Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Please note – this document replaces the version originally published on 7th November 2016.

Supporting information

Biomass-derived Interconnected Carbon Nanoring Electrochemical Capacitors with High Performance in both Strongly Acidic and Alkaline Electrolytes

Xianjun Wei,*[a] Yongbin Li, Shuyan Gao*[a]

[a] Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions (Ministry of Education), School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China.

Mechanism of KOH activation

It is worth noting that KOH as the activator plays a critical role in constructing porous structure and increasing surface area for TDICN. In general, there are two main activation mechanisms, physical and chemical activations. In chemical activation over 400 ^oC, the reaction between carbon materials and KOH occurs (equ. (s1)).[2, 3] When the temperature is higher than 700 ^oC, the as-formed K_2CO_3 (equ. (s1)) transforms into CO_2 and K_2O (equ. (s2)),[3] and the latter can be further reduced by carbon to form metallic K (equ. (s3)).[4, 5] In addition, K can diffuse into the graphite layers and then expands the lattice (equ. (s1) and equ. (s3)).[6, 7] After removing these intercalated materials by hydrochloric acid washing, the expanded carbon lattices are no longer restored, therefore reasonably generating pores. The physical activation can also facilitate the pore opening through gasification of biomass carbon (equ. (s4)), [8, 9] e.g., the escape of CO_2 (equ. (s2)) and CO (equ. (s2) and equ. (s_4)) gas from the biomass carbon transforms some micropores into mesopores. However, the activation mechanisms are dependent not only on the activation temperature, but also on the mass of KOH. At low mass of KOH, the number of KOH is inadequate to cover and etch the carbon, that is to say, the activation will be very weak. [10] If KOH is excessive, it would promote gasification reaction and then destroy the carbon framework (equ. (s5) and equ. (s6)). In the presence of KOH with optimal mass, the intermediate products H_2O (equ. (s5)) and K_2O (equ. (s5)) react with carbon (equ. (s6) and equ. (s3)), resulting in development of porous structure inside the carbon framework.[11, 12]

$$6\ KOH + 2\,C \rightarrow 2\,K + 3\,H_2 + 2\,K_2CO_3 \tag{s1}$$

$$K_2CO_3 \rightarrow CO_2 + K_2O \tag{s2}$$

$$C + K_2O \rightarrow 2\,K + CO \tag{s3}$$

$$CO_2 + C \rightarrow 2\,CO \tag{s4}$$

$$2\,KOH \rightarrow K_2O + H_2O \tag{s5}$$

$$H_2O + C \rightarrow CO + H_2 \tag{s6}$$

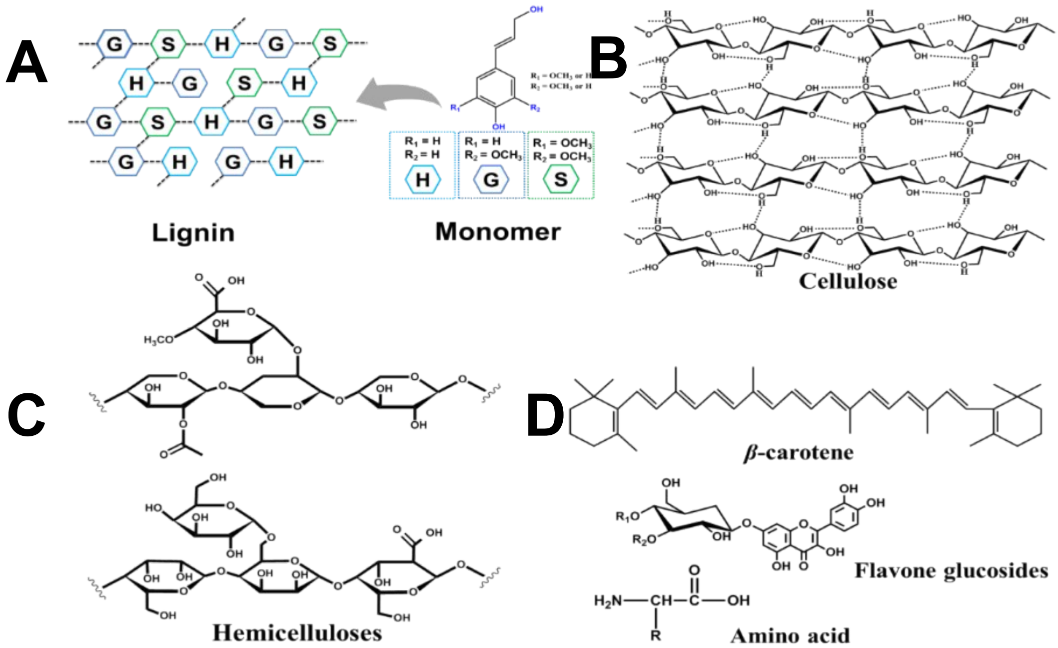

Figure S1. Chemical structure of constituents about sweet potato stem and leaf.

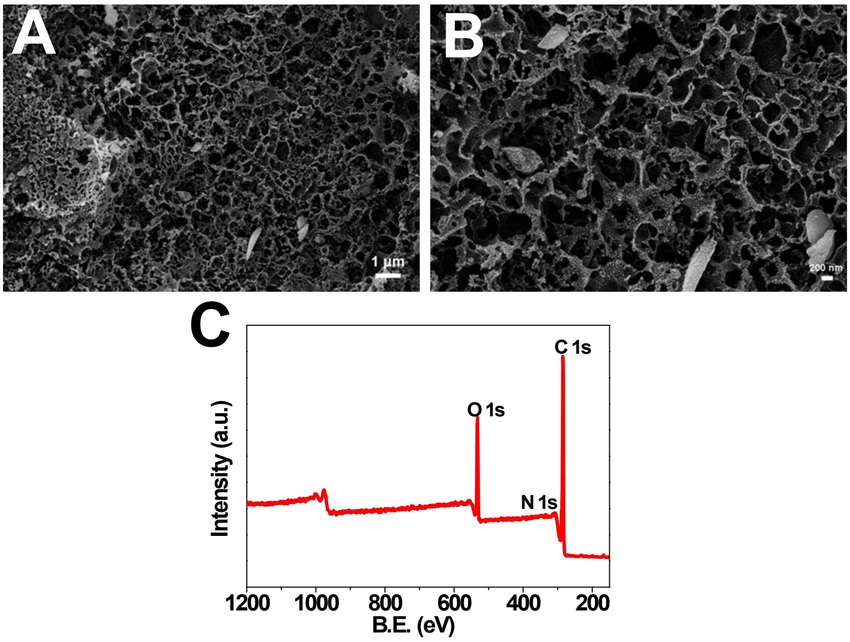

Figure S2. FESEM images (A and B) and the XPS survey spectrum (C) of TDICN.

Table S1. Comparison of the properties of carbon materials synthesized from waste and their use in supercapacitors.

Biomass precursor	*SSA* [a] ($m^2\ g^{-1}$)	*P* [b] ($W\ kg^{-1}$)	*E* [c] ($W\ h\ kg^{-1}$)	*C* [d] ($F\ g^{-1}$)	Electrolyte	Reference
Sago bark	58 (M)	400	5	180 (2t)	5 mol L^{-1} KOH	1
Coffee grounds	1945.7 (M)	11 250	35.4	121 (2t)	BMIM BF_4/AN	13
Cotton	1563 (Q)			314 (3t)	6 mol L^{-1} KOH	14
Shiitake mushroom	2988 (M)	13 000	8.2	306 (3t)	6 mol L^{-1} KOH	15
Walnut shell	1072.7 (M)			117.4 (2t)	6 mol L^{-1} KOH	16
Pomelo peel	2725 (Q)	96	9.4	342 (3t)	6 mol L^{-1} KOH	17
Broussonetia papyrifera	1212 (M)			320 (3t)	6 mol L^{-1} KOH	18
Willow catkins	645 (M)			340 (3t)	6 mol L^{-1} KOH	19
Corncob residues	1210 (M)	8 276	6.8	314 (3t)	6 mol L^{-1} KOH	20
Paulownia flower	224.8 (M)	3 781	44.5	297 (2t)	1 mol L^{-1} H_2SO_4	21
Big bluestem	2490 (M)			283 (2t)	6 mol L^{-1} KOH	22
Rice husk	1442 (M)		8.36	243 (2t)	6 mol L^{-1} KOH	23
Soybean	580 (Q)			426 (3t)	6 mol L^{-1} KOH	24
Sugar cane bagasse	1788 (Q)	10 000	10	300 (3t)	1 mol L^{-1} H_2SO_4	25
Argan seed shells	2132 (Q)			325 (3t)	1 mol L^{-1} H_2SO_4	26
Celtuce leaves	3239 (M)			421 (3t)	2 mol L^{-1} KOH	27

