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

Supporting Information for

Chemical-enzymatic fractionation to unlock the potential of biomass-derived carbon materials for sodium ion batteries

Yiming Feng,[£1] Lei Tao,[£2,3] Yanhong He,[1] Qing Jin,[1] Chunguang Kuai[3], Yunwu Zheng,[4] Mengqiao Li[5], Qingping Hou,[3] Zhifeng Zheng,[2,] Feng Lin,[3,]* Haibo Huang[1,]*

1. Department of Food Science and Technology, Virginia Tech, Blacksburg, Virginia 24061, United States.
2. College of Energy, Xiamen University, Xiamen, Fujian 361102, China.
3. Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States.
4. College of Materials Engineering, Southwest Forestry University, Kunming 650224, China.
5. Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052, United States

[£]The authors contributed equally to this work.

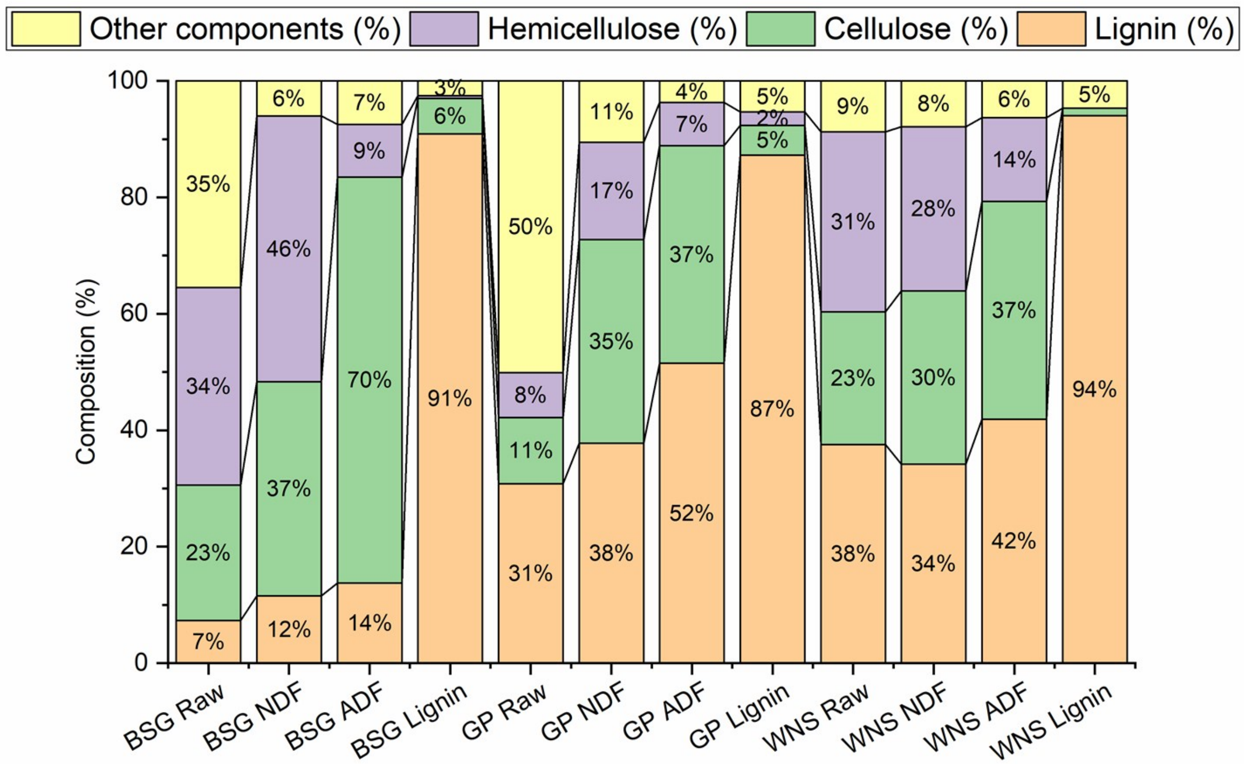

Fig. S1. Composition analysis of fractionated samples used in this work.

