

Supplementary Information

Direct Carbonization of Black Liquor Powders into 3D Honeycomb-Like Porous Carbons with Tunable Disordered Degree for Sodium-Ion Battery

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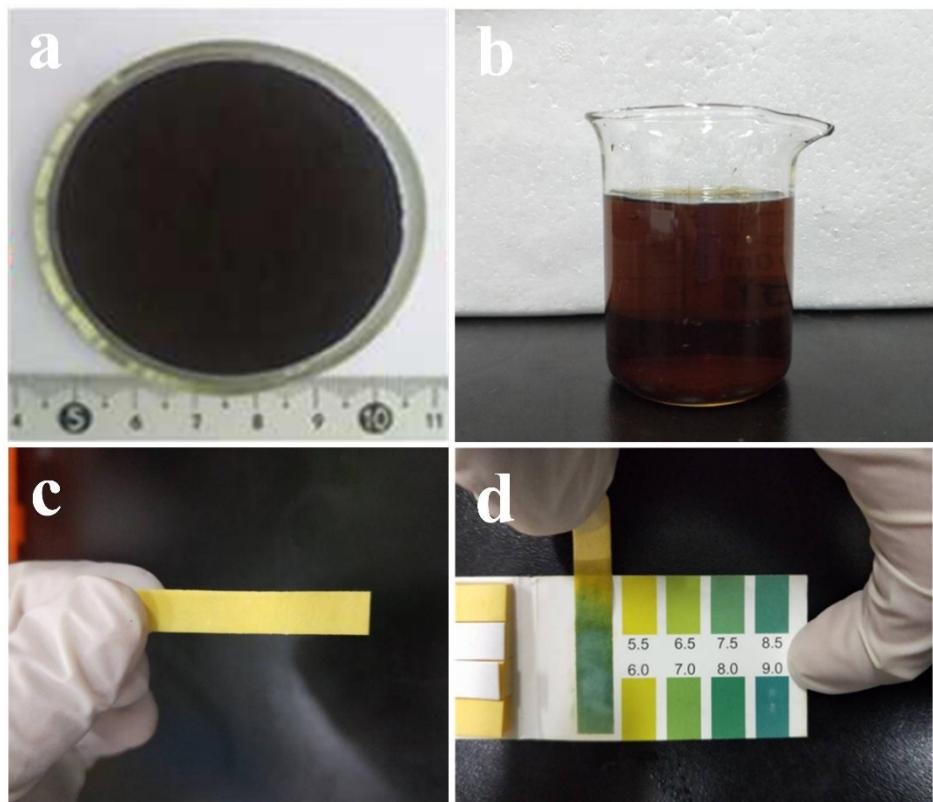


Fig. S1 Photographs of (a) the black liquid powder, (b) the black liquid aqueous solution, pH test paper without (c) and with (d) the addition of black liquid.

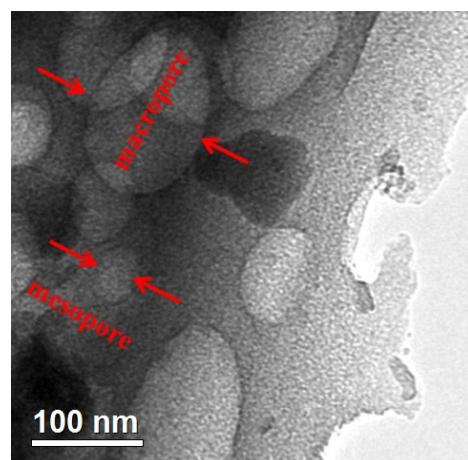


Fig. S2 TEM image of the BL-PC-1.

