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

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SO<sub>2</sub> emissions not only affect local air quality but can also contribute to other environmental issues. Developing low-cost and robust adsorbents with high uptake and selectivity is needed to reduce SO<sub>2</sub> emissions. Here, we show the SO<sub>2</sub> adsorption-desorption capacity of carbon microfibers (CMFs) at 298 K. CMFs showed a reversible SO<sub>2</sub> uptake capacity (5 mmol g<sup>-1</sup>), cyclability over ten adsorption cycles with fast kinetics and good selectivity towards SO2/CO2 at lowpressure values. Additionally, CMFs' photoluminescence response to SO<sub>2</sub> and CO<sub>2</sub> was evaluated.

Sulphur dioxide (SO<sub>2</sub>) is a highly toxic gas that is accountable for severe respiratory illnesses, even at very low concentrations. For example, exposure to small amounts of SO<sub>2</sub> (as low as 1.5 ppm) for only a few minutes can cause momentary incapacity to breathe, and at higher concentrations (above 100 ppm) can cause death.1

Different strategies to remove SO2 (flue gas desulphurisation processes FGD) have been typically used with acceptable results. These include limestone scrubbers (producing calcium sulphite)<sup>2</sup> and even SO<sub>2</sub> fixation (disulfitomercurate).<sup>3</sup> However, these procedures exhibited drawbacks associated with large amounts of wastewater, high toxicity, corrosion of pipelines, and high recuperation fees. Other SO<sub>2</sub> capture alternatives, such as silicas, zeolites, metal oxides, and activated carbons, have exhibited low SO<sub>2</sub> efficiency.<sup>4,5</sup> Although metalorganic frameworks (MOFs) have demonstrated promising SO<sub>2</sub> capture results, for example, MOF-177 and MIL-101(Cr) showing high SO<sub>2</sub> capture values, the crystal structure of these materials collapsed after being in contact with SO<sub>2</sub>.6

Most of the current research on SO2 has been narrowly focused on capturing this corrosive gas. However, the SO2 capture is not the only relevant; SO2 detection is as suitable as the capture and conversion of SO<sub>2</sub>. Efficient materials for SO<sub>2</sub> detection are required to comply with the following characteristics: (i) high chemical stability towards SO2 under more realistic conditions (60% of relative humidity), (ii) nondependency on relatively high surface areas, and (iii) high processability.6 In addition to remarkable chemical and structural stability, such "detector materials" are characterised for showing high SO<sub>2</sub> uptake at low pressure, providing feasible applicability in SO<sub>2</sub> detection devices.8 Cooper et al. demonstrated outstanding SO<sub>2</sub> capture in porous organic cages (POCs) at low pressure. 9,10 Therefore, new porous platforms have appeared as exciting alternatives to capture and detect corrosive and explosive gases. For example, Hiraoka and co-workers reported a functionalised organic nanotube with optimal selective fluorescence properties to detect liquefied petroleum gas.<sup>11</sup>

Carbon materials have been explored for SO<sub>2</sub> capture. Yi et al., tested coconut shell-based activated carbon (SAC) and coal-based activated carbon (CAC), where SAC was the best adsorbent for SO<sub>2</sub>. 12 Muñiz et al. performed thermal and chemical treatments to enhance the SO2 uptake on activated carbon fibres, and they concluded that the superficial functionalities with a basic character seem to be the most important characteristic concerning SO<sub>2</sub> capture. <sup>13</sup> Wang et al., developed a series of N-doped coal-based porous carbons (NCPCs) by calcining a mixture of anthracite, MgO, KOH and carbamide at 1073 K; their results showed that the balance between nitrogen doping content and specific surface area (microporosity) improved the number of active adsorption sites of SO<sub>2</sub>. 14 In this context, the carbon microfibers (CMFs) obtained

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by calcination of polyacrylonitrile microfibers (PANMFs)<sup>15</sup> present an opportunity for SO2 detection due to the following aspects: (i) chemical composition based on nitrogen and oxygen functional groups resulting from the polymer precursor (PAN), (ii) high microporosity controllable depending on calcination temperature, (iii) good thermal stability, and (iv) reversible gas adsorption (e.g., CO2 or CH4). Concerning nitrogen functional groups, there have been identified four groups in the CMFs: N-6 (pyridine-N), N-5 (pyrrolic-N), N-X (pyridine-N-oxide) and N-Q (quaternary-N or graphitic-N). 15 Some of these groups have improved the performance of CMFs in oxygen reduction reactions (ORR) in fuel cells16 and their gas adsorption properties (CO<sub>2</sub> and CH<sub>4</sub>).<sup>15</sup>

Textural, chemical, and structural characterisation of the CMFs have been reported previously (Fig. S1, ESI†). To CMFs were obtained by calcination of PANMFs at 1173 K; this material has a specific surface area of 731 m<sup>2</sup> g<sup>-1</sup>, a total pore volume of  $0.348 \text{ cm}^3 \text{ g}^{-1}$ , and a microporosity above 70%. An average pore size of 0.78 nm was calculated from the N<sub>2</sub> adsorption isotherm at 77 K, and 0.5 nm was estimated using the CO<sub>2</sub> adsorption isotherm at 273 K.<sup>17</sup> The CMFs average chemical composition is C: 89%, N: 6%, and O: 5%. It is important to mention that the fibrous structure of PANMFs is preserved after calcination with fibre diameters between 200 and 400 nm.