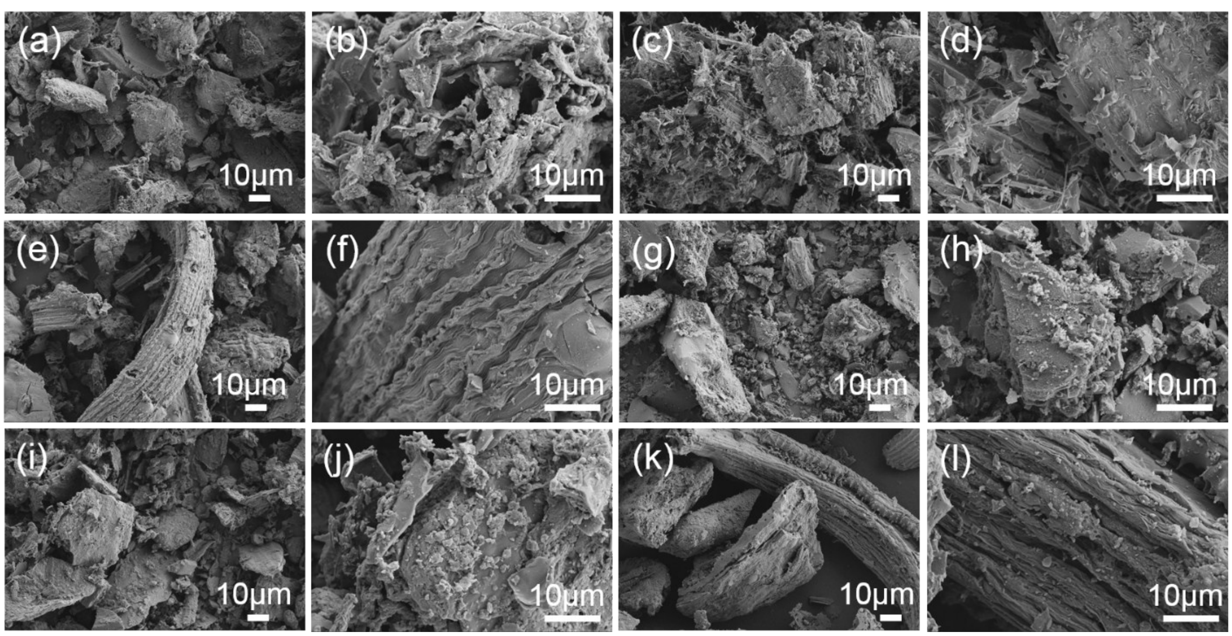

Fig S2. SEM images of carbonized BSG from different fractions and temperatures that have been studied in this work.(a, b) BSG Raw_1050C, (c, d) BSG NDF_1050C. (e, f) BSG ADF_1050C. (g, h) BSG Lignin_1050C, (i, j) BSG Raw_800C, (k, l) BSG ADF-1050C.

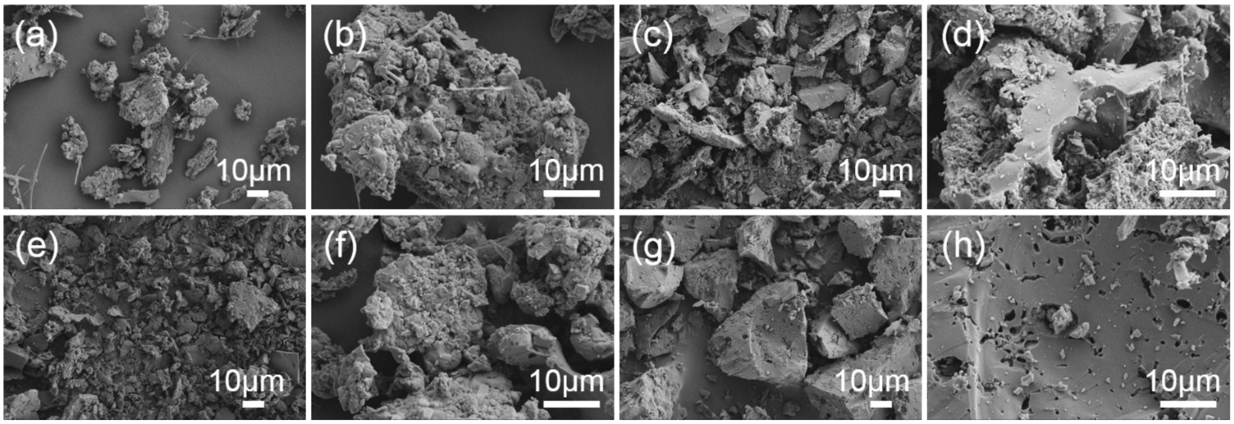

Fig. S3. SEM images of carbonized GP from different fractions and temperatures that have been studied in this work. (a, b) GP Raw_1050C, (c, d) GP ADF_1050C, (e, f) GP Raw_800C, (g, h) GP ADF_800C.