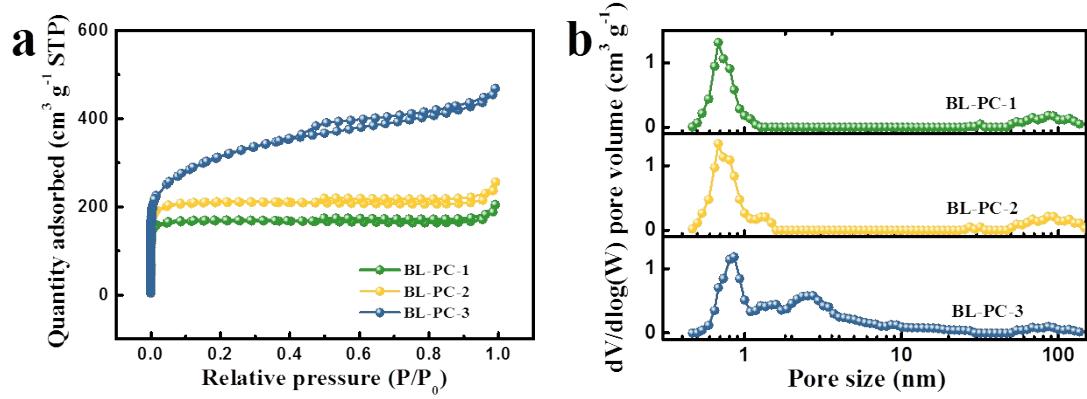


Fig. S3 (a) N₂ adsorption–desorption isotherms and (b) DFT pore size distribution curves of the typical samples.

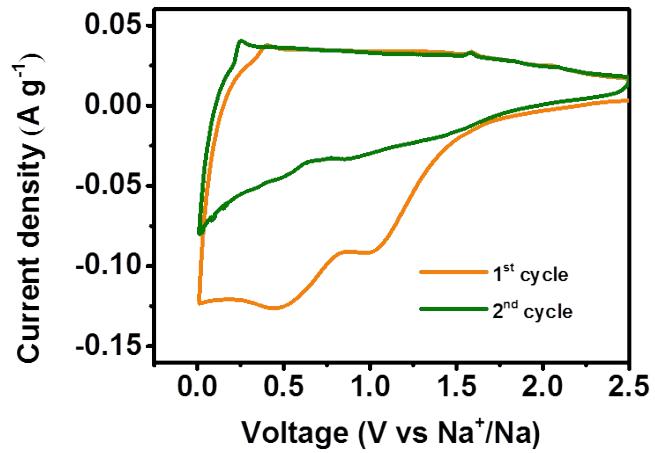


Fig. S4 CV curves of BL-PC-1 for the first two cycles for at a scan rate of 0.1mV s⁻¹.

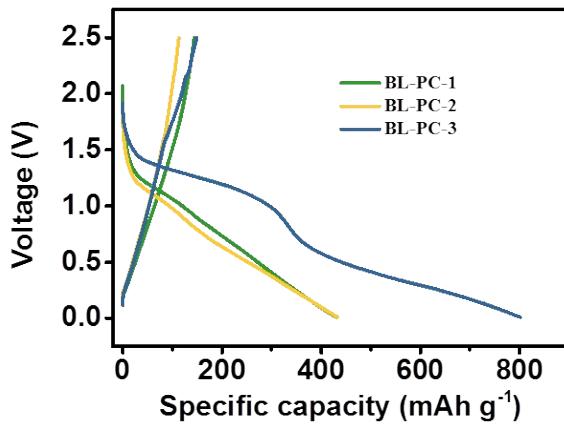


Fig. S5 Galvanostatic charge–discharge curves for the first discharge/charge profile of BL-PC-1, BL-PC-2 and BL-PC-3 at a current density of 100 mA g⁻¹.

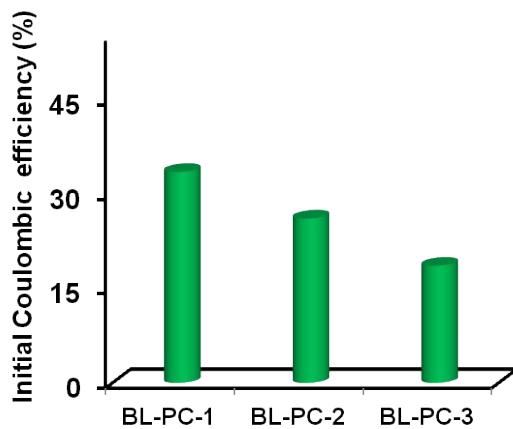


Fig. S6 The initial Coulombic efficiency for the BL-PCs.