Since CMFs contain several nitrogen sites, which can be potential SO<sub>2</sub>-adsorption sites, we measured the SO<sub>2</sub> adsorption

a) 30 25 SO<sub>2</sub> uptake (mmol/g) SO<sub>2</sub> uptake (wt%) 20 des CMF@298 K - - des CMF@303 K 0.2 0.4 0.6 0.8 1.0 b) SO, uptake (mmol g<sup>-1</sup>)

Fig. 1 (a) SO<sub>2</sub> adsorption-desorption isotherms at 298, 303, and 308 K, (b) ten SO<sub>2</sub> adsorption-desorption cycles on CMFs.

at 298, 303 and 308 K (Fig. 1a). SO2 isotherms showed a type-I profile based on IUPAC18 with a small hysteresis. CMFs showed a maximum uptake of 5.2, 4.9 and 4.6 mmol g<sup>-1</sup> at 1 bar for 298, 303 and 308 K, respectively. This value is higher than several reported in the literature compared to other carbonaceous or inorganic materials in the function of superficial area BET (Fig. S4, ESI†). The three SO2 adsorption isotherms were used to calculate the isosteric enthalpy of adsorption, obtaining values around  $-30 \text{ kJ} \text{ mol}^{-1}$  (see Fig. S3, ESI†), consistent with a physisorption process and mild regeneration conditions.

Then, cyclability tests were carried out to evaluate the reusability of the material at the conditions where the highest SO<sub>2</sub> capture was obtained. Ten SO<sub>2</sub> adsorption-desorption cycles were performed at 298 K until 1 bar. The amount of  $SO_2$  captured in each cycle is stable, around 5 mmol  $g^{-1}$ (Fig. 1b). Between each cycle, a vacuum activation process was enough to desorb almost all the SO2 adsorbed, leading to the slight increase in the baseline and thus, the maximum SO<sub>2</sub> uptake in each cycle.

FTIR-ATR and SEM measurements were performed to characterise the CMFs in the SO<sub>2</sub> capture process (Fig. 2). In the three different stages during the SO2 uptake (before and after the first adsorption cycle and after ten desorption cycles indicated by pink, yellow and purple colours, respectively, in Fig. 1 and 2), the IR-ATR spectra showed the presence of ester groups between 2250 to 2000 cm<sup>-1</sup>, and coupling C-N stretching and N-H deformation modes of C-N-H groups (amide)

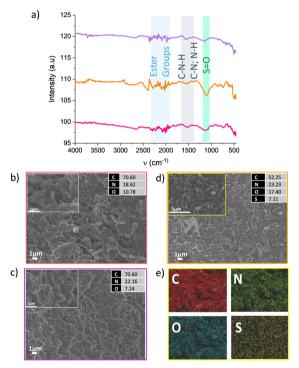


Fig. 2 (a) IR-ATR spectra at different stages according to the points marked in Fig. 1b, pristine sample (pink), after SO<sub>2</sub> uptake (yellow), and after 10 desorption cycles (violet). SEM micrographs with their EDX results on (b) pristine sample, (c) after 10 desorption cycles, (d) after SO<sub>2</sub> uptake, and (e) the EDX mapping results of the rectangular area inside panel (d).

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a)

around 1522 cm<sup>-1</sup>. For the SO<sub>2</sub>-saturated CMFs sample, a characteristic band in 1050 cm<sup>-1</sup> was identified, indicating the S=O group was present (Fig. 2a). 19,20 These results are in good agreement with the SEM micrographs and EDX analyses. Carbon microfibres morphology only changes when the SO<sub>2</sub> capture process occurs; the surface showed small globularities protruding from the fibre channels, and the EDX results showed sulphur presence of around 7 wt% and an increment of the oxygen percentage as well (Fig. 2d). The EDX mapping displayed a homogeneous distribution of C, N, O and S on the surface in the area shown inside the 5 µm scale micrograph in Fig. 2d. The sample showed the same morphology and composition before starting the cycles (Fig. 2b), with the sample pristine and after the last desorption cycle (Fig. 2c). These results indicate that the CMFs are stable against SO2 for ten adsorption-desorption cycles.

Considering that  $SO_2$  is often found as a minor component of flue gas mixtures (diluted in  $CO_2$  and/or  $N_2$ ), the separation selectivity is a crucial factor to consider. The  $SO_2/CO_2$  separation selectivity was determined employing the ideal adsorbed solution theory (IAST) using two monocomponent isotherms of  $SO_2$  and  $CO_2$  at 298 K (Fig. 3a, details on ESI†). The CMFs exhibited good selectivity values for the binary mixtures  $SO_2/CO_2$  in the low-pressure domain, 122, 118 and 110 for

1%, 5% and 10% of  $SO_2$  at 0.05 bar, respectively (Fig. 3b). The IAST selectivity result is comparable with similar superficial area BET adsorbents such as zeolite Y (180, 930 m² g $^{-1}$ ), <sup>21</sup> Mggallate (321, 576 m² g $^{-1}$ ), <sup>22</sup> Co-gallate (143, 494 m² g $^{-1}$ ), <sup>23</sup> DMOF-TM (169, 900 m² g $^{-1}$ ), <sup>23</sup> MIL-160 (128, 1170 m² g $^{-1}$ ), <sup>24</sup> Cu-ATC (114, 600 m² g $^{-1}$ ), <sup>25</sup> NbOFFIVE-Cu-TPA (78, 1179 m² g $^{-1}$ ), <sup>26</sup> Granted, the SO<sub>2</sub> uptake of CMFs falls short in front of benchmark materials. However, these results invite us to explore another application of the CMFs, SO<sub>2</sub> detection, where the reversible adsorption and selectivity are relevant.

Photoluminescence experiments were carried out on the CMFs using a  $\lambda_{\rm ex}$  = 370 nm after exposure to an SO<sub>2</sub>-saturated atmosphere (details on ESI†). The PL intensity increased by about 50% after the SO<sub>2</sub> exposure, compared to the activated sample (Fig. 4a). This switch-on emission decreased over time: after 15 min of exposure, the emission returned to the value of the reference sample. However, when the sample is not activated and has been left in contact with the environment, the signal increases, indicating that it detects other molecules, such as H<sub>2</sub>O or CO<sub>2</sub>. To evaluate this hypothesis, PL measurements were performed by saturating the CMFs with CO<sub>2</sub> and H<sub>2</sub>O separately (Fig. S6, ESI†). The results showed a positive response for carbon dioxide but not for water. The presence of specific functional groups on carbon materials as the nitrogen-

SO<sub>2</sub> saturated CMFs
As synthesised CMFs
CMFs 15 min after SO<sub>2</sub> saturation

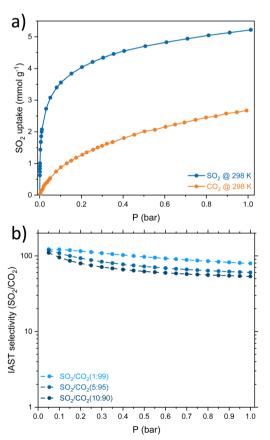


Fig. 3 (a) Comparison of the  $SO_2$  and  $CO_2$  adsorption isotherms at 298 K on CMFs. (b) IAST selectivity of  $SO_2/CO_2$  on MCFs for different concentrations of the binary mixture.

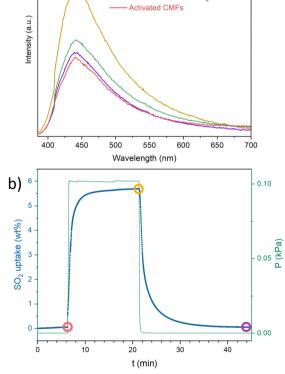


Fig. 4 (a) Photoluminescence CMFs spectra ( $\lambda_{ex}$  = 370 nm) of as synthesised, activated, SO<sub>2</sub> saturated and after the exposure to SO<sub>2</sub> samples. (b) Profile of adsorption–desorption kinetics of SO<sub>2</sub> on CMFs (gravimetric experiment with controlled SO<sub>2</sub> atmosphere).

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bearing active sites in the CMFs (in the form of NH<sub>2</sub>, for example, where nitrogen acts as an electron donor) may enhance the interaction with SO2 and the resulting photoluminescent response. The interaction between these gases with free electron pairs favours light absorption and subsequent emission for detection.<sup>27</sup> For the SO<sub>2</sub> interaction, the observed reversibility agrees with the observed adsorption-desorption kinetics of SO<sub>2</sub> obtained by gravimetric experiments (Fig. 4b). However, even though a similar PL intensity was observed for CO<sub>2</sub> exposed sample compared to SO<sub>2</sub>, the PL emission of the CO<sub>2</sub> exposed sample remained after several hours, indicating a slow desorption of this gas molecule (Fig. S7, ESI†).

In summary, SO<sub>2</sub> adsorption-desorption capacity at room temperature and 1 bar of CMFs was around 5 g mol<sup>-1</sup>. It maintained good chemical and morphological stability during 10 adsorption-desorption cycles of SO<sub>2</sub> and a good SO<sub>2</sub>/CO<sub>2</sub> selectivity, achieving a reasonable degree of reuse. When evaluating the photoluminescence of the material, it was determined that it can detect SO<sub>2</sub> and CO<sub>2</sub> but not H<sub>2</sub>O and that SO<sub>2</sub> desorption is faster than CO2. CMFs may be functionalised to improve their textural properties, SO<sub>2</sub> uptake and selectivity overall.

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### Conflicts of interest

There are no conflicts to declare.

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