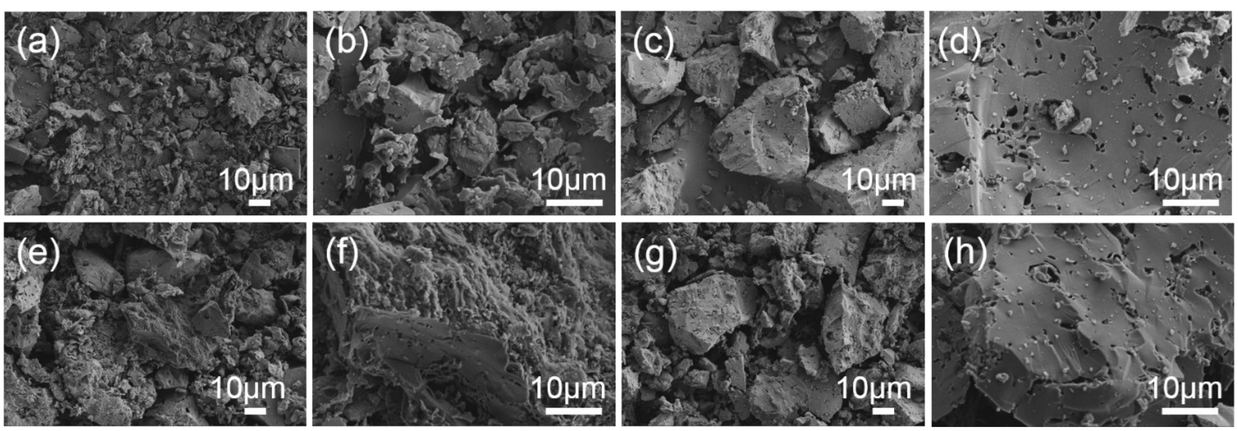

Fig. S4. SEM images of carbonized WNS from different fractions and temperatures that have been studied in this work. (a, b) WNS Raw_1050C, (c, d) WNS ADF-1050C, (e, f) WNS Raw_800C, (g, h) WNS ADF_1050C.