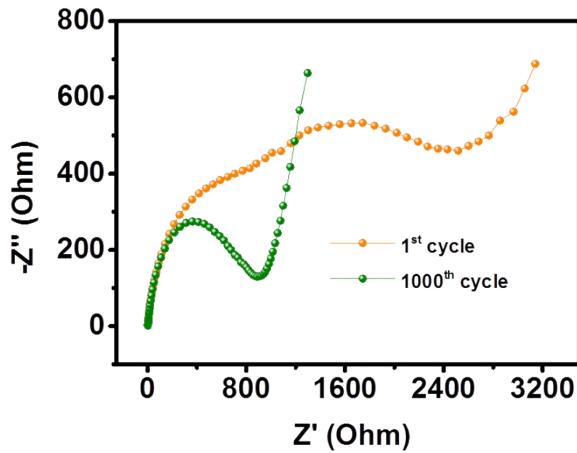


Fig. S7 Electrochemical impedance spectra of the BL-PC-1.

Table S1 Summary of BET specific surface area and total pore volume of the samples.

Samples	S_{BET} ($m^2 g^{-1}$)	V_t ($cm^3 g^{-1}$)
BL-PC-1	683	0.27
BL-PC-2	829	0.33
BL-PC-3	1146	0.72

Table S2 Electrochemical performance comparison of various anodes materials for sodium-ion batteries

Samples	Capacity (mAh g ⁻¹) at high current density	Range of current density (mA g ⁻¹)	Capacity retention (%)	Refer. number
BL-PC-1	83 (1000 mA g⁻¹)	100-1000	60	This work
Hard carbon	50 (1000 mA g ⁻¹)	50-1000	22	[1]
Porous hard carbons	75 (500 mA g ⁻¹)	40-500	28	[2]
Sugar-derived carbons	62 (1000 mA g ⁻¹)	100-1000	28	[3]
Reed straw derived hard carbon	46 (1000 mA g ⁻¹)	100-1000	22	[4]
Water caltrop shell-derived hard carbons	51 (1000 mA g ⁻¹)	100-1000	18	[5]
Hierarchically porous carbon monoliths	63 (1000 mA g ⁻¹)	100-1000	58	[6]
Mesocarbon microbeads	30 (800 mA g ⁻¹)	100-800	13	[7]
Hierarchical porous carbons	105 (1000 mA g ⁻¹)	100-1000	60	[8]
Reduced graphene oxide	96 (1000 mA g ⁻¹)	80-1000	54	[9]
Hollow carbon sphere	120 (1000 mA g ⁻¹)	200-1000	54	[10]
Hollow carbon nanowires	149 (500 mA g ⁻¹)	50-500	59	[11]
Carbon nanoparticle	78 (1000 mA g ⁻¹)	100-1000	28	[12]
Surface-carboxylated carbon nanoparticles	82 (1000 mA g ⁻¹)	100-1000	30	[12]
Carbon nanotubes	36 (1000 mA g ⁻¹)	100-1000	52	[13]
Carbon nanosheets	80 (1000 mA g ⁻¹)	100-1000	23	[14]
Microporous spherical carbon	67 (1000 mA g ⁻¹)	100-1000	51	[15]
Carbon nanofibers	75 (1000 mA g ⁻¹)	100-1000	34	[16]
Crumpled graphene paper	100 (1000 mA g ⁻¹)	100-1000	59	[17]
Hard carbon nanoparticles	72 (1250 mA g ⁻¹)	125-1250	31	[18]