Cassava peel	1352 (Q)			153 (3t)	0.5 mol L^{-1} H_2SO_4	28
Waste news paper	416 (M)			180 (2t)	6 mol L^{-1} KOH	29
Waste coffee beans	1019 (Q)	6 000	20	368 (3t)	1 mol L^{-1} H_2SO_4	30
Seaweeds	746 (Q)		19.5	264 (3t)	1 mol L^{-1} H_2SO_4	31
Auricularia	80 (Q)		8.9	196 (2t)	2 mol L^{-1} KOH	32
Seaweed biopolymer	273 (Q)	10 000	10	198 (3t)	1 mol L^{-1} H_2SO_4	33
Cotton stalk	1481 (M)			114 (2t)	1 mol L^{-1} Et_4NBF_4	34
Bamboo	1251 (M)			268 (2t)	30 wt% H_2SO_4	35
Sunflower seed shell	2509 (M)	2 400	4.8	311 (3t)	30 wt% KOH	36
Corn grains	3199 (M)			257 (3t)	6 mol L^{-1} KOH	37
Seaweed, undaria pinnatifida	3270 (M Ar)	390	42	210 (2t)	1 mol L^{-1} TEA BF_4/AN	38
Ginkgo shells	1775 (Q)			178 (3t)	6 mol L^{-1} KOH	39
Fallen leaves	1078 (Q)	1 080	33.9	310 (3t)	6 mol L^{-1} KOH	40
Coconut shells	2440 (Q)	4 500	7.6	246 (2t)	0.5 mol L^{-1} H_2SO_4	41
Horseweed	1469 (Q)			184.2 (2t)	6 mol L^{-1} KOH	42
Wood sawdust	2294 (Q)	250	7.8	225 (2t)	6 mol L^{-1} KOH	43
Auricularia	1607 (Q)	213	22	347 (3t)	6 mol L^{-1} KOH	44
Elm samara	1947 (Q)	20 000	22.2	310 (2t)	6 mol L^{-1} KOH	45
TDICN	3114.7	6 534	12.9	532.5 (3t)	1 mol L^{-1}	This work

	(M Ar)				H_2SO_4	
TDICN	3114.7(M Ar)	6 459	12.3	350 (3t)	6 mol L^{-1} KOH	This work
TDICN	3114.7 (M Ar)	6 534	12.9	371.9 (2t)	1 mol L^{-1} H_2SO_4	This work
TDICN	3114.7(M Ar)	6 459	12.3	354.3 (2t)	6 mol L^{-1} KOH	This work

[a] BET surface area, [b] Power density, [c] Energy density, [d] Gravimetric capacitance, 2t/3t refers to a two-electrode/three-electrode system test. M refers to N_2 adsorption measurement was performed on micromeritics instrument, Q refers to N_2 adsorption measurement was performed on quantachrome instrument. M Ar refers to Ar adsorption measurement was performed on micromeritics instrument.

