma, C.C. Hu, J. Power Sources,2015,27, 8218-229.

13 K. Wang, L.W. Li, T.Z. Zhang, Z.F. Liu, Energy,2014,70, 612-617.

14 B. Xu, S.S. Hou, G.P. Cao, F. Wu, Y.S. Yang, J. Mater. Chem.,2012, 22,19088-19093.

15 Q.H. Liang, L. Ye, Z.H. Huang, Q. Xu, Y. Bai, F.Y. Kang, Q.H. Yang, Nanoscale,2014, 6, 13831-13837.

16J. Tan, H.B. Chen, Y. Gao, H.M. Li, Electrochim. Acta,2015,178,144-152.

17 Q. Xu, X.L. Yu, Q.H. Liang, Y. Bai, Z.H. Huang, F.Y. Kang, J. Electroanal. Chem.,2015, 739, 84-88.

18 G. lota, K. Lota, E. Frackowiak, Electrochem.Commun.,2007, 9, 1828-1832.

19 C.L. Wang, Y. Zhou, L. Sun, P. Wan, Z. Zhang, J.S. Qiu, J. Power Sources,2013, 239, 81-88.

20 W.F. Zhang, Z.H. Huang, G.P. Cao, F.Y. Kang, Y.S. Yang, J. Power Sources,2012, 204, 230-235.

21 X.M. Fan, C.Yu, J. Yang, Z. Ling, J.S. Qiu, Carbon,2014, 70, 130-141.

22 J.W. Jeon, R. Sharma, P. Meduri, B.W. Arey, H.T. Schaef, J.L. Lutkenhaus, J.P. Lemmon, P.K. Thallapally, M.I. Nandasiri, B.P. McGrail, S.K. Nune, ACS Appl. Mater. Interf.,2014,6, 7214-7222.

23 A.J. Amali, J.K. Sun, Q. Xu, Chem. Commun.,2014, 50, 1519-1522.

24 J.L. Huang, J.Y. Wang, C.W. Wang, H.N. Zhang, C.X. Lu, J.Z. Wang, Chem. Mater.,2015, 27, 2107-2113.

25 Y.Y. Yao, C. Ma, J.T. Wang, W.M. Qiao, L.C. Ling, D.H. Long, ACS Appl. Mater.Interf.,2015, 7, 4817-4825.

26 J.H. Hou, C.B. Cao, F. Idrees, X.L. Ma, ACS Nano,2015,9,2556-2564.

27 X.C. Liu, S.M. Li, R. Mi, J. Mei, L.M. Liu, L.J. Cao, W.M. Lau, H. Liu, Appl. Energy,2015,153,32-40.

28 C.W. Wang, M.J. O'Connell, C.K. Chan, ACS Appl. Mater. Interf.,2015,7, 8952-

8960.

29 E. Frackowiak, G. Lota, J. Machnikowski, C.V. Guterl, F. Beguin, Electrochim. Acta,2006,51, 2209-2214.

30T.H. Le, Y. Yang, Z.H. Huang, F.Y. Kang, J. Power Sources,2015, 278,683-692.