



# Sulfate ionic liquids impregnated 2D boron nitride nanosheets for trace SO<sub>2</sub> capture with high capacity and selectivity

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## ABSTRACT

Owing to the abundant ionic sites and good molecular recognition ability of ionic liquids (ILs), the impregnation of ILs on support materials is an attractive strategy for trace SO<sub>2</sub> capture with both desired capacity and high selectivity. Herein, we successfully prepared a kind of hexagonal boron nitride (*h*-BN) nanosheets impregnated sulfate functionalized ILs tetramethylethylenediamine ethylsulfate ( $x$ [TMEDA][DES]@BN,  $x$  = mass ratio) for capture of low-concentration SO<sub>2</sub>. It is found that the low-concentration SO<sub>2</sub> uptakes of 1.5[TMEDA][DES]@BN were extremely high, with the amount of 2.3 mmol g<sup>-1</sup> at 293.2 K and 0.01 bar, and 0.82 mmol g<sup>-1</sup> at 293.2 K and 0.002 bar. Meanwhile, 1.5[TMEDA][DES]@BN showed a very fast SO<sub>2</sub> adsorption rate and reached an unprecedented SO<sub>2</sub>/CO<sub>2</sub> selectivity (2714) for the mixture of 1% SO<sub>2</sub> and 99% CO<sub>2</sub>. Finally, dynamic column breakthrough tests further confirmed the excellent separation performance and good reversibility of 1.5[TMEDA][DES]@BN in deeply removing 2000 ppm SO<sub>2</sub> in the mixture of SO<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>.

## 1. Introduction

Sulfur dioxide (SO<sub>2</sub>) released from the burning of low-grade coal and fuel is unfavorable to human health and the environment [1]. The excessive emission of low concentration SO<sub>2</sub> (such as 1000–3000 ppm) would cause serious concerns such as heavy smog and acid rain. Nowadays, various kinds of flue gas desulfurization (FGD) techniques are applied for the removal of SO<sub>2</sub> from flue gas. However, there still exist many inherent drawbacks in these FGDs, such as low efficiency, huge energy consumption, and production of sulfur-containing solid waste. Therefore, the selective elimination of trace SO<sub>2</sub> with high efficiency and excellent reversibility is highly demanded and desirable.

Ionic liquids (ILs), as a type of spotlighting gas absorbents, have been widely studied in various acid gas captures such as CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>x</sub>, owing to their specific properties such as negligible vapor pressure, good solubility, and designable structure [2–4]. Many kinds of ILs were found and considered to be excellent absorbents for highly efficient absorption of acid gas, especially SO<sub>2</sub> capture [5,6]. However, the homogeneous ILs absorbents usually have the intrinsic nature of high viscosity, which tends to cause poor mass/heat transport and insufficient desorption of acid gas [6,7]. To overcome these problems, many efforts have been made to explore the immobilization of ILs on various porous support

materials, where the supported ILs not only retain the natural features of ILs, but also possess the advantages of porosity. Till now, various porous materials such as silica gels, porous carbons, metal organic frameworks (MOFs), and zeolite have widely been reported for supporting ILs [8–12].

Recently, Zhang et al. [13] demonstrated that the composite material of one-dimensional (1D) mesoporous MCM-41 supported an IL, tetramethylguanidinium lactate, showed an SO<sub>2</sub> capacity of 3.48 mmol g<sup>-1</sup> at 1.0 bar. After that, Wang et al. [14] reported that imidazolium tetrazolate IL functionalized three-dimensional (3D) mesoporous FDU-12 materials could be used as great adsorbents for SO<sub>2</sub> uptake with 8.19 mmol g<sup>-1</sup> at 1.0 bar. However, it is well known that the concentration of SO<sub>2</sub> in flue gas is significantly less than the CO<sub>2</sub> concentration (e.g., 2000 ppm SO<sub>2</sub> vs. 10–15 v/v% CO<sub>2</sub>). Most materials supported ILs reported so far exhibited very low capacities for low-concentration SO<sub>2</sub> capture, and thus could not efficiently remove trace SO<sub>2</sub> in flue gas [9,15–17].

