Energy Materials

Supplementary Materials

Cross-linked coal-derived hard carbon with expanded interlayers and nanopores for high-plateau sodium storage

Cuiying Lu[1], Qianggong Dong[1], ChangXiang Guo[1], Zhen Wang[1], Yunqi Feng[1], Guangfeng Hu[1], Ting Su[1], Huarui Hao[1], Xingbin Yan[2], Bingjun Yang[3], Dong Cao[1]

[1]Shaanxi Key Laboratory of Low Metamorphic Coal Clean Utilization, School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, Shaanxi, China.

[2]School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, Guangdong, China.

[3]Key Laboratory of Energy Conservation and Energy Storage Materials of Gansu Province, Research Center for Resource Chemistry and Energy Materials, State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China.

[*]**Correspondence to:** Dr. ChangXiang Guo, Dr. Dong Cao, Shaanxi Key Laboratory of Low Metamorphic Coal Clean Utilization, School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, Shaanxi, China. E-mail: guo.cx168@yulinu.edu.cn; caodbit@yulinu.edu.cn

Supporting Figures

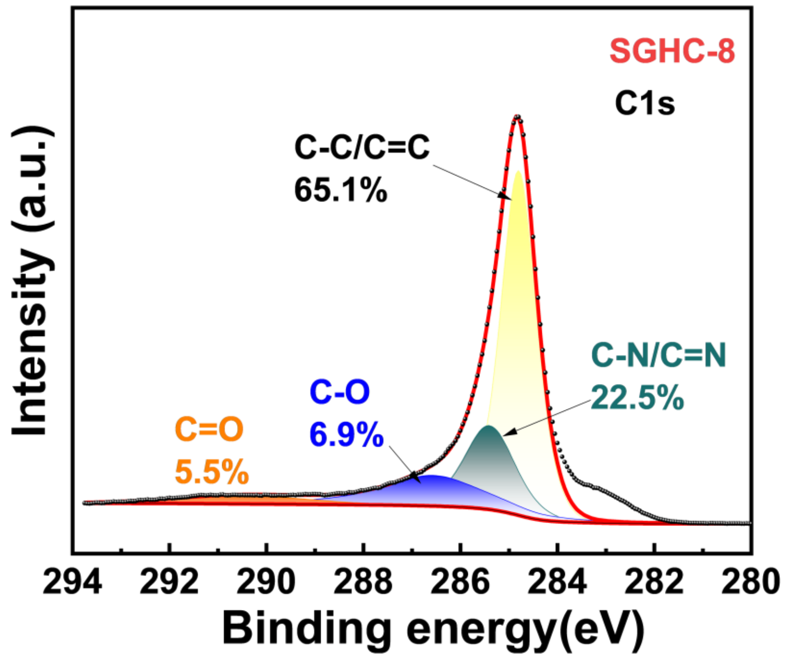

Figure S1. High-resolution C 1s XPS spectrum of SGHC-8.

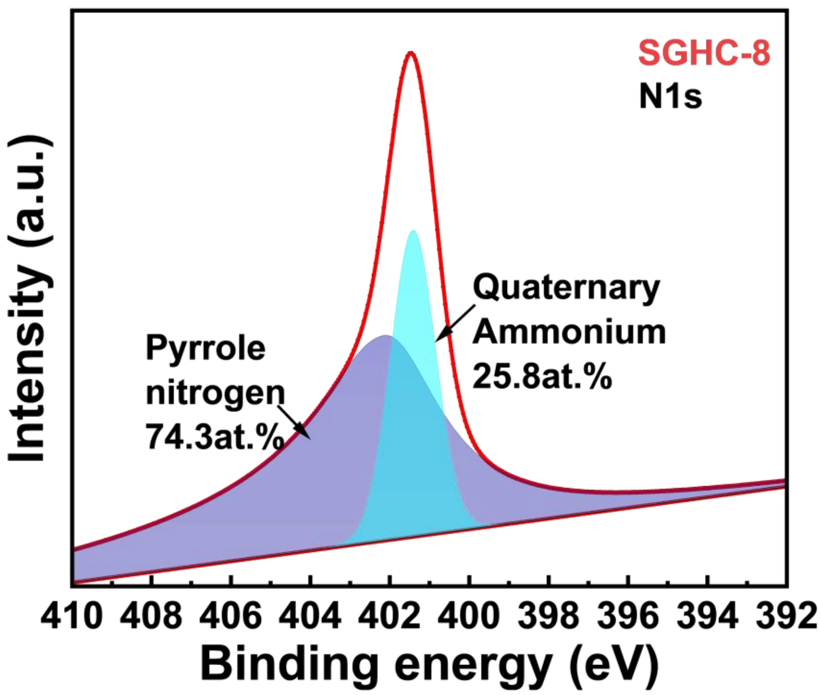

Figure S2. High-resolution N 1s XPS spectrum of SGHC-8.

