**Fabrication of coconut shell-derived porous carbons for $CO_2$ adsorption application**

**(Supplementary materials)**

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## Synthesis

In a typical preparation, coconut shell (CS) was mixed with a KOH aqueous solution to achieve KOH/CS mass ratios of 0.3:1, 0.5:1, and 1:1. After thorough stirring, the blend was put into a convection oven with the temperature 120 °C

overnight. Afterward, the achieved slurry mixture was put into a tubular furnace under the protection of $N_2$ flow. First, the temperature was elevated to and kept at 200 °C for 1 h and then further raised to the designed activation temperature (700, 750, or 800 °C). The resulting samples were rinsed multiple times with distilled water until the pH value of filtrate reached 7. Then, the as-obtained samples were heated at 150 °C under vacuum for 24 h. The resultant carbonaceous sorbents were designated as CSC-T-m; T and m are the activation temperature and the KOH/CS mass ratio, respectively.

**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 0.001 and 0.01. 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 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 Kα 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. 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:

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

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:

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

Where $C_A$ is the adsorbate concentration at the column outlet.

**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**

$CO_2$ heat of adsorption was calculated using a variant of the Clausius-Clapeyron equation taking both the 273K and 298K $CO_2$ adsorption data.

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

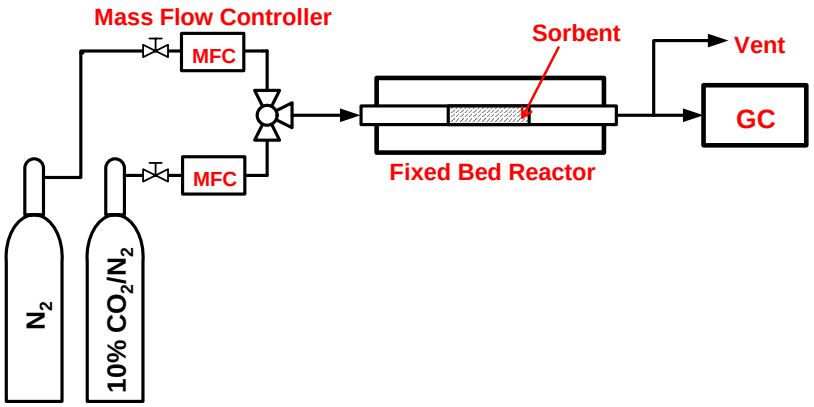
Where $P_n$ : Pressure for isotherm n

$T_n$: 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.




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

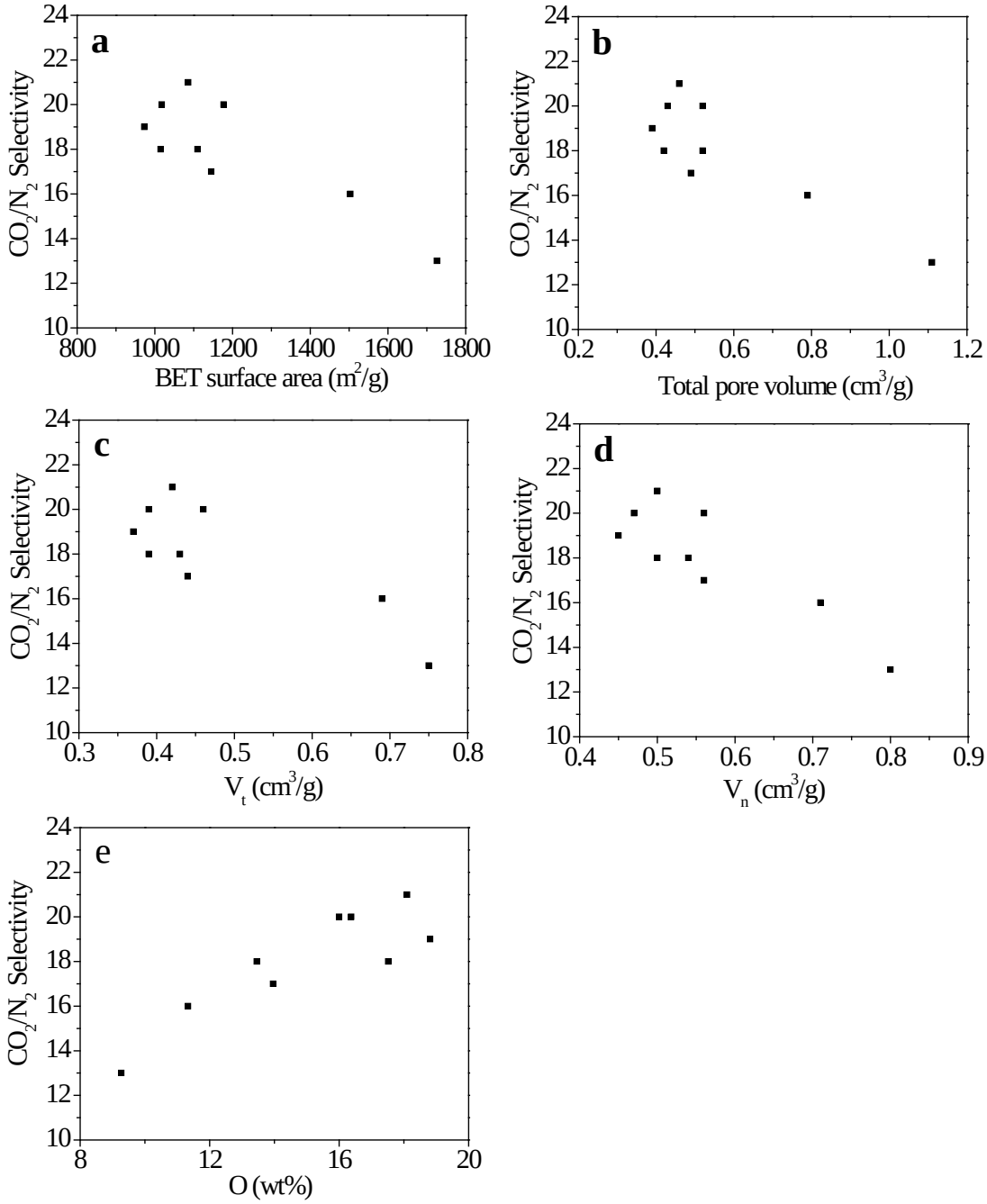



**Figure S1**. Plot of each porous properties characteristics (a) $S_{BET}$, (b) $V_0$, (c) $V_t$ ,(d) $V_n$ , and (e) oxygen content versus $CO_2/N_2$ selectivity.

Table S1. 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 |
| NAC | 4.0 | S7 |
| PC-700 | 3.6 | S8 |
| CEMFAET | 3.8 | S9 |
| AC-2-635 | 3.9 | S10 |
| AC1040 | 4.3 | S11 |
| CP-2-600 | 3.9 | S12 |
| CPTHB-7 | 3.7 | S12 |
| Cell-UK | 4.4 | S13 |
| TOK-900 | 4.3 | S14 |
| MOF-2 | 0.6 | S15 |
| MOF-505 | 3.3 | S16 |
| ZIF-78 | 2.7 | S17 |
| UFC-600-3 | 3.5 | S18 |
| PSK-2-650 | 3.5 | S19 |
| CSC-750-0.5 | 4.2 | This study |

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