So far, hexagonal boron nitride (*h*-BN) nanosheets has attracted increasing interests because of its two-dimensional (2D) layer-structure and high specific surface area [18,19]. There are some researches on the utilization of *h*-BN nanosheets for efficient adsorption of acidic gas such as CO<sub>2</sub> and SO<sub>2</sub> [20,21]. It is thus clear that *h*-BN will be applied as a

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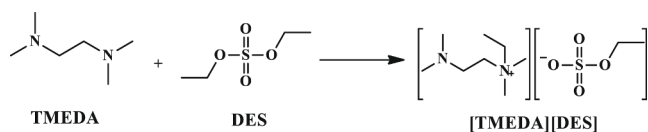
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**Scheme 1.** The one-pot procedure of synthesis of sulfate ionic liquids.

support for immobilization and high-dispersion of ILs, which can enhance  $\text{SO}_2$  adsorption capacity and desulphurization efficiency. Herein, a kind of *h*-BN nanosheets supported sulfate ILs was prepared and used as an efficient adsorbent for trace  $\text{SO}_2$  capture with both high uptake and superior selectivity simultaneously. Detail investigation indicated that trace  $\text{SO}_2$  uptake capacities of *h*-BN nanosheets supported sulfate ILs were extremely high, with the amount of  $2.3 \text{ mmol g}^{-1}$  at 293.2 K and 0.01 bar, and  $0.82 \text{ mmol g}^{-1}$  at 293.2 K and 0.002 bar. Also, the  $\text{SO}_2/\text{CO}_2$  selectivity could reach as high as 2714 for the mixture of 1%  $\text{SO}_2$  and 99%  $\text{CO}_2$ . Furthermore, the excellent separation performance and good reversibility of 2000 ppm  $\text{SO}_2$  capture were confirmed through column breakthrough tests with the  $\text{SO}_2/\text{N}_2/\text{CO}_2$  mixed gas.

## 2. Experimental

### 2.1. Materials

Tetramethylethylenediamine (TMEDA, >99%), diethyl sulfate (DES, >99%), urea (99.5%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Boric acid (99.5%), ethanol (>99%), methanol (>99%), and ethyl acetate (>99%) were purchased by Tianjin Fuchen Chemical Reagent Co., Ltd.  $\text{SO}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  were purchased with a grade of 99.99% from Jiangxi Huahong Gas Co., Ltd. Other chemicals were high purity and used without further purification.

### 2.2. Synthesis of sulfate ionic liquids

In a typical run, a solution of TMEDA (0.01 mol) in ethyl acetate (20 mL) was poured into a round-bottomed flask. Then DES (0.01 mol) slowly dripped into the flask. The mixture was further stirred for 12 h in an ice-water bath. After reaction, the system formed a liquid–liquid biphas, and the lower phase containing sulfate ILs could be easily separated by simple decantation. Then the lower phase was further dried in an oven under vacuum at 343 K for 18 h to eliminate other solvents and residues. Finally, the sulfate IL was obtained and denoted as [TMEDA][DES] (Scheme 1). The water content of [TMEDA][DES] was measured to be less than 0.05 wt% by the Karl Fisher titration, and the purity of [TMEDA][DES] was found to be 99.2 wt% confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Fig. S1–2, Supplementary data).

### 2.3. Preparation of $x[\text{TMEDA}][\text{DES}]/\text{BN}$ adsorbent

Firstly, *h*-BN nanosheets were prepared in accordance with the previous literature [18,19]. Then, the sulfate IL impregnated *h*-BN nanosheets ( $x[\text{TMEDA}][\text{DES}]/\text{BN}$ ,  $x$  = mass ratio) were prepared and obtained by the mixing of these two precursors with different mass ratios. The detailed procedure was as follows: In a typical run, [TMEDA][DES] (1.0 g), *h*-BN (1.0 g), and ethanol (40 mL) were charged into a flask at 298.2 K, respectively. The mixture was then put into a sonic bath for 1 h to obtain the suspension. After that, the solvent ethanol in the suspension was distilled by rotary evaporation. Thus, the white solid was further dried in an oven under vacuum at 343.2 K for 6 h to obtain the sample  $1.0[\text{TMEDA}][\text{DES}]/\text{BN}$ .

The preparation of the other three samples  $0.5[\text{TMEDA}][\text{DES}]/\text{BN}$ ,  $1.5[\text{TMEDA}][\text{DES}]/\text{BN}$ , and  $2.0[\text{TMEDA}][\text{DES}]/\text{BN}$  were prepared in accordance with the above-mentioned process excepting the mass ratio of 0.5:1, 1.5:1, and 2:1.