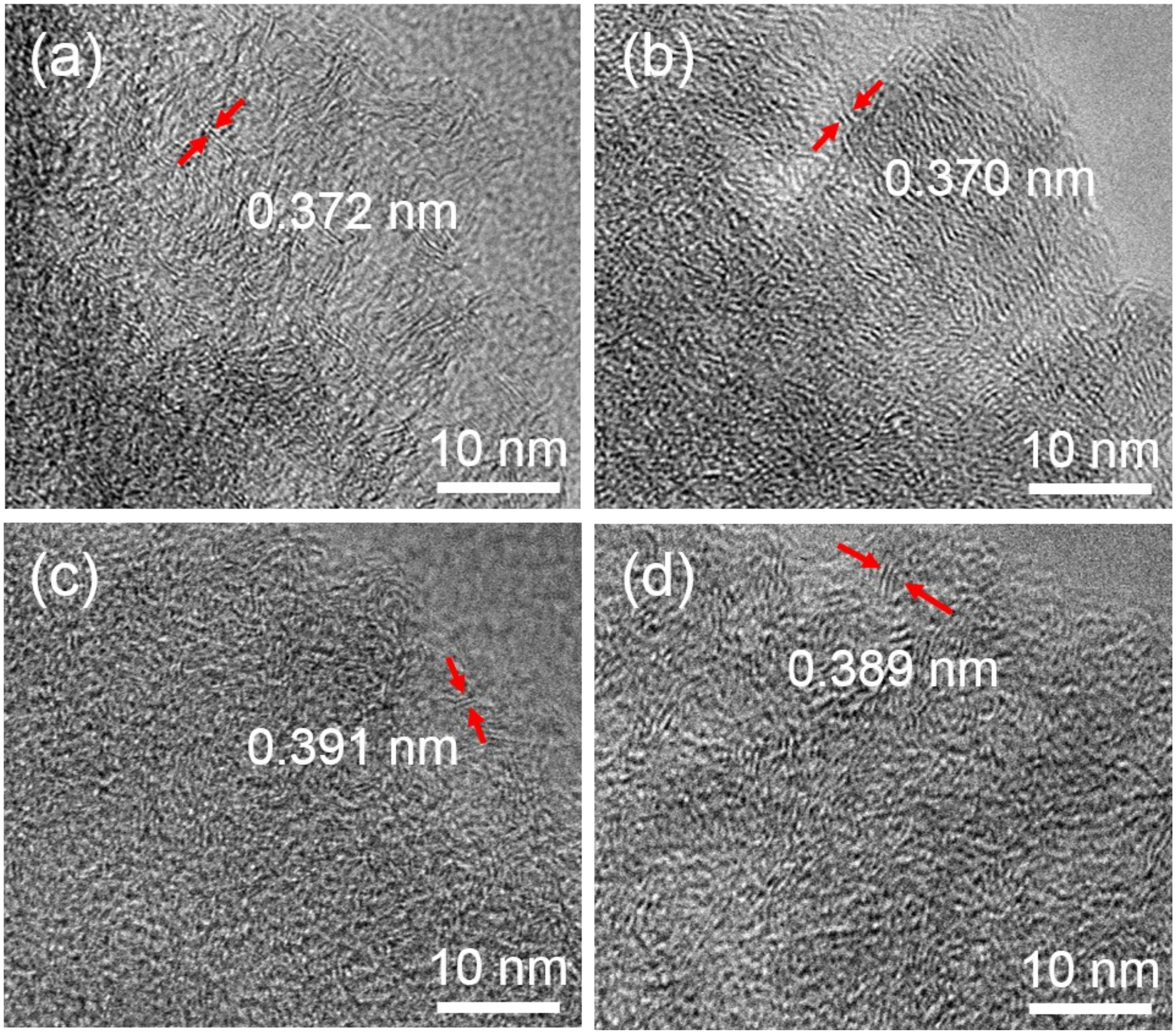

Fig. S5. HRTEM images of carbonized BSG from different fractions. (a) BSG Raw_1050C, (b) BSG NDF_1050C, (c) BSG ADF_1050C, (d) BSG Lignin_1050C.

