

Supporting Information

Biomass-derived 3D honeycomb-like N and S dual-doped hierarchically porous carbons for high-efficient CO₂ capture

Weiwei Shi^a, Rongzhen Wang^a, Huili Liu^a, Binbin Chang^{a*}, Baocheng Yang^{*}, Zuling Zhang^b

^aHenan Provincial Key Laboratory of Nanocomposites and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, Henan 450006, China

^bHenan Provincial Chemi-Industries Research Station Co., Ltd, Zhengzhou 450000, China

*Corresponding author. Tel. Fax: +86 571 87541018.

E-mail address: binbinchang@infm.hhstu.edu.cn (B. Chang);
baochengyang@infm.hhstu.edu.cn (B. Yang)

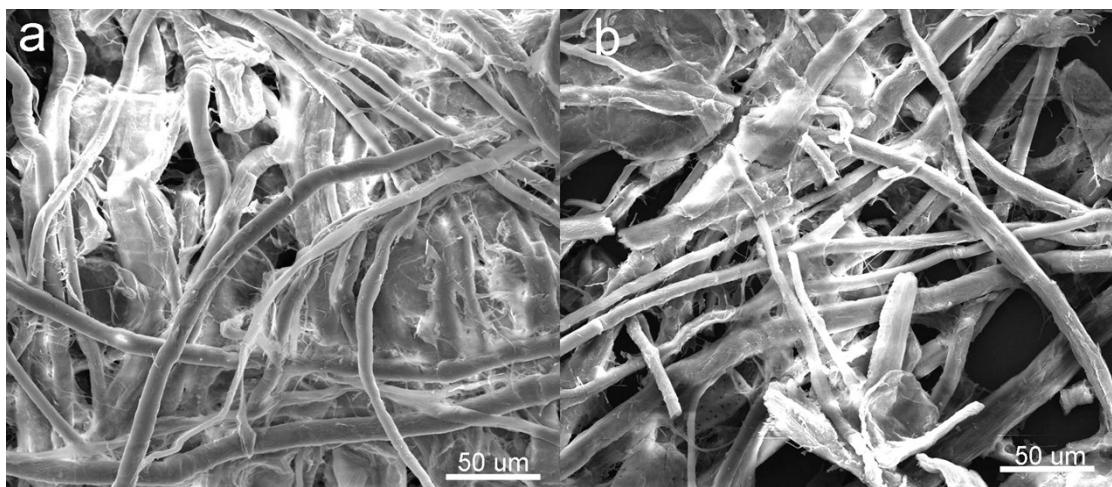


Fig. S1 The SEM images of waste paper towel (a) and hydrothermally synthesized precursors at 200 °C (b)

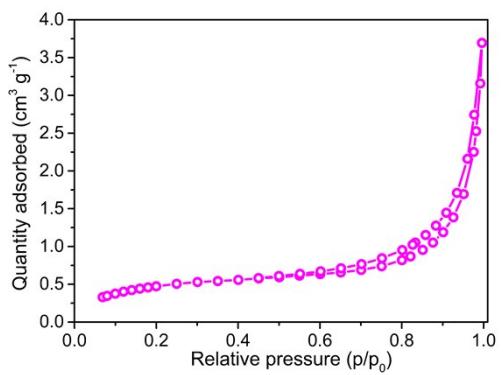


Fig. S2 The N₂ adsorption-desorption isotherm of hydrothermally synthesized precursor at 200 °C

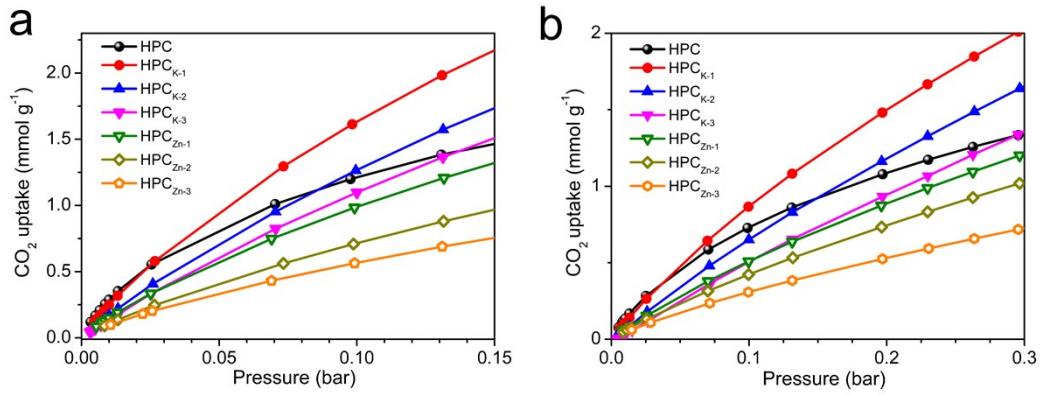


Fig. S3 CO₂ adsorption isotherms of all the resultant samples: (a) at 273 K below 0.15 bar; (b) at 298 K below 0.3 bar.

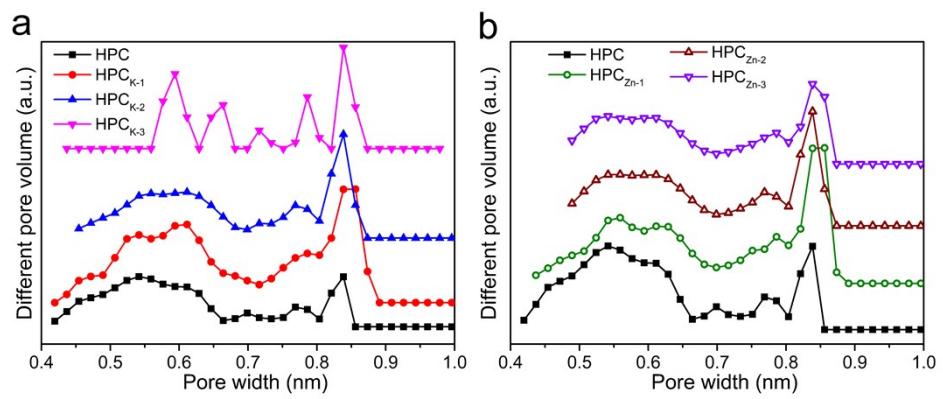


Fig. S4 Micropore (<1 nm) size distribution of all as-obtained materials measured by CO₂ adsorption at 273 K using the DFT method: (a) HPC_{K-x}; (b) HPC_{Zn-x}

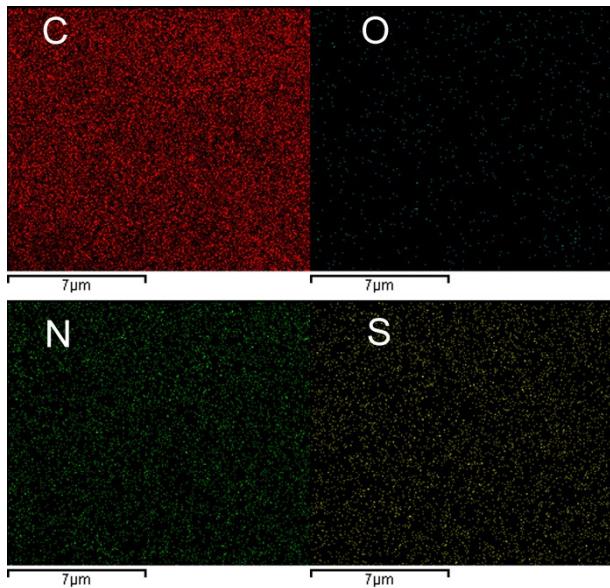


Fig. S5 The element mapping of N,S-HPC_{K-1} sample

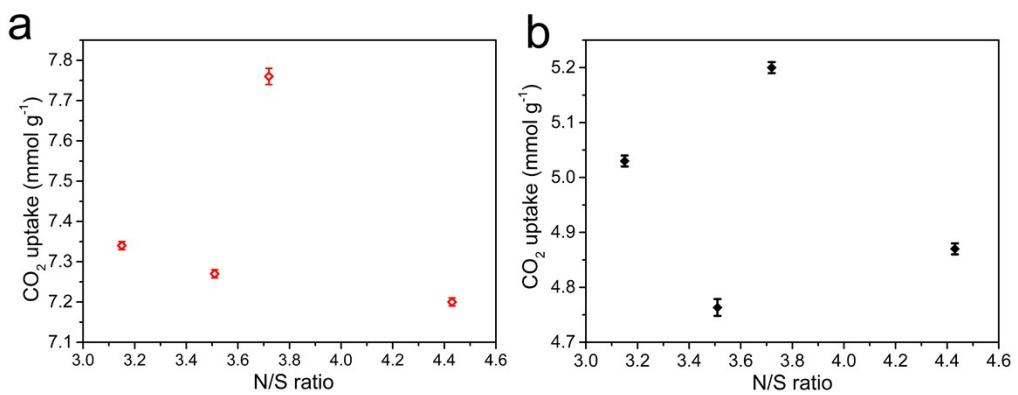


Fig. S6 The effect of different N/S ratios on CO₂ capture: (a) at 273 K under 1 bar; (b) at 298 K under 1 bar

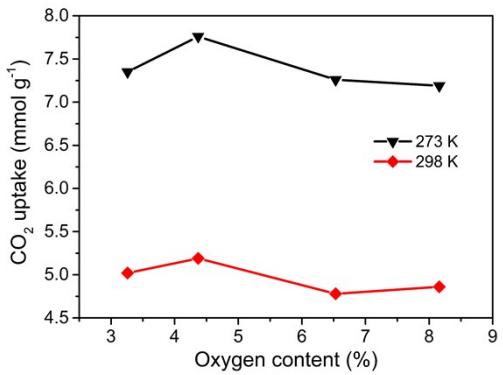


Fig. S7 The effect of oxygen content on CO₂ capture

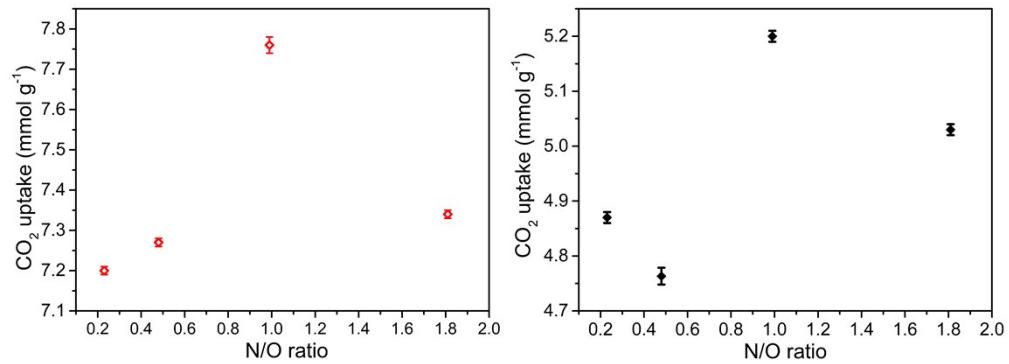


Fig. S8 The effect of different N/O ratios on CO₂ capture: (a) at 273 K under 1 bar; (b) at 298 K under 1 bar

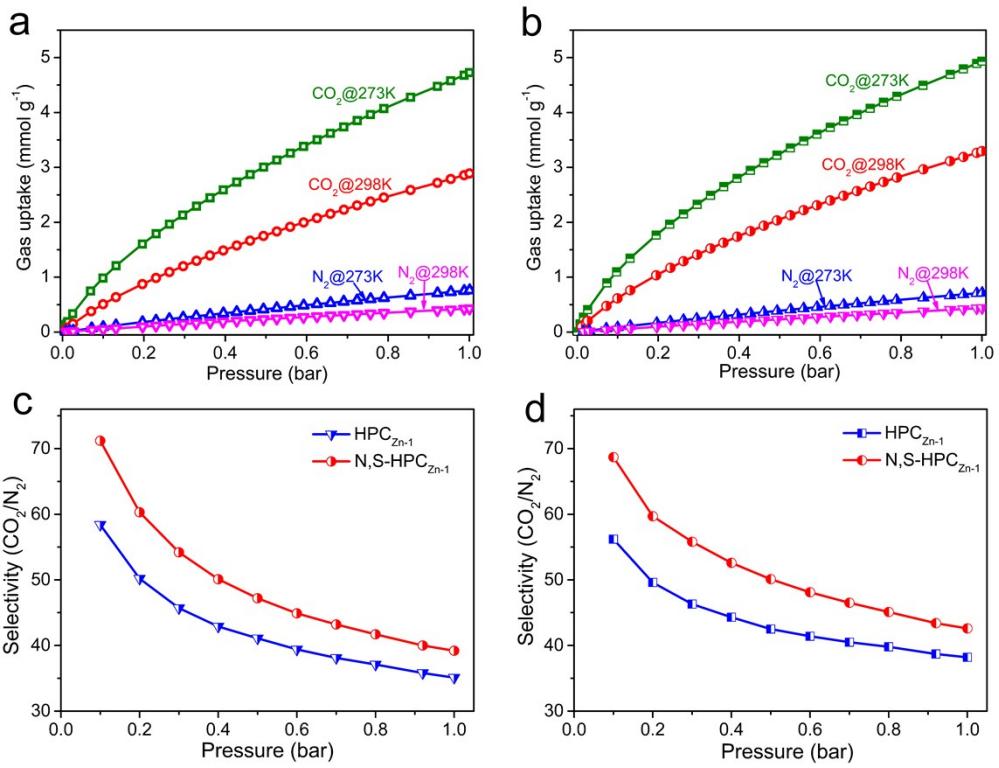


Fig. S9 Adsorption selectivities. (a) CO₂ and N₂ adsorption isotherms of HPC_{K-1} at 273 and 298 K. (b) CO₂ and N₂ adsorption isotherms of N,S-HPC_{K-1} at 273 and 298 K. (c) IAST-calculated selectivities of CO₂/N₂ on HPC_{K-1} and N,S-HPC_{K-1} at 273 K. (d) IAST-calculated selectivities of CO₂/N₂ on HPC_{K-1} and N,S-HPC_{K-1} at 298 K.

Table S1 Comparison of the CO₂ uptake with different carbon-based adsorbents

Sample	S _{BET} (m ² g ⁻¹)	Nitrogen content (wt %)	CO ₂ uptake at 0.15 bar (mmol g ⁻¹)	CO ₂ uptake at 1 bar (mmol g ⁻¹)	Temperatur e (K)	Reference
Commercial activated carbons	2000–3000	—	—	2.1–2.5	298	—
N-doped porous carbon nanofiber	1923	12.27	1.25 at 298 K	6.44/4.42	273/298	1
Popcorn-derived porous carbon	~850	2.47	~1.3 at 298 K	4.6	298	2
Dialdehyde and diamine derived microporous carbons	1881	0.36	—	4.92/2.86	273/298	3
Conjugated microporous polymers aerogels	1701	—	—	3.47	273	4
N-doped mesoporous carbons	748	11.67	1.16 at 298 K	2.73	298	5
N-doped porous carbon microflowers	2309	2.45	—	3.75	298	6
N-doped porous carbon hollow sphere	775	8.39	—	4.42/2.96	273/298	7
Hierarchically porous carbons	829	1.23	—	4.6	273	8
N-doped hierarchical porous carbon nanosheets	1120	17.4	~0.8 at 298 K	4.37	273	9
Wheat-derived activated microporous carbon	1438	—	~1.0 at 298 K	5.7/3.48	273/298	10
Salt-templated porous carbon with arginine	857	2.94	—	3.36	273	11
N-rich microporous carbon sphere	648	7.9	~2.0 at 298 K	5.4/4.3	273/298	12
N-doped porous carbon nanofibers/NiO	330.7	7.86	~0.89 at 298 K	2.46/1.79	273/298	13
Hierarchically porous carbons	~2700	—	—	3.7	298	14
N-enriched hierarchically porous carbon nanosheet	1354	6.47	~0.8 at 298 K	2.50	298	15
Biomass-derived microporous carbons	2511	—	—	3.71	298	16
Plant-derived porous graphene nanosheets	355.4	—	—	2.43	298	17
N and S co-doped hierarchically porous carbons	1770.7	4.32	1.51 at 298 K	7.76/5.19	273/298	This work

References

- [1] Y. Li, B. Zou, C.W. Hu, M.H. Cao, Nitrogen-doped porous carbon nanofiber webs for efficient CO₂ capture and conversion, *Carbon*, 99 (2016) 79–89.
- [2] T. Liang, C.L. Chen, X. Li, J. Zhang, Popcorn-derived porous carbon for energy storage and CO₂ capture, *Langmuir*, 32 (2016) 8042–8049.
- [3] J.C. Wang, Q. Liu, An efficient one-step condensation and activation strategy to synthesize porous carbons with optimal micropore sizes for highly selective CO₂ adsorption, *Nanoscale*, 6 (2014) 4148–4156.
- [4] R. Du, N. Zhang, H. Xu, N.N. Mao, W.J. Duan, J.Y. Wang, Q.C. Zhao, Z.F. Liu, J. Zhang, CMP aerogels: ultrahigh-surface-area carbon-based monolithic materials with superb sorption performance, *Adv. Mater.*, 26 (2014) 8053–8058.
- [5] Z. Zhang, B. Wang, C. Zhu, P. Gao, Z. Tang, N. Sun, W. Wei, Y. Sun, Facile one-pot synthesis of mesoporous carbon and N-doped carbon for CO₂ capture by a novel melting-assisted solvent-free method, *J. Mater. Chem. A*, 3 (2015) 23990–23999.
- [6] Y. Li, M.H. Cao, Synthesis of high-surface-area nitrogen-doped porous carbon microflowers and their efficient carbon dioxide capture performance, *Chem. Asian J.*, 10 (2015) 1496–1504.
- [7] Y. Wang, H.B. Zou, S.J. Zeng, Y. Pan, R.W. Wang, X. Wang, Q.L. Sun, Z.T. Zhang, S.L. Qiu, A one-step carbonization route towards nitrogen-doped porous carbon hollow spheres with ultrahigh nitrogen content for CO₂ adsorption, *Chem. Commun.*, 51 (2015) 12423–12426.
- [8] S.J. Yang, M. Antonietti, N. Fechler, Self-assembly of metal phenolic mesocrystals and morphosynthetic transformation toward hierarchically porous carbons, *J. Am. Chem. Soc.*, 137 (2015) 8269–8273.
- [9] J. Gong, H.J. Lin, M. Antonietti, J.Y. Yuan, Nitrogen-doped porous carbon nanosheets derived from poly(ionic liquid)s: hierarchical pore structures for efficient CO₂ capture and dye removal, *J. Mater. Chem. A*, 4 (2016) 7313–7321.
- [10] S.M. Hong, E. Jang, A.D. Dysart, V.G. Pol, K.B. Lee, CO₂ Capture in the Sustainable Wheat-Derived Activated Microporous Carbon Compartments, *Sci Rep.*, 6 (2016) 34590.
- [11] K.V. Kumar, S. Gadipelli, K. Preuss, H. Porwal, T.T. Zhao, Z.X. Guo, M.M. Titirici, Salt templating with pore padding: hierarchical pore tailoring towards functionalised porous carbons, *ChemSusChem*, 10 (2017) 199–209.

- [12] L. Liu, Z.H. Xie, Q.F. Deng, X.X. Hou, Z.Y. Yuan, One-pot carbonization enrichment of nitrogen in microporous carbon spheres for efficient CO₂ capture, *J. Mater. Chem. A*, 5 (2017) 418–425.
- [13] Q. Li, J. N. Guo, D. Xu, J. Q. Guo, X. Qu, Y. Hu, H. J. Qi, F. Yan, Electrospun N-doped porous carbon nanofibers incorporated with NiO nanoparticles as free-standing film electrodes for high-performance supercapacitors and CO₂ capture, *Small*, 14 (2018) 1704203.
- [14] L. Esterez, D. Barpaga, J. Zheng, S. Sabale, R. L. Patel, J. G. Zhang, B. P. McGrail, P. K. Motkri, Hierarchically porous carbon materials for CO₂ capture: the role of pore structure, *Ind. Eng. Chem. Res.*, 57 (2018) 1262–1268.
- [15] Q.R. Guo, C. Chen, Z. Li, X. Li, H.J. Wang, N.J. Feng, H. Wan, G.F. Guan, Controllable construction of N-enriched hierarchically porous carbon nanosheets with enhanced performance for CO₂ capture, *Chem. Eng. J.*, 371 (2019) 414–423.
- [16] G.K. Parshetti, S. Chowdhury, R. Balasubramanian. Biomass derived low-cost microporous adsorbents for efficient CO₂ capture. *Fuel*, 2015, 148, 246-254.
- [17] G.K. Parshetti, S. Chowdhury, R. Balasubramanian. Plant derived porous graphene nanosheets for efficient CO₂ capture. *RSC Adv.*, 2014, 4, 44634-44643.