Lignin-derived carbon	75 (1000 mA g ⁻¹)	100-1000	50	[3]
Oak sawdust-derived	3.5 (1000 mA g ⁻¹)	100-1000	1.9	[3]
Densified graphene	91 (1000 mA g ⁻¹)	100-1000	72	[19]
Hard carbon derived from cucumber stem	73 (1000 mA g ⁻¹)	100-1000	31	[20]
Hard carbon	52 (1000 mA g ⁻¹)	100-1000	32	[21]
Kraft lignin/ cellulose acetate derived carbon powder	50 (500 mA g ⁻¹)	50-500	29	[22]
Kraft lignin derived carbon powder	42 (500 mA g ⁻¹)	50-500	23	[22]
Cellulose acetate nanofibers	19 (500 mA g ⁻¹)	50-500	32	[22]
Hard carbon microspherules	78 (600 mA g ⁻¹)	60-600	30	[23]
Metal organic framework-derived carbons	85 (200 mA g ⁻¹)	50-200	53	[24]
Mesoporous disordered carbon	115 (1000 mA g ⁻¹)	100-1000	40	[25]
Mesoporous soft carbon	105 (1000 mA g ⁻¹)	100-1000	47	[26]
Porous Carbon/Sn composite	80 (1000 mA g ⁻¹)	100-1000	32	[27]
Sn/micron-sized disordered carbon	90 (610 mA g ⁻¹)	12-610	50	[28]
Sn thin film on conductive wood fiber	50 (170 mA g ⁻¹)	84-170	38	[29]
Trisodium 1,2,4-benzenetricarboxylate	53 (400 mA g ⁻¹)	50-400	28	[30]
paracyclophane-1,9,17,25-tetraene	70 (1000 mA g ⁻¹)	100-1000	47	[31]
Sodium Naphthalene Dicarboxylate	85 (500 mA g ⁻¹)	31-500	40	[32]

References:

- [1]. Xiao, B., et al., Lithium-Pretreated Hard Carbon as High-Performance Sodium-Ion Battery Anodes. *Advanced Energy Materials*, 2018. 8(24): p. 1801441.
- [2]. Zhang, N., et al., High capacity hard carbon derived from lotus stem as anode for sodium ion batteries. *Journal of Power Sources*, 2018. 378: p. 331-337.
- [3]. Yoon, D., et al., Carbon with Expanded and Well-Developed Graphene Planes Derived Directly from Condensed Lignin as a High-Performance Anode for Sodium-Ion Batteries. *ACS Applied Materials & Interfaces*, 2017. 10(1): p. 569-581.
- [4]. Wang, J., et al., Facile hydrothermal treatment route of reed straw-derived hard carbon for high performance sodium ion battery. *Electrochimica Acta*, 2018. 291: p. 188-196.
- [5]. Wang, P., et al., Low-cost water caltrop shell-derived hard carbons with high initial coulombic efficiency for sodium-ion battery anodes. *Journal of Alloys and Compounds*, 2019. 775: p. 1028-1035.
- [6]. Gong, J., et al., A Novel Method of Fabricating Free-Standing and Nitrogen-Doped 3D Hierarchically Porous Carbon Monoliths as Anodes for High-Performance Sodium-Ion Batteries by Supercritical CO₂ Foaming. *ACS Applied Materials & Interfaces*, 2019.
- [7]. Song, L., et al., Anode performance of mesocarbon microbeads for sodium-ion batteries. *Carbon*, 2015. 95: p. 972-977.
- [8]. Wang, H., et al., Biomass derived hierarchical porous carbons as high-performance anodes for sodium-ion batteries. *Electrochimica Acta*, 2016. 188: p. 103-110.
- [9]. Wang, Y., et al., Reduced graphene oxide with superior cycling stability and rate capability for sodium storage. *Carbon*, 2013. 57: p. 202-208.
- [10]. Tang, K., et al., Hollow Carbon Nanospheres with Superior Rate Capability for Sodium-Based Batteries. *Advanced Energy Materials*, 2012. 2(7): p. 873-877.
- [11]. Cao, Y., et al., Sodium Ion Insertion in Hollow Carbon Nanowires for Battery Applications. *Nano Letters*, 2012. 12(7): p. 3783-3787.
- [12]. Gaddam, R.R., et al., Biomass derived carbon nanoparticle as anodes for high performance sodium and lithium ion batteries. *Nano Energy*, 2016. 26: p. 346-352.
- [13]. Luo, X., et al., Graphene nanosheets, carbon nanotubes, graphite, and activated carbon as anode materials for sodium-ion batteries. *Journal of Materials Chemistry A*, 2015. 3(19): p. 10320-10326.
- [14]. Wang, H., et al., Nitrogen-Doped Porous Carbon Nanosheets as Low-Cost, High-Performance Anode Material for Sodium-Ion Batteries. *ChemSusChem*, 2013. 6(1): p. 56-60.
- [15]. Zhou, D., et al., Long cycle life microporous spherical carbon anodes for sodium-ion batteries derived from furfuryl alcohol. *JOURNAL OF MATERIALS CHEMISTRY A*, 2016. 4(17): p. 6271-6275.
- [16]. Zhao, P., et al., Electrochemical performance of fulvic acid-based electrospun hard carbon nanofibers as promising anodes for sodium-ion batteries. *Journal of Power Sources*, 2016. 334: p. 170-178.
- [17]. Yun, Y.S., et al., Crumpled graphene paper for high power sodium battery anode. *Carbon*, 2016. 99: p. 658-664.
- [18]. Xiao, L., et al., Hard carbon nanoparticles as high-capacity, high-stability anodic materials for Na-ion batteries. *Nano Energy*, 2016. 19: p. 279-288.
- [19]. Zhang, J., et al., The Interplay of Oxygen Functional Groups and Folded Texture in Densified Graphene Electrodes for Compact Sodium-Ion Capacitors. *Advanced Energy Materials*, 2018. 8(11): p. 1702395.
- [20]. Li, C., et al., Heteroatom-doped hierarchically porous carbons derived from cucumber stem as high-performance anodes for sodium-ion batteries. *Journal of Materials Science*, 2019. 54(7): p. 5641-5657.
- [21]. Liu, X., et al., High Capacity and Cycle-Stable Hard Carbon Anode for Nonflammable Sodium-Ion Batteries. *ACS Applied Materials & Interfaces*, 2018. 10(44): p. 38141-38150.
- [22]. Jia, H., et al., Electrospun Kraft Lignin/Cellulose Acetate-Derived Nanocarbon Network as an Anode for High-Performance Sodium-Ion Batteries. *ACS Applied Materials & Interfaces*, 2018. 10(51): p. 44368-44375.
- [23]. Li, Y., et al., Amorphous monodispersed hard carbon micro-spherules derived from biomass as a high performance negative electrode material for sodium-ion batteries. *Journal of Materials Chemistry A*, 2015. 3(1): p. 71-77.
- [24]. Ingersoll, N., et al., Metal organic framework-derived carbon structures for sodium-ion battery anodes. *Electrochimica Acta*, 2019. 297: p. 129-136.
- [25]. Raj K, A., et al., Bio-derived mesoporous disordered carbon: An excellent anode in sodium-ion