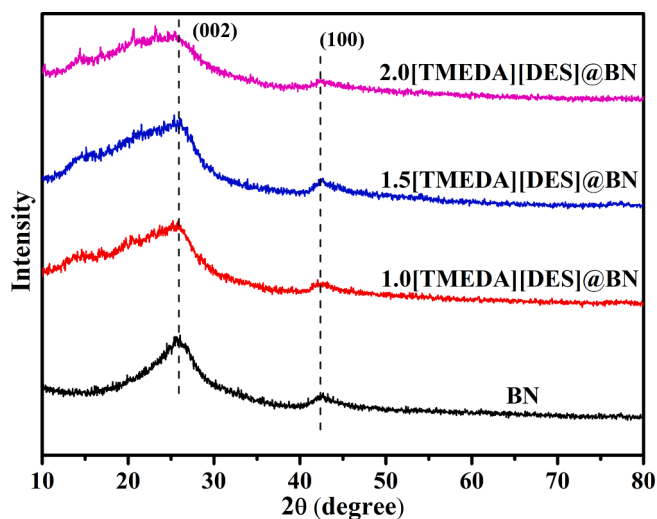


**Fig. 1.** XRD patterns of  $x[\text{TMEDA}][\text{DES}]/\text{BN}$  and *h*-BN samples.

### 2.4. Characterizations

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were characterized on a Bruker Avance III spectrometer. XRD patterns of samples were carried out on a Rigaku RINT-2200 X-ray diffractometer with a scanning rate of 3 K/min. Transmission electron microscope (TEM) images were recorded on a JEOL JEM-2100. Scanning electron microscope (SEM) images were obtained using an S-3400 electron microscope. Fourier transform infrared (FTIR) spectra were carried out on a Nicolet 6700 spectrometer.  $\text{N}_2$  adsorption–desorption analysis was carried out on a Micromeritics TriStar II 3020 apparatus. The thermostability of adsorbents was determined by PerkinElmer Diamond TG/DTA apparatus under flowing  $\text{N}_2$ . The chemical structures and surface electronic states of adsorbents were determined by X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS SUPRA).

### 2.5. Pure gas adsorption

The experiments for adsorption of  $\text{SO}_2$  at 293.2–313.2 K were carried out using a home-made apparatus (Fig. S3, Supplementary data) that was reported in our previous studies [22,23]. The detailed experimental processes are listed in the Supplementary data. The  $\text{SO}_2$  uptake capacity was determined through the pressure changes of the two chambers. Also, Micromeritics TriStar 3020 apparatus was employed to record the adsorption isotherm of  $\text{N}_2$  and  $\text{CO}_2$  at 298.2 K. The ideal adsorption solution theory (IAST) selectivity of  $\text{SO}_2/\text{N}_2$  and  $\text{SO}_2/\text{CO}_2$  was then calculated based on the model equation proposed by Myers et al [24,25].

### 2.6. Trace $\text{SO}_2$ adsorption

The homemade apparatus for trace  $\text{SO}_2$  breakthrough tests at 303.2 K and 1.0 bar was shown in Fig. S4 in the Supplementary data. The simulated flue gas is composed of 0.2%  $\text{SO}_2$  (2000 ppm), 84.8%  $\text{N}_2$ , and 15%  $\text{CO}_2$ . In a typical run, a given amount of  $1.5[\text{TMEDA}][\text{DES}]/\text{BN}$  adsorbent was added and placed in a quartz tube at a certain temperature under the following He. Then the He flow was treated by a flowing simulated flue gas containing  $\text{SO}_2/\text{CO}_2/\text{N}_2$  at a rate of  $23.53 \text{ mL min}^{-1}$ . The composition of outlet simulated flue gas was monitored and detected by mass spectrometry. For the recycle test,  $\text{SO}_2$ -loaded  $1.5[\text{TMEDA}][\text{DES}]/\text{BN}$  was heated to 323.2 K for releasing  $\text{SO}_2$  with the He flow for 2 h. The regenerated  $1.5[\text{TMEDA}][\text{DES}]/\text{BN}$  was employed for the next breakthrough experiments.

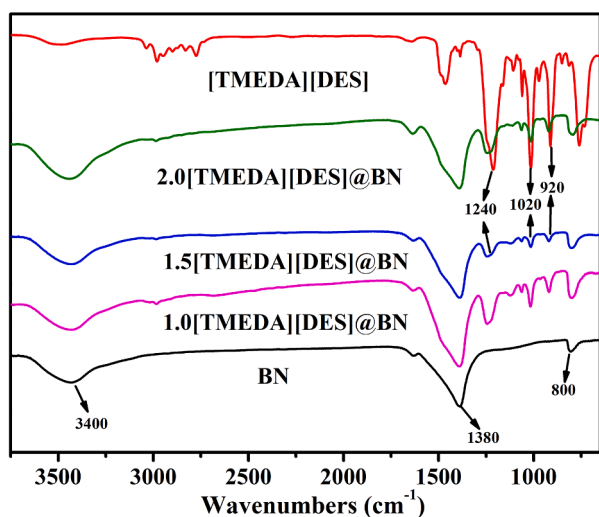


Fig. 2. FTIR spectra of *h*-BN, [TMEDA][DES], and *x*[TMEDA][DES]@BN samples.

### 3. Results and discussion

#### 3.1. Characterization results

Fig. 1 illustrates the XRD patterns of *x*[TMEDA][DES]@BN adsorbents and precursor *h*-BN nanosheets. It is observed that two diffraction peaks appeared at  $25.8^\circ$  and  $42.6^\circ$ , which ascribes to the (002) and (100) crystalline levels diffraction of *h*-BN nanosheets [26]. After

impregnation with [TMEