

Sustainable CO₂ Capture: N, S-Codoped Porous Carbons Derived from Petroleum Coke with High Selectivity and Stability

(Supplementary materials)

Jiawei Shao¹, Yingyi Wang¹, Mingyang Che¹, Ya Liu¹, Yongfu Jiang¹, Qiang Xiao^{2, *},
Muslum Demir^{3,4}, Linlin Wang⁵, Xin Hu^{1, *}

¹ Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua 321004, China; shaojw2001@outlook.com (J.S.); wangyingyi0@126.com (Y.W.); 13154843717@163.com (M.C.); sky48@zjnu.cn (Y.L.); yongfujiang@zjnu.cn (Y.J.)

² Institute of Plant Nutrition, Resources and Environment, Beijing Academy of Agriculture and Forestry Science, Beijing 100097, China

³ Department of Chemical Engineering, Bogazici University, 34342 Istanbul, Türkiye; demirm@alumni.vcu.edu

⁴ TUBITAK Marmara Research Center, Material Institute, 41470 Gebze, Türkiye

⁵ Key Laboratory of Urban Rail Transit Intelligent Operation and Maintenance Technology and Equipment of Zhejiang Province, College of Engineering, Zhejiang Normal University, Jinhua 321004, China; wanglinlin@zjnu.cn

* Correspondence: xqiang1978@163.com (Q.X.); huxin@zjnu.cn (X.H.);
Tel.: +86-151-0579-0257 (X.H.); Fax: +86-579-8228-8269 (X.H.)

N, S co-doping

A mixture of PC and thiourea (mass ratio 1:1) was heated in N₂ at 500 °C for 2 h. The collected samples were rinsed with hot distilled water a few times to get rid of any unreacted thiourea. Finally, the resulting products were put into the oven to dry at 120 °C overnight. The resulting sample was denoted as PCT.

KOH activation

For a typical reaction, 2 g PCT was combined with a solution that contained 8g KOH. 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 700 °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 PCTK-700-4.

Characterization

Powdered X-ray diffraction (XRD) patterns were carried out on a PHILIPS PW3040/60 powder diffractometer using CuK α radiation ($\lambda = 0.15406\text{nm}$). 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°C . Ultrahigh-purity N₂ (99.999%, Shanghai Pujiang Gas Co., Ltd) was used for measurement. Before measurement, the samples were degassed in a vacuum at 200°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 0.001 and 0.01. The total micropore volume (V_t) was deduced from the N₂ 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 density functional theory (DFT) method. In addition, X-ray photoelectron (XPS) measurements were performed using an AXIS Nova spectrometer (Kratos Inc., NY, USA) equipped with a monochromatic Al K α X-ray source (1486.6 eV). XPS survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV.

The CO₂ adsorption isotherms were measured using the Beshide 3H-2000PS2 sorption analyzer at 0°C and 25°C , respectively. Pure CO₂ (99.99%, Shanghai Pujiang

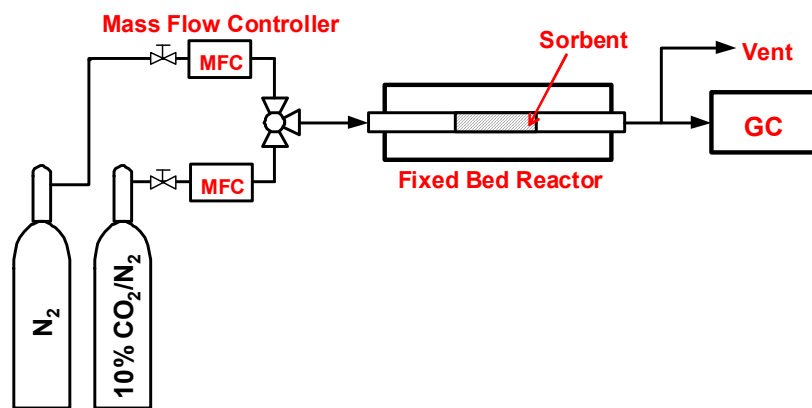
Gas Co., Ltd) was used for adsorption. Prior to each adsorption experiment, the sample was degassed for 12 h at 200°C to remove the guest molecules from the pores. The volume of narrow micropores (with sizes <1 nm), V_n , was calculated from CO₂ adsorption at 0°C using the Dubinin–Radushkevich (D-R) equation. The measurements were repeated for each sample, until the values fell within $\pm 2\%$ of each other.

Measurement of dynamic CO₂ uptake of the sorbents

The dynamic CO₂ uptake of the sorbents was tested on a fixed-bed reactor schematically illustrated in Scheme S1 at 1 bar and 25 °C. First, the sample was heated at 100°C for 1 h under N₂ at a flow rate of 20 mL/min. The gas flow was shifted from nitrogen to a 10% mixture of CO₂ in N₂ 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). From the breakthrough curves, the dynamic CO₂ capture capacity on an adsorbent was calculated. The error for this measurement falls within 2%.

Measurement of CO₂ adsorption kinetics

The adsorption kinetics of CO₂ 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 CO₂ gas was fed into the test chamber with a flow rate of 50 mL/min and the weight variation with time was recorded. The measurement's error is within 2%.



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

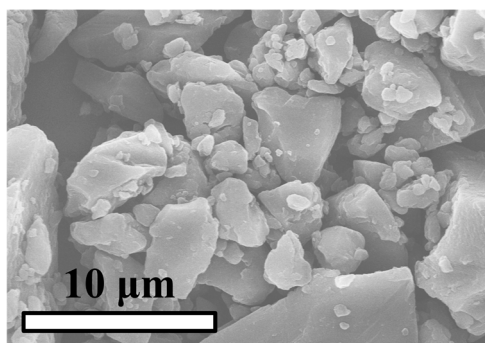


Figure S1. SEM image of PC

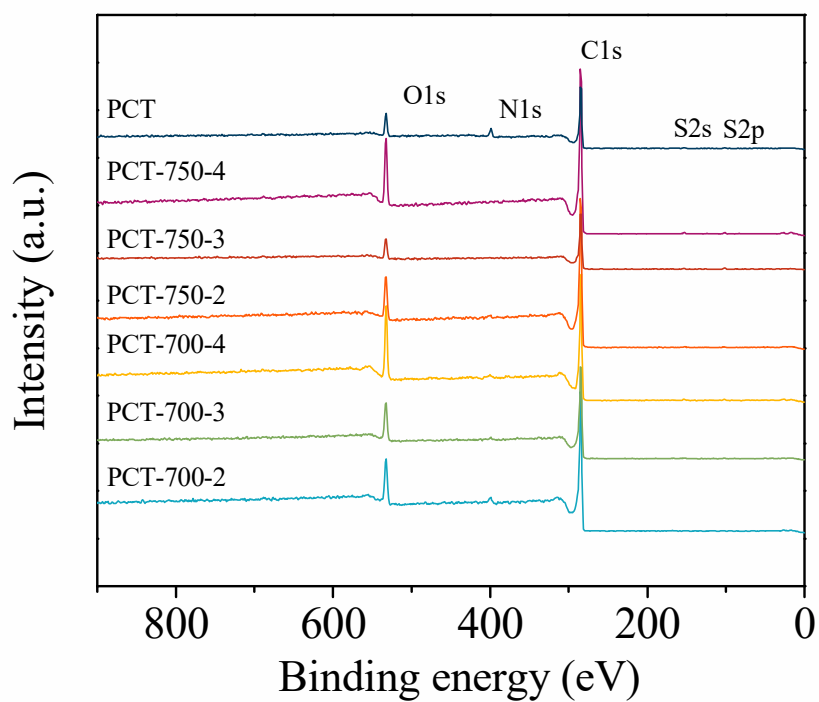


Figure S2. XPS survey scan spectrum of PCT and PCTK-T-m samples

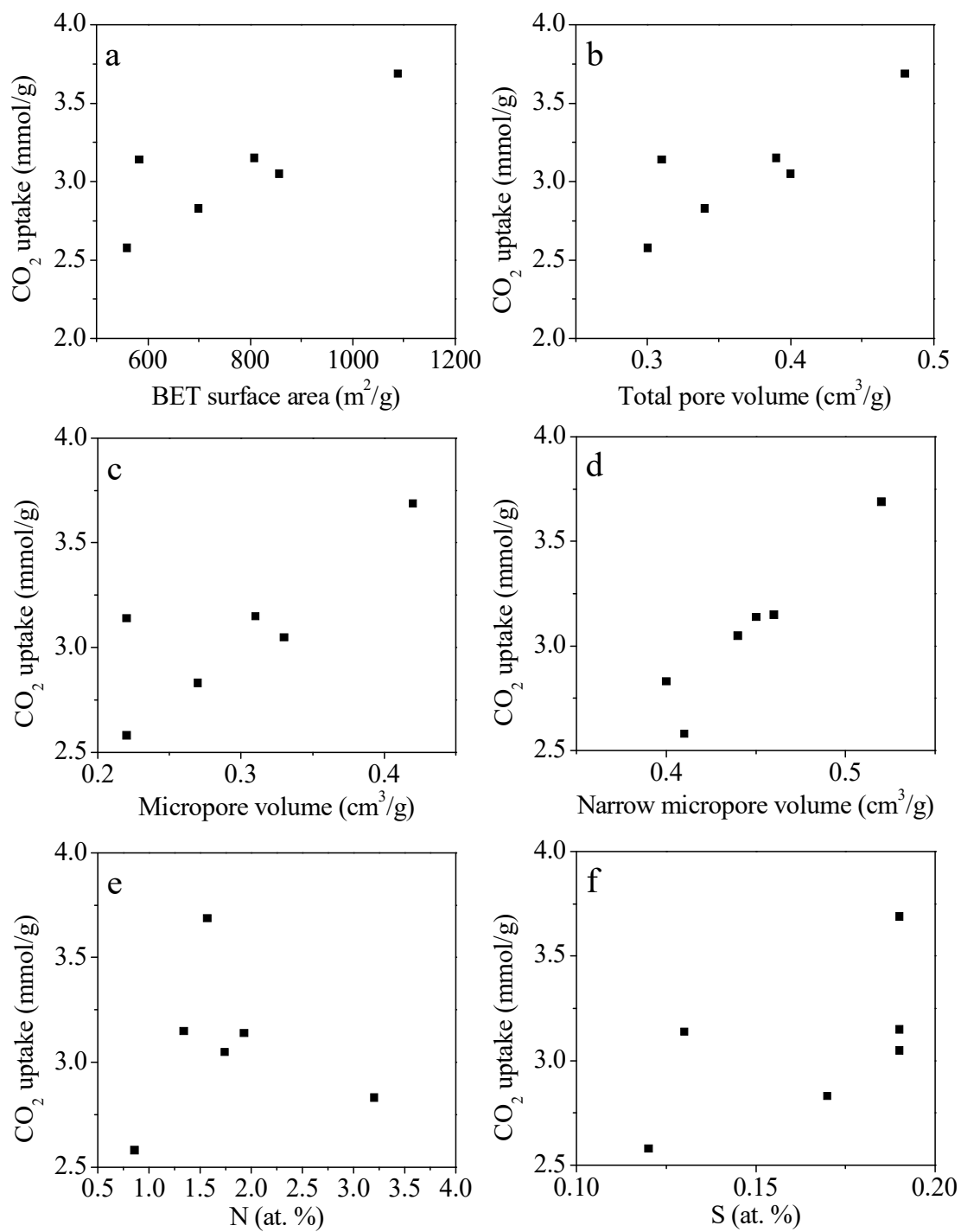