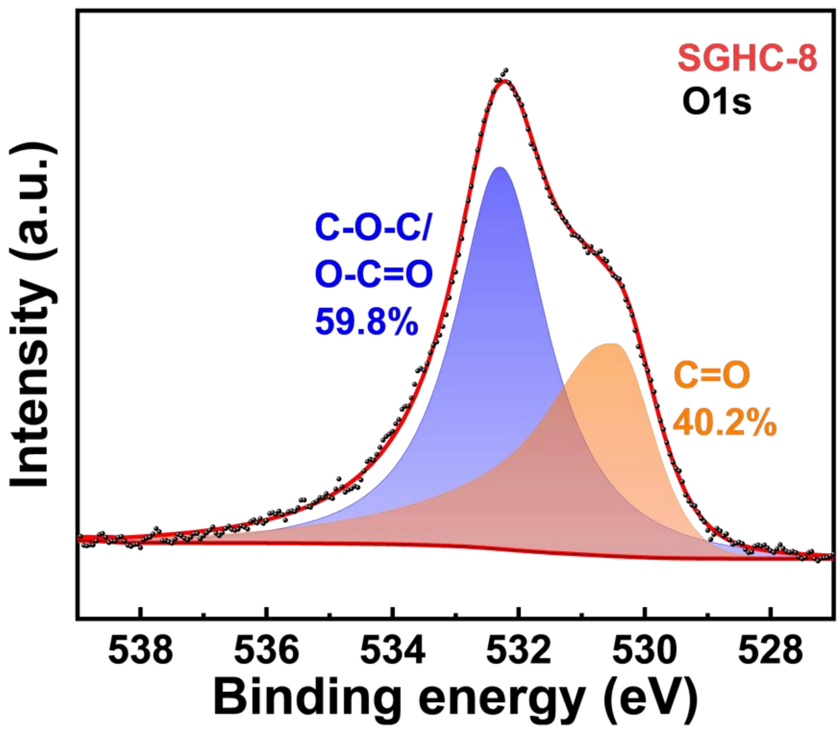

Figure S3. High-resolution O 1s XPS spectrum of SGHC-8.

Table S1. Sodium-storage performance comparison of SGHC-8 and representative coal-derived hard carbon anodes reported in the literature

Material	Preparation method	Capacity (mAh g^{-1})	ICE (%)	Current density (mA g^{-1})	Reference
Bituminous	Flash-pyrolyzed	111	65	-	[S1]
Anthracite	Carbonization	267.7	80	100	[S2]
Bituminous	HF/HCl deashing	270	86.8	30	[S3]
Lignite	HNO_3	256	82	20	[S4]
Bituminous	NaOH/HCl	270	84.4	35	[S5]
Anthracite	HF/HCl	233	69.3	20	[S6]
Bituminous	Direct-carbonization	317	80.0	20	[S6]
Sub-bituminous	Direct-carbonization	326	79.8	20	[S6]
Lignite	Purification carbonization	338.8	84.1	20	[S6]

Lignite	Density-gradient separation-carbonization	260	80.0	20	[S7]
Lignite	Thermal extraction carbonization	306	54.3	100	[S8]
Anthracite	NaOH/HCl/HF	308.3	82.3	30	[S9]
Lignite	Crosslinking- carbonization	356	82.9	30	[S10]
Bituminous	HCl/HF-preoxidation carbonization	274.2	74.8	30	[S11]
Semi-coke	Precarbonization -NaOH etching -carbonization	326.8	84.7	20	[S12]
Anthracite	Carbonization-ballmilling HCl purification	382	47.7	30	[S13]
Anthracite	Oxidation- intercalation-rapid thermal reduction	326	20.7	30	[S14]
Anthracite	Ball milling-N-doping	316.4	45.2	30	[S15]
Lignite	Coating carbonization	312.2	85.3	30	[S16]
Anthracite	HCl purification-carbonization	325	77	50	[S17]
Anthracite	Direct carbonization	252	70	50	[S17]
SGHC-8	CS/GA crosslinking-carbonization	350.5	80.6	20	This work

REFERENCES

[S1] Moon, J.V.; Karimi, Z.; Prline, A.; *et al*. Flash-pyrolyzed coal char as a high-performance anode for sodium-ion batteries. *Fuel Process Technol.,* 2023, 252, 107998. https://doi.org/10.1016/j.fuproc.2023.107998.

[S2] Li, Q.; Gao, Y.Z.; Wen, H.Y. *et al*. Investigation of pyrolyzed anthracite as an anode material for sodium ion batteries. *New J. Chem.,* 2022, 46, 13575-81. https://doi.org/10.1039/D2NJ01258H.