Notes and references

1 G. Hegde, S. A. A. Manaf, A. Kumar, G. A. M. Ali, K. F. Chong, Z. Ngaini and K. V. Sharma, *ACS Sustainable Chem. Eng*., 2015, **3**, 2247–2253.
2 T. Otowa, R. Tanibata and M. Itoh, *Gas Sep. Purif*., 1993, **7**, 241-245.
3 D. Lozano-Castelló, J. M. Calo, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 2007, **45**, 2529-2536.
4 J. Gañan, C. M. González-Garcı́a, J. F. González, E. Sabio, A. Macı́as-Garcı́a and M. A. Dı́az-Dı́ez, *Appl. Surf. Sci*., 2004, **238**, 347–354.
5 Y. Sudaryanto, S. B. Hartono, W. Irawaty, H. Hindarso and S. Ismadji, *Bioresour. Technol.*, 2006, **97**, 734–739.
6 A. Ahmadpour and D. D. Do, *Carbon*, 1997, **35**, 1723–1732.
7 E. Raymundo-Piñero, K. Kierzek, J. Machnikowski and F. Béguin, *Carbon*, 2006, **44**, 2498–2507.
8 J. Wang and S. Kaskel, *J. Mater. Chem*., 2012, **22**, 23710–23725.
9 J. Romanos, M. Beckner, T. Rash, L. Firlej, B. Kuchta, P. Yu, G. Suppes, C. Wexler and P. Pfeifer, *Nanotechnology*, 2012, **23**, 015401-015407.
10 F.-C. Wu, R.-L. Tseng and R.-S. Juang, *Sep. Purif. Technol*., 2005, **47**, 10–19.
11 D. Adinata, W. M. A. W. Daud and M. K. Aroua, *Bioresour. Technol.,* 2007, **98**, 145–149.
12 Q. Cao, K.-C. Xie, Y.-K. Lv and W.-R. Bao, *Bioresour. Technol.,* 2006, **97**, 110–115.
13 Y. S. Yun, M. H. Park, S. J. Hong, M. E. Lee, Y. W. Park and H.-J. Jin, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3684−3690.
14 K. Song, W.-L. Song and L.-Z. Fan, *J. Mater. Chem. A*, 2015, **3**, 16104-16111.
15 P. Cheng, S. Gao, P. Zang, X. Yang, Y. Bai, H. Xu, Z. Liu and Z. Lei, *Carbon*, 2015, **93**, 315–324.
16 Y. Li and X. Liu, *Mater. Chem. Phys*., 2014, **148**, 380–386.
17 Q. Liang, L. Ye, Z.-H. Huang, Q. Xu, Y. Bai, F. Kang and Q.-H. Yang, *Nanoscale*, 2014, **6**, 13831–13837.
18 T. Wei, X. Wei, Y. Gao and H. Li, *Electrochim. Acta*, 2015, **169**, 186–194.
19 K. Wang, N. Zhao, S. Lei, R. Yan, X. Tian, J. Wang, Y. Song, D. Xu, Q. Guo and L. Liu, *Electrochim. Acta*, 2015, **166**, 1–11.
20 W.-H. Qu, Y.-Y. Xu, A.-H. Lu, X.-Q. Zhang and W.-C. Li, *Bioresour. Technol.*, 2015, **189**, 285–291.
21 J. Chang, Z. Gao, X. Wang, D. Wu, F. Xu, X. Wang, Y. Guo and K. Jiang, *Electrochim. Acta*, 2015, **157**, 290–298.
22 H. Jin, X. Wang, Z. Gu, J. D. Hoefelmeyer, K. Muthukumarappana and J. Julson, *RSC Adv*. 2014, **4**, 14136–14142.
23 X. He, P. Ling, M. Yu, X. Wang, X. Zhang and M. Zheng, *Electrochim. Acta*, 2013, **105**, 635–641.
24 C. Long, L. Jiang, X. Wu, Y. Jiang, D. Yang, C. Wang, T. Wei and Z. Fan, *Carbon*, 2015, **93**, 412–420.
25 T. E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu and G. Q. Lu, *J Power Sources* 2010, **195**, 912–918.
26 A. Elmouwahidi, Z. Zapata-Benabithe, F. Carrasco-Marín and C. Moreno-Castilla, *Bioresour. Technol.*,2012, **111**, 185–190.
27 R. Wang, P. Wang, X. Yan, J. Lang, C. Peng and Q. Xue, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5800–5806.
28 A. E. Ismanto, S. Wang, F. E. Soetaredjo and S. Ismadji, *Bioresour. Technol.*, 2010, **101**, 3534–3540.
29 D. Kalpana, S. H. Cho, S. B. Lee, Y. S. Lee, R. Misra and N. G. Renganathan, *J. Power Sources*, 2009, **190**, 587–591.
30 T. E. Rufford, D. Hulicova-Jurcakova, Z. Zhu and G. Q. Lu, *Electrochem Commun*., 2008, **10**, 1594–1597.
31 E. Raymundo-Piñero, M. Cadek and F. Béguin, *Adv. Funct. Mater*., 2009, **19**, 1032–1039.
32 H. Zhu, X. Wang, F. Yang and X. Yang, *Adv. Mater*., 2011, **23**, 2745–2758.
33 E. Raymundo-Piñero, F. Leroux and F. Béguin, *Adv. Mater*., 2006, **18**, 1877–1882.
34 M. Chen, X. Kang, T. Wumaier, J. Dou, B. Gao, Y. Han, G. Xu, Z. Liu and L. Zhang, *J. Solid State Electrochem*., 2013, **17**, 1005–1012.

35 Y.-J. Kim, B.-J. Lee, H. Suezaki, T. Chino, Y. Abe, T. Yanagiura, K. C. Park and M. Endo, *Carbon*, 2006, **44**, 1592–1595.
36 X. Li, W. Xing, S. Zhuo, J. Zhou, F. Li, S.-Z. Qiao and G.-Q. Lu, *Bioresour. Technol.*, 2011, **102**, 1118–1123.
37 M. S. Balathanigaimani, W.-G. Shim, M.-J. Lee, C. Kim, J.-W. Lee and H. Moon, *Electrochem. Commun.*, 2008, **10**, 868–871.
38 D. Kang, Q. Liu, J. Gu, Y. Su, W. Zhang and D. Zhang, *Acs Nano*, 2015, **9**, 11225-11233.
39 L. Jiang, J. Yan, L. Hao, R. Xue, G. Sun and B. Yi, *Carbon*, 2013, **56**, 146-154.
40 Y.-T. Li, Y.-T. Pi, L.-M. Lu, S.-H. Xu and T.-Z. Ren, *J. Power Sources*, 2015, **299**, 519-528.
41 A. Jain, C. Xu, S. Jayaraman, R. Balasubramanian, J. Y. Lee and M. P. Srinivasan, *Microporous Mesoporous Mater.*, 2015, **218**, 55-61.
42 L. Yuan, C. Feng, C. Wang, Z. Fu, X. Yang and Y. Tang, *J Mater. Sci.*, 2016, **51**, 3880-3887.
43 Y. Huang, L. Peng, Y. Liu, G. Zhao, J. Y. Chen and G. Yu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15205-15215.
44 L. Jiang, L. Sheng, X. Chen, T. Wei and Z. Fan, *J. Mater. Chem. A*, 2016, **4**, 11388-11396.
45 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.