Sulfur-Enriched Nanoporous Carbon: A Novel Approach to CO_2 Adsorption

(Supporting Information)

Chen Liu[a], Yue Zhi[a], Qiyun Yu[a], Lifeng Tian[a], Muslum Demir*[,b,c], Suleyman Gokhan Colak[d], Ahmed A. Farghaly[e], Linlin Wang[f], Xin Hu*[, a]

[a]Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua, Zhejiang, 321004, PR China

[b] Department of Chemical Engineering, Bogazici University, 34342 Istanbul, Türkiye

[c]TUBITAK Marmara Research Center, Material Institute, Gebze 41470, Türkiye

[d]Department of Biomedical Engineering, Faculty of Engineering and Natural Sciences, Iskenderun Technical University, 31200 Hatay, Turkey

[e]Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

[f]Key Laboratory of Urban Rail Transit Intelligent Operation and Maintenance Technology and Equipment of Zhejiang Province, College of Engineering, Zhejiang Normal University, Jinhua, Zhejiang, 321004, PR China

*Corresponding author's e-mail: demirm@alumni.vcu.edu (M. D.) and huxin@zjnu.cn (X. H.); phone: 86-151-0579-0257; fax: 86-579-8228-8269

Details for sorbents synthesis

Coconut shell was carbonized at 500°C for 2 h under the flow of N_2 (100 mL/min). The obtained sample was named as C. For a typical reaction, 2 g C was combined with a solution that contained 2g potassium persulfate (PP). After stirring vigorously for 6 h, the mixture was left overnight to dry at 120 °C in an oven. Afterwards, the sample was activated to 750 °C for 2 h. During the activation process, the heating rate is 5 °C/min and nitrogen flow rate is 400 mL/min. Following activation, the sorbent was rinsed with distilled water until the pH value of the filtrate was roughly 7. The wet sample was then dried at 150 °C under vacuum for 24 h. The obtained sample was denoted as C-PP-750-2.

Characterization

Powdered X-ray diffraction (XRD) patterns were carried out on a PHILIPS PW3040/60 powder diffractometer using CuKα radiation (λ =0.15406nm). Scanning electron microscopy (SEM Hitachi S-4800) was used to observe the morphology of the samples of carbon materials. Further details of the pore structure were determined by transmission electron microscopy (TEM, JEOL-2100F) operated at 200 kV. The CHN elements were analyzed using a VarioEL III Elemental Analyzer. Nitrogen adsorption and desorption isotherms were measured on a Beishide 3H-2000PS2 sorption analyzer at -196^{o}C. Ultrahigh-purity N_2 (99.999%, Shanghai Pujiang Gas Co., Ltd) was used for measurement. Before measurement, the samples were degassed in a vacuum at 200^{o}C for at least 12h. The specific surface area (S_{BET}) was calculated according to the multipoint Brunauer-Emmett-Teller (BET) method from the adsorption data in the relative pressure range between 0.005 and 0.05. The total micropore volume (V_t) was deduced from the N_2 adsorption data by the t-plot method, and the total pore volume (V_0) was estimated from the adsorbed amount of liquid nitrogen at a relative pressure of 0.99. The error of porosity measurement is within 3%. The pore size distribution was calculated using the non-local density functional theory (NLDFT) method. XPS survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV. A non-linear least squares curve fitting program (Peak-Fit version 4) with a Gaussian-Lorentzian mix function and Shirley background subtraction was used to deconvolve the XPS subpeaks

The CO_2 adsorption isotherms were measured using the Beshide 3H-2000PS2 sorption analyzer at 0^{o}C and 25^{o}C, respectively. Pure CO_2 (99.99%, Shanghai Pujiang Gas Co., Ltd) was used for adsorption. Prior to each adsorption experiment, the sample was degassed for 12 h at 200^{o}C to remove the guest molecules from the pores. The volume of narrow micropores (with sizes <1 nm), V_n, was calculated from CO_2 adsorption at 0°C using the Dubinin–Radushkevich (D-R) equation. The measurements were repeated for each sample, until the values fell within ± 2% of each other.

Measurement of dynamic CO_2 uptake of the sorbents

The dynamic CO_2 uptake of the sorbents was tested on a fixed-bed reactor schematically illustrated in Scheme S1 at 1 bar and 25 °C. First, sample was heated at 100°C for 1 h under N_2 at a flow rate of 20 mL/min. The gas flow was shifted from nitrogen to a 10% mixture of CO_2 in N_2 at a flow rate of 10 mL/min, when the sample temperature was lowered to 25°C. The effluent gases were monitored online using an

Agilent 7820A gas chromatograph with a thermal conductivity detector (TCD) to obtain the breakthrough curve.

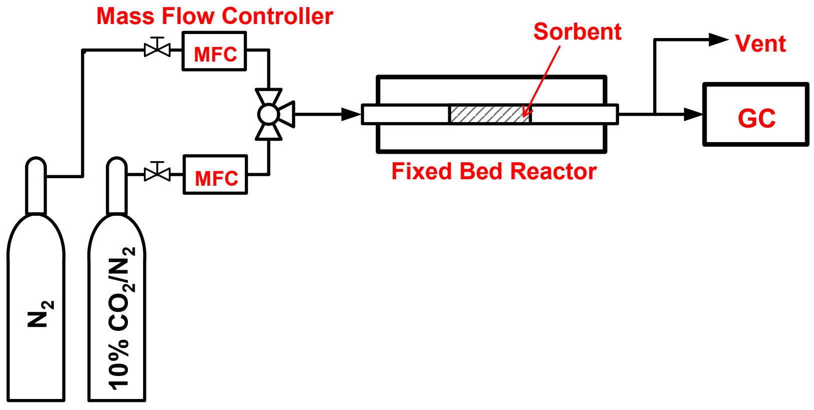
The dynamic CO_2 uptake of the sorbent (q_d) was calculated from the breakthrough curves using the following equation:

$$q_d = \frac{Q_F C_0 t_s}{w} \quad (1)$$

In the above equation, Q_F is the feed molar flow rate, C_0 is the concentration of the adsorbate in the feed stream, w is the weight of the adsorbent materials loaded in the column and t_s is the stoichiometric time, which can be estimated from breakthrough curves using the equation below:

$$t_s = \int_0^\infty \left(1 - \frac{C_A}{C_0}\right) \partial t \quad (2)$$

Where C_A is the adsorbate concentration at the column outlet.



Scheme S1. Schematic of the fixed-bed reactor system.

Measurement of CO_2 adsorption kinetics

The adsorption kinetics of CO_2 was measured in a thermogravimetric analyzer (NETZSCH STA 449C). In the kinetic analysis, the sample (~5 mg) was degassed under a He stream at 200°C for 1 h. Next, the temperature was cooled to the experimental temperature of 25°C. Then the CO_2 gas was fed into the test chamber with a flow rate of 50 mL/min and the weight variation with time was recorded.

IAST CO_2/N_2 selectivity

To calculate the IAST CO_2/N_2 selectivity, the CO_2 adsorption isotherm was fitted with a Langmuir–Freundlich equation and N_2 isotherm was fitted with a linear equation, respectively.

The adsorption selectivity of carbon dioxide over nitrogen was calculated according to the following equation:

$$S = \frac{V_1/V_2}{P_1/P_2}$$

where V_1 and V_2 are the adsorbed amount of carbon dioxide at 0.1 bar and nitrogen at 0.9 bar, respectively, which can be derived from the fitted equation; P_1 and P_2 are the equilibrium partial pressure of carbon dioxide (0.1 bar) and nitrogen (0.9 bar) in the bulk gas phase, respectively.

CO_2 heat of adsorption (Q_{st})

CO_2 heat of adsorption was calculated using a variant of the Clausius-Clapeyron equation taking both the 0 and 25°C CO_2 adsorption data.

$$\ln\left(\frac{P_1}{P_2}\right) = Q_{st} * \frac{T_2 - T_1}{R * T_1 * T_2}$$

Where P_n : Pressure for isotherm n

T_n: Temperature for the isotherm n

R: Gas constant

Pressure as the function of the adsorbed amount was determined by using

Langmuir–Freundlich equation. This Langmuir–Freundlich equation gives an accurate fit over the pressure up to 1 bar and with the goodness of fit (R^2) above 0.99. The corresponding P_1 and P_2 at a certain CO_2 adsorbed amount of both temperatures can be obtained by the simulated Langmuir–Freundlich equation. Then input these numbers into the above equation, the corresponding CO_2 heat of adsorption was calculated.

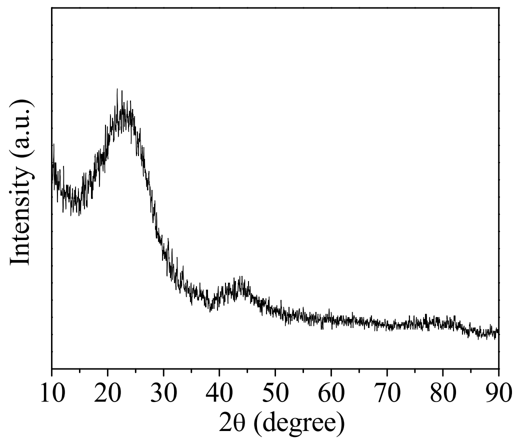


Figure S1. XRD pattern for C-PP-750-1

Table S1. S-species contributions in total S obtained from fitting of the S 2p XPS spectra

Sample	Oxidized sulphur (at. %)	S $2p_{1/2}$ (at. %)	S $2p_{3/2}$ (at. %)
C-PP-700-3	36.22	21.26	42.52
C-PP-750-1	59.82	13.39	26.78
C-PP-750-2	58.05	13.98	27.96
C-PP-750-3	64.00	12.00	24.00

Table S2. Comparison of the CO_2 adsorption (25 °C and 1 bar) for different sorbents

Sample	CO_2 uptake (mmol/g)	Ref.
AA750	2.7	S1
GEPM-1	2.5	S2
GMNO-4	2.6	S3
GTCF-3	2.7	S4
MRF-2	2.5	S5
OM-CNS	3.0	S6
SU-MC	1.0	S7
NDPC-2-800	0.8	S8
COP-122	0.4	S9
ZIF-78	2.7	S10
C-PP-750-1	2.6	This study

References

S1. Balahmar, N.; Mitchell, A. C.; Mokaya, R., Generalized Mechanochemical Synthesis of Biomass-Derived Sustainable Carbons for High Performance CO_2 Storage. *Adv. Energy Mater.* **2015,** *5*, (22), 1500867.

S2. Sui, Z.Y.; Cui, Y.; Zhu, J.H.; Han, B.H., Preparation of Three-Dimensional Graphene Oxide–Polyethylenimine Porous Materials as Dye and Gas Adsorbents. *ACS Appl. Mater. Interfaces* **2013,** *5*, (18), 9172-9179.

S3. Zhou, D.; Liu, Q.; Cheng, Q.; Zhao, Y.; Cui, Y.; Wang, T.; Han, B., Graphene-manganese oxide hybrid porous material and its application in carbon dioxide adsorption. *Chin. Sci. Bull*. **2012,** *57*, (23), 3059-3064.

S4. Zhou, D.; Cheng, Q.Y.; Cui, Y.; Wang, T.; Li, X.; Han, B. H., Graphene-terpyridine complex hybrid porous material for carbon dioxide adsorption. *Carbon* **2014,** *66*, 592-598.

S5. Zhou, H.; Xu, S.; Su, H.; Wang, M.; Qiao, W.; Ling, L.; Long, D., Facile preparation and ultra-microporous structure of melamine-resorcinol-formaldehyde polymeric microspheres. *Chem. Commun.* **2013,** *49*, (36), 3763-3765.

S6. Zheng, L.; Li, W. B.; Chen, J. L., Nitrogen doped hierarchical activated carbons derived from polyacrylonitrile fibers for CO2 adsorption and supercapacitor electrodes. *RSC Adv.* **2018,** *8*, (52), 29767-29774.

S7. To, J. W. F.; He, J.; Mei, J.; Haghpanah, R.; Chen, Z.; Kurosawa, T.; Chen, S.; Bae, W.-G.; Pan, L.; Tok, J. B. H.; Wilcox, J.; Bao, Z., Hierarchical N-Doped Carbon as CO_2 Adsorbent with High CO_2 Selectivity from Rationally Designed Polypyrrole Precursor. *J. Am. Chem. Soc.* **2016,** 138, (3), 1001-1009.

S8. Fu, N.; Wei, H.-M.; Lin, H.-L.; Li, L.; Ji, C.-H.; Yu, N.-B.; Chen, H.-J.; Han, S.; Xiao, G.-Y., Iron Nanoclusters as Template/Activator for the Synthesis of Nitrogen Doped Porous Carbon and Its CO_2 Adsorption Application. *ACS Appl. Mater. Interfaces* **2017,** 9, (11), 9955-9963.

S9. Dogan, N. A.; Ozdemir, E.; Yavuz, C. T., Direct Access to Primary Amines and Particle Morphology Control in Nanoporous CO_2 Sorbents. *ChemSusChem* **2017,** 10, (10), 2130-2134.

S10. Furukawa, H.; Yaghi, O. M., Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009,** *131*, (25), 8875-8883.