Figure S3. Plot of each porous properties characteristics (a) S_{BET} , (b) V_o , (c) V_t , (d) V_n , (e) nitrogen and (f) sulfur content versus CO₂ uptake.

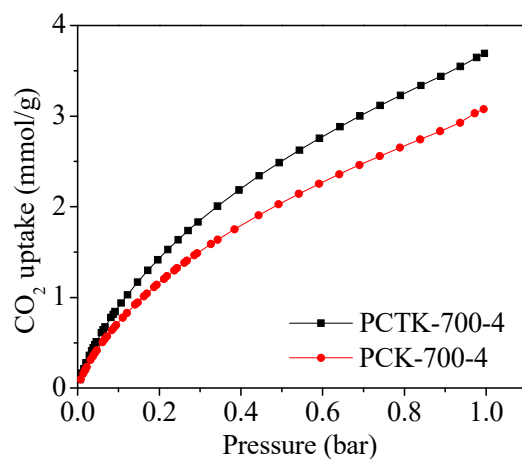


Figure S4. CO₂ adsorption isotherms of PCTK-700-4 vs PCK-700-4 at 25°C and 1 bar

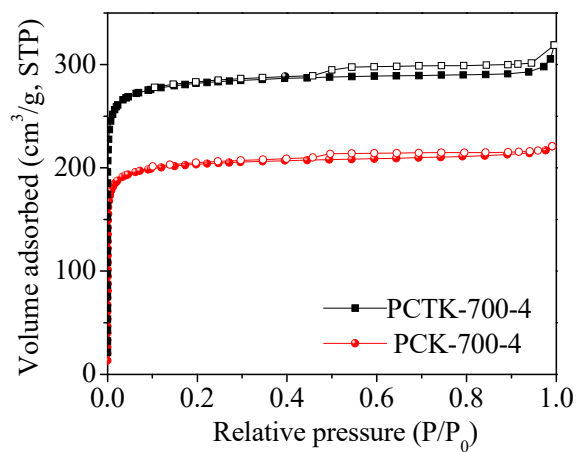


Figure S5. N₂ sorption isotherms of PCTK-700-4 vs PCK-700-4

Table S1. Comparison of the CO₂ 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	S11
4-FSAC-HPC	3.3	S12
PSK-2-650	3.5	S13
Zeolite 13x	4.6	S14
Mg-MOF-74	7.1	S15
UiO-66(Zr)-(OH) ₂	6.2	S16
PCTK-700-4	3.7	This study

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