- battery and full-cell lab prototype. *Carbon*, 2019, 143: p. 402-412.
- [26]. Cao, B., et al., Mesoporous soft carbon as an anode material for sodium ion batteries with superior rate and cycling performance. *Journal of Materials Chemistry A*, 2016, 4(17): p. 6472-6478.
- [27]. Xu Y., et al., Electrochemical Performance of Porous Carbon/Tin Composite Anodes for Sodium-Ion and Lithium-Ion Batteries. *Adv Energy Mater*, 2013: p. 128-133.
- [28]. Bresser D., et al., Embedding tin nanoparticles in micron-sized disordered carbon for lithium- and sodium-ion anodes. *Electrochim Acta*, 2014, 128: p. 163-71.
- [29]. Zhu H., et al., Tin Anode for Sodium-Ion Batteries Using Natural Wood Fiber as a Mechanical Buffer and Electrolyte Reservoir. *Nano Lett* 2013, 13: p. 3093-3100.
- [30]. Luo C, Shea JJ, Huang J. A carboxylate group-based organic anode for sustainable and stable sodium ion batteries. *J Power Sources* 2020, 453: p. 227904.
- [31]. Eder S., et al. Switching between local and global aromaticity in a conjugated macrocycle enables high-performance organic sodium-ion battery anodes. *Angewandte Chemie International Edition*, 2020. [Doi.org/10.1002/anie.202003386](https://doi.org/10.1002/anie.202003386).
- [32]. Medabalmi V., et al., Sodium Naphthalene Dicarboxylate Anode Material for Inorganic-Organic Hybrid Rechargeable Sodium-Ion Batteries. *J Electrochem Soc*, 2018, 165: p. A175-A180.