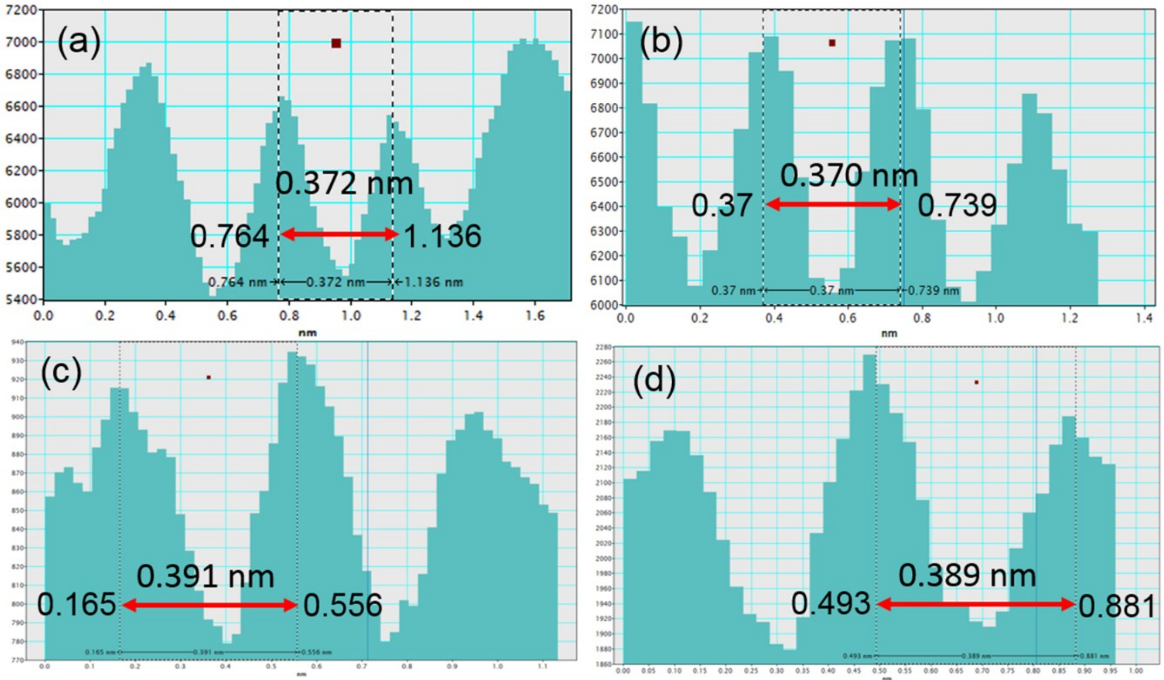

Fig. S6. d_{002} estimation of carbonized BSG from different fractions, using Fast Fourier transformation (FFT) filtered HRTEM images. (a) BSG Raw_1050C, (b) BSG NDF_1050C, (c) BSG ADF_1050C, (d) BSG Lignin_1050C

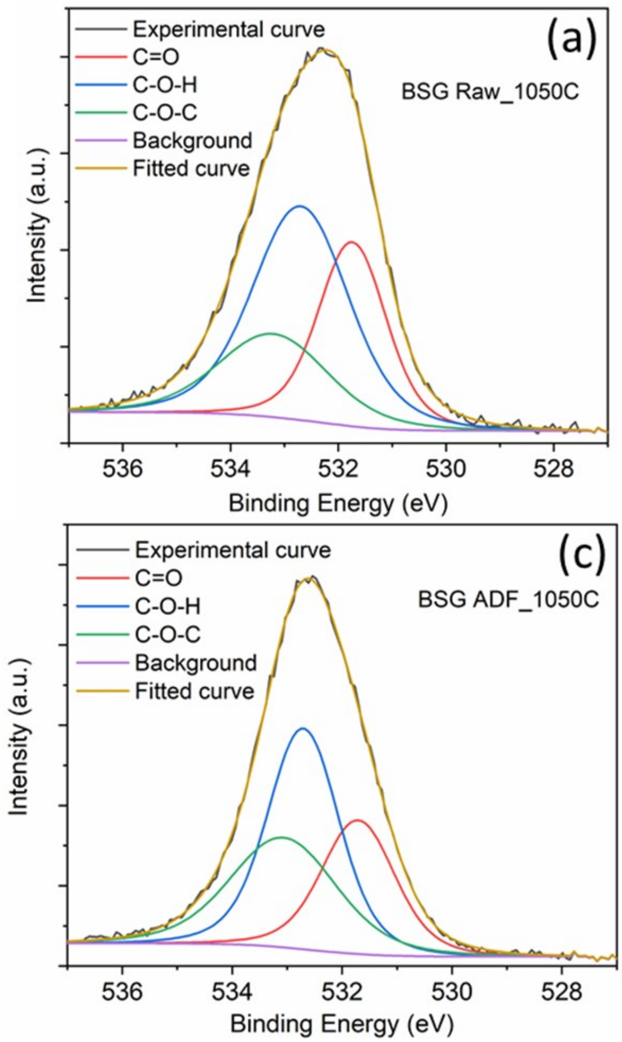

Fig. S7. XPS O1s spectrum of carbons derived from BSG. (a) BSG Raw 1050C (b) BSG NDF_1050C (c) BSG ADF_1050C (d) BSG Lignin_1050C

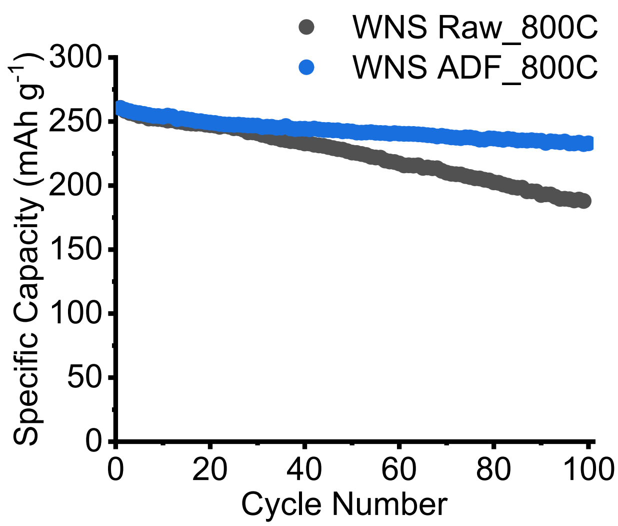

Fig. S8. Cycling performance comparison between WNS Raw_800C & WNS ADF_800C.

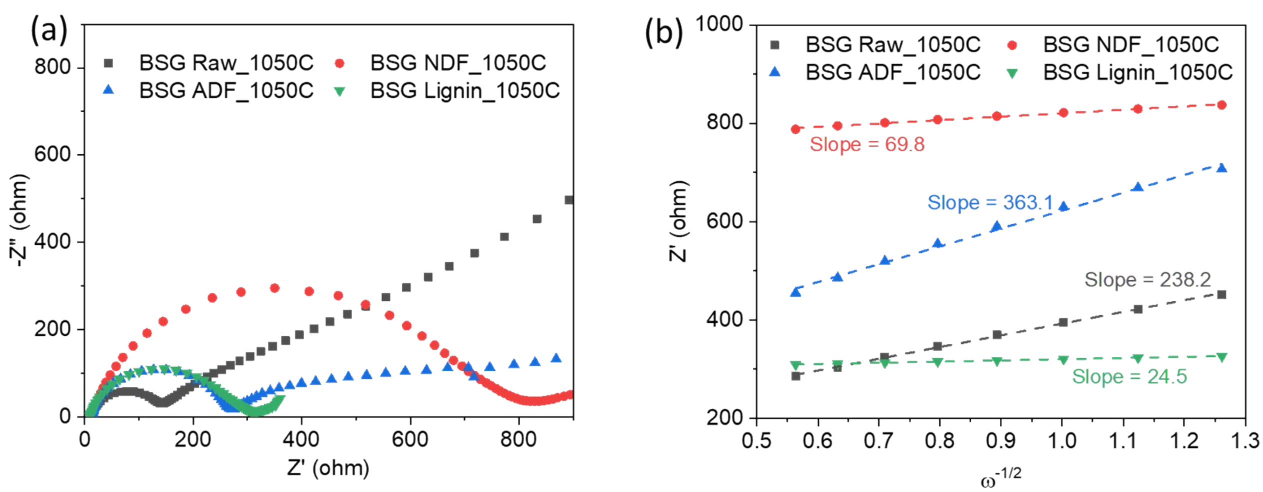

Fig. S9. (a) Electrochemical impedance spectroscopy (EIS) Nyquist plot of carbons. (b) Fitting curves for the EIS plots.

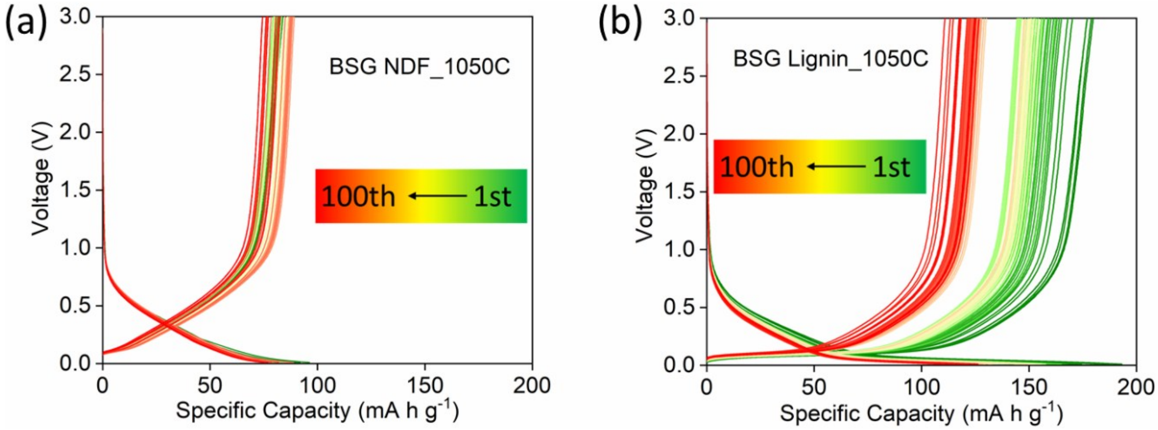

Fig. S10. Charge-discharge curves for 100 cycles of (a) BSG NDF_1050C and (b) BSG Lignin_1050C.

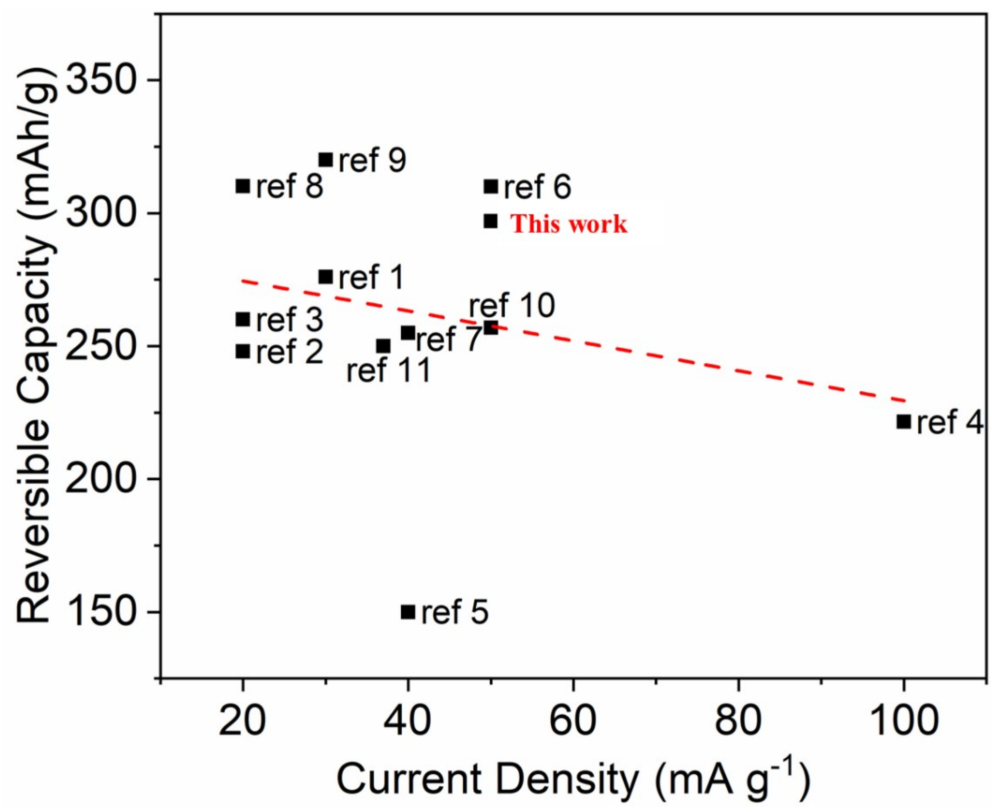

Fig. S11. Comparison of the electrochemical performance of hard carbons for sodium ion battery at different current densities.

Table S1. Comparison of d_{002} calculated from XRD and HRTEM

Sample name	d_{002} (Å) from XRD	d_{002} (Å) from HRTEM
BSG Raw_1050C	3.76	3.72
BSG NDF_1050C	3.75	3.70
BSG ADF_1050C	3.86	3.91
BSG lignin_1050C	3.84	3.89

Table S2. Surface functional group analysis based on XPS O1s spectrums

	BSG Raw_1050C	BSG NDF_1050C	BSG ADF_1050C	BSG Lignin_1050C
C=O	29.8%	31.4%	26.4%	27.3%
C-O-H	48.6%	52.9%	42.4%	42.9%
C-O-C	21.7%	15.8%	31.2%	29.9%

Table S3. Atomic ratio of carbon and oxygen

	BSG Raw_1050C	BSG NDF_1050C	BSG ADF_1050C	BSG Lignin_1050C

C%	86.1%	84.0%	85.0%	87.1%
O%	10.5%	14.0%	12.5%	11.3%

Table S4. EIS parameters of carbon materials derived from different fractions of BSG

	R_s (Ω)	**R_{ct} (Ω)**	**σ_ω(Ω s^{-1})**
BSG Raw_1050C	10.5	144.1	239.2
BSG NDF_1050C	11.6	739.2	69.8
BSG ADF_1050C	12.7	246.8	363.1
BSG Lignin_1050C	9.9	285.9	24.5

Table S5. Sodium diffusivity calculated using Randles Sevcik equation.

Sample	Na^+ diffusivity (cm^2/s)
BSG Raw_1050C	2.47×10^{-10}
BSG NDF_1050C	1.52×10^{-09}
BSG ADF_1050C	8.40×10^{-09}
BSG Lignin_1050C	2.47×10^{-09}

Table S6. Comparison of the electrochemical performance.