[S3] Tian, Q. Q.; Li, X M.; Xie, L.J.; *et al*. Insights into the carbonization mechanism of bituminous coal-derived carbon materials for lithium-ion and sodium-ion batteries. *New Carbon Mater.,* 2023, 38, 939-53. https://doi.org/10.1016/s1872-5805(23)60759-0.

[S4] Zou Y.J.; Li H.; Qin K.Y.; *et al*. Low-cost lignite-derived hard carbon for high-performance sodium-ion storage. *J. Mater. Sci,* 2020, 55, 5994-6004. https://doi.org/10.1007/s10853-020-04420-0.

[S5] Kong, J.L.; Pan, G.H.; Su, Z.J. The coal as high performance and low cost anodes for sodium-ion batteries. *Mater. Lett., X,* 2022, 13, 100123. https://doi.org/10.1016/j.mlblux.2022.100123.

[S6] Wang, B.Y.; Xia, J.L.; Dong, X.L.; *et al*. Study on sodium storage behavior of hard carbons derived from coal with different grades of metamorphism. *CIESC J.* 2021, 72, 5738–50. https://doi.org/10.11949/0438-1157.20210668.

[S7] Liu, Z.Y.; Huang, G.X.; Kang, W.W.; *et al*. Non-graphitic carbon as sodium-ion battery anode materials with improved ratio of plateau to sloping capacities prepared from lignite-based organic maceral. *Appl. Surf. Sci.,* 2024, 655, 159528. https://doi.org/10.1016/j.apsusc.2024.159528.

[S8] Xiao, N.; Wei, Y.B.; Li, H.Q. *et al*.; Boosting the sodium storage performance of coal-based carbon materials through structure modification by solvent extraction. *Carbon,* 2020, 162, 431-7. https://doi.org/10.1016/j.carbon.2020.02.015.

[S9] Zhang, Z.H.; Huang G.X.; Qu, X.X.; *et al*. An effective strategy to prepare non-graphitic carbon with increased pseudo-graphitic content for sodium-ion battery anode with enhanced plateau capacity. *Chem. Eng. J.,* 2023, 477, 147188.

https://doi.org/10.1016/j.cej.2023.147188.

[S10] Wang, K.F.; Sun F.; Wang, H.; *et al*. Altering thermal transformation pathway to create closed pores in coal-derived hard carbon and boosting of Na+ plateau storage for high-performance sodium-ion battery and sodium-ion capacitor. *Adv. Funct. Mater.* 2022, 32, 2203725. https://doi.org/10.1002/adfm.202203725.

[S11] Chen, H.; Sun, N.; Zhu, Q.Z.; *et al*. Microcrystalline hybridization enhanced coal-based carbon anode for advanced sodium- ion batteries. *Adv. Sci.,* 2022, 9, 2200023. https://doi.org/10.1002/advs.202200023.

[S12] Lou Z.J.; Wang H.; Wu D.Y.; *et al*. Microcrystalline regulation of bituminous coal derived hard carbon by pre-oxidation strategy for improved sodium-ion storage. *Fuel,* 2022, 310, 122072. https://doi.org/10.1016/j.fuel.2021.122072.

[S13] Sun, F.; Wang, H.; Qu, Z.B.; *et al*. Carboxyl-dominant oxygen rich carbon for improved sodium ion storage synergistic enhancement of adsorption and intercalation mechanisms. *Adv. Energy Mater.,* 2021, 11, 2002981. https://doi.org/10.1002/aenm.202002981.

[S14] Jiang, Z.D.; Xing, B.L.; Qu, X.X.; *et al*. Anthracite-based expanded graphite as anode materials for sodium-ion batteries with exceptional sodium storage performances. *J. Energy Storage,* 2024, 83, 110667. https://doi.org/10.1016/j.est.2024.110667.

[S15] Gao, X.M.; Chang, G.B.; Huang, C.; *et al*. Mechanochemical regulation of microcrystalline in coal-derived disordered carbon for improved sodium storage: metamorphic grade. *Appl. Surf. Sci.,* 2024, 658, 159868. https://doi.org/10.1016/j.apsusc.2024.159868.

[S16] Chen, H.; Sun, N.; Wang, Y.; *et al*. One stone two birds: pitch assisted microcrystalline regulation and defect engineering in coal-based carbon anodes for sodium-ion batteries. *Energy Storage Mater.,* 2023, 56, 532–41. https://doi.org/10.1016/j.ensm.2023.01.042.

[S17] Dong, Y.; Yuan, S.H.; Zhao, W.Q.; *et al*. Tailoring natural anthracite carbon materials towards considerable electrochemical properties with exploration of ester/ether-based electrolyte. *J. Mater. Chem. A,* 2023, 11, 9668–81. https://doi.org/10.1039/D2TA09704D.