# SO<sub>2</sub> capture and detection with carbon microfibers (CMFs) synthesised from polyacrylonitrile

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# **Materials and Methods**

#### **CMFs synthesis**

The polymer precursor, polyacrylonitrile (PAN), was acquired from Sigma-Aldrich, with a molecular mass average of 150,000 amu, and it was used as received without additional purification. The solvent *N*,*N*-dimethylformamide (DMF) grade anhydrous (99.8%) was also acquired from Sigma-Aldrich. PANMFs were synthesised with a concentration of 10wt% of PAN and 90wt% of DMF, and the mixture was stirred for 6 h at 343 K. The electrospinning apparatus was set at a flow rate of 0.5 mL h<sup>-1</sup>, a voltage of 15 kV, and a 10 cm distance between the syringe tip and the collector.<sup>1, 2</sup> CMFs were obtained by calcination of PANMFs in two stages: i) stabilisation at 353 K (air atmosphere) for 30 min and ii) carbonisation at 1173 K for 90 min (nitrogen atmosphere).

# Characterisation

IR spectra were obtained in the 4000-450 cm<sup>-1</sup> range on a spectrometer (Thermo-Scientific, iS5) with a diamond window ATR attachment. SEM Micrographs were collected on a scanning electron microscope (JEOL, JMS-7600 F) to characterise the microstructure of the samples, the morphology, surface features and EDX analysis and mapping.

# SO<sub>2</sub> adsorption experiments

Isotherms were measured on a gravimetric sorption analyser (Surface Measurement Systems, DVS Vacuum) using SO<sub>2</sub> (99.95%). Samples were degassed in a dynamic vacuum (1 x  $10^{-6}$  Torr) at 453 K for 4 h. After cooling to the desired temperature, the isotherms at 298, 303 and 308 K and cyclic experiments at 298 K were measured from 0 to 1 bar.

# $N_2$ and $CO_2$ adsorption experiment

Isotherms were measured on Autosorb 1 instrument (Quantachrome) using high-purity gases  $N_2$  (99.995%) and  $CO_2$  (99.8%). Before the measurements, samples were outgassed at 453 K for 4 h with a heating ramp of 1 K min<sup>-1</sup> under a dynamic vacuum.

# Ex-situ gas-saturated samples

Saturated samples were prepared by exposing a vial with a previously activated sample to a saturated atmosphere of the desired gas. Samples were activated in a small vial with a dynamic vacuum at 453 K for 2 h. Then, once the samples were cooled to room temperature, the vials were exposed for 2 h to a saturated atmosphere of the selected gas. The CO<sub>2</sub>-saturated atmosphere was achieved with a CO<sub>2</sub>-filled balloon. The H<sub>2</sub>O-saturated atmosphere was achieved by placing the vial in a closed container with water, keeping the water from entering the vial. The SO<sub>2</sub> atmosphere required an ex-situ SO<sub>2</sub> saturator (see below).

# Ex-situ SO<sub>2</sub> saturator system

# Caution! The $SO_2$ generation process was carried out inside a fume hood and in small volumes to avoid over-pressure.

The system contains two principal parts:  $SO_2$  gas generator (A), an addition funnel with  $H_2SO_4$  connected to a Schlenk flask with  $Na_2SO_3$  under stirring, and the saturation chamber (B), constructed from a round flask connected to a vacuum line. First, around 20 mg of the sample was placed in a 1.5 mL glass vial and activated (see above). Second, the vial was quickly put in the saturation chamber, and the system was evacuated. Finally,  $SO_2$  gas was generated by dripping concentrated sulfuric acid over  $Na_2SO_3$ , filling the system's volume and letting it stand for 2 h. Carefully, the vial was removed from the saturation chamber, quickly closed and taken to the required measurement.

# The fluorescence experiments

They were carried out in an Edinburgh Instruments FS5 spectrofluorometer coupled with the SC-10 solid-state sample holder. The samples were packed into quartz sample holders and positioned into the instrument. The samples were packed right after being removed from the activation and saturation processes.



**Fig. S1** Chemical and textural characterisation of CMFs a) PXRD pattern, b) FTIR spectrum, c) XPS spectrum, and d)  $N_2$  adsorption isotherm at 77K (inset: relevant surface parameters).

# Calculation of isosteric enthalpy of adsorption

Isosteric enthalpy of adsorption was calculated using the Calusius-Clapeyron (eq. S1) approach from the adsorption branch of three isotherms collected a t 298, 303 and 308 K.<sup>3</sup> The SO<sub>2</sub> isotherms were fitted to a Freundlich-Langmuir isotherm (eq. S2). Then, a Van't Hoff type plot (isosteric ln(p) vs 1/T for different n loadings, Fig. S2a) was used to obtain the  $\Delta$ Hads at low loadings (eq. S3, Fig. S3b).

$$\Delta H_{ads}(n) = -R \cdot \ln\left(\frac{p_2}{p_1}\right) \frac{T_1 T_2}{T_2 - T_1}$$
 eq. S1

 $n = \frac{a \cdot b \cdot p^c}{1 + b \cdot p^c}$  eq. S2

$$\Delta H_{ads}(n) = R \cdot slope$$

eq. S3



Fig. S2 a) Freundlich-Langmuir fits for the MCFs SO<sub>2</sub> adsorption isotherms at 298, 303 and 308 K.

Table S1 Freundlich-Lan	gmuir fitting para	meters for the fitted	d MCFs SO <sub>2</sub> adsorp	otion isotherms.
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т [К]	а	b	C	R <sup>2</sup>
298	7.343	2.356	0.398	0.9993
303	6.890	2.435	0.406	0.9997
308	6.508	2.485	0.407	0.9997



**Fig. S3** a) Plot of isosteric ln(p) vs 1/T for different *n* loadings (mmol g<sup>-1</sup>) and b) Isosteric enthalpy of adsorption of SO<sub>2</sub> for the MCFs.



Fig. S4. Comparison of  $SO_2$  uptake at 1 bar and 298 K vs surface area BET of representative inorganic adsorbents.<sup>4-10</sup>

#### **Calculation of IAST selectivity**

The binary mixture  $SO_2/CO_2$  selectivity was estimated using the pyIAST package.<sup>11</sup> First, the adsorption branch for the single-component isotherms of  $SO_2$  and  $CO_2$  collected at 298 K were fitted using the dual-site Langmuir equation (eq. S4).

$$n = M_1 \frac{K_1 p}{1 + K_1 p} + M_2 \frac{K_2 p}{1 + K_2 p}$$
 eq. 54

IAST selectivity was calculated using the following formula:

$$S = \frac{\frac{q_1}{q_2}}{\frac{y_1}{y_2}}$$
 eq. S5

where  $q_i$  is the adsorption loading and  $y_i$  the molar fraction of each gas.



Fig. S5. Dual-Site Langmuir fits of the SO<sub>2</sub> and CO<sub>2</sub> adsorption isotherms of CMFs at 298 K.

**Table S2.** Dual-Site Langmuir fitting parameters of the  $SO_2$  and  $CO_2$  adsorption isotherms of CMFs at 298 K.

Fitting parameters	SO <sub>2</sub>	CO <sub>2</sub>	
M <sub>1</sub>	0.821672	0.855777	
Kı	161.930246	1.960471	
M <sub>2</sub>	5.943032	0.057985	

K <sub>2</sub>	0.867382	547.869866
RMSE	0.033557	0.005885

Additional photoluminescence experiments



Fig. S6 Photoluminescence spectra ( $\lambda_{ex}$ =370 nm) as synthesised sample activated sample and after the exposure to several small gas/vapour molecules.



Fig. S7 Photoluminescence spectra ( $\lambda_{ex}$ =370 nm) as synthesised sample activated sample and after

the exposure to CO<sub>2</sub>.

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