Biomass precursor	Reversible capacity	Current density	Plateau capacity	Initial Coulombic efficiency	Cycling performance	ref
Rice husk	276 mAh/g	30 mA/g	54%	50%	93% after 100 cycles	1
Apple	248 mAh/g	20 mA/g	~ 40%	63%	81% after 100 cycles	2
Almond Shell	260 mAh/g	20 mA/g	50%	80%	N/A	3
Pine Pollen	221.5 mAh/g	100 mA/g	~20%	59.8%	91.6% after 200 cycles	4
pistachio shell	150 mAh/g	40 mA/g	50%	74.9%	86.3% after 50 cycles	5
Corn straw pitch	310 mAh/g	50 mA/g	60%	~60%	79% after 700 cycles	6
bleached pulp	255 mAh/g	40 mA/g	~50%	~70%	69% after 600 cycles	7
cherry petals	310.2 mAh/g	20 mA/g	~45%	67.3%	42.4% after 500 cycles	8
loofah sponge	320 mAh/g	30 mA/g	~55%	63%	93% after 100 cycles	9
Walnut shell	257 mAh/g	50 mA/g	60%	N/A	70% after 300 cycles	10
Cellulose	250 mAh/g	37 mA/g	66%	84%	N/A	11
Walnut shell	297 mAh/g	50 mA/g	60%	73.7%	86.4% after 200 cycles	This work

Table S7. Yield of carbon products

Sample	Yield	Sample	Yield
BSG Raw_1050C	18.80%	WNS NDF_1050C	28.40%
BSG NDF_1050C	22.60%	WNS ADF_1050C	26.40%
BSG ADF_1050C	27.80%	WNS lignin_1050C	48.10%
BSG lignin_1050C	46.40%	BSG Raw_800C	28.90%
GP Raw_1050C	29.20%	BSG ADF_800C	30%
GP NDF_1050C	26.80%	GP Raw_800C	32%
GP ADF_1050C	30.20%	GP ADF_800C	30.60%
GP lignin_1050C	36.70%	WNS Raw_800C	28%
WNS Raw_1050C	28.00%	WNS ADF_800C	26%

References used in the supplementary materials

1 M. K. Rybarczyk, Y. Li, M. Qiao, Y. S. Hu, M. M. Titirici and M. Lieder, *J. Energy Chem.*, 2018, **29**, 17–22.

2 L. Wu, D. Buchholz, C. Vaalma, G. A. Giffin and S. Passerini, *ChemElectroChem*, 2016, **3**, 292–298.

3 C. Marino, J. Cabanero, M. Povia and C. Villevieille, *J. Electrochem. Soc.*, 2018, **165**, A1400–A1408.

4 Y. Zhang, X. Li, P. Dong, G. Wu, J. Xiao, X. Zeng, Y. Zhang and X. Sun, *ACS Appl. Mater. Interfaces*, 2018, **10**, 42796–42803.

5 K. Kim, D. G. Lim, C. W. Han, S. Osswald, V. Ortalan, J. P. Youngblood and V. G. Pol, *ACS Sustain. Chem. Eng.*, 2017, **5**, 8720–8728.

6 Y. E. Zhu, H. Gu, Y. N. Chen, D. Yang, J. Wei and Z. Zhou, *Ionics (Kiel).*, 2018, **24**, 1075–1081.

7 W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen and X. Ji, *J. Mater. Chem. A*, 2013, **1**, 10662–10666.

8 Z. Zhu, F. Liang, Z. Zhou, X. Zeng, D. Wang, P. Dong, J. Zhao, S. Sun, Y. Zhang and X. Li, *J. Mater. Chem. A*, 2018, **6**, 1513–1522.

9 Y. E. Zhu, L. Yang, X. Zhou, F. Li, J. Wei and Z. Zhou, *J. Mater. Chem. A*, 2017, **5**, 9528–9532.

10 M. Wahid, Y. Gawli, D. Puthusseri, A. Kumar, M. V. Shelke and S. Ogale, *ACS Omega*, 2017, **2**, 3601–3609.

11 V. Simone, A. Boulineau, A. de Geyer, D. Rouchon, L. Simonin and S. Martinet, *J. Energy Chem.*, 2016, **25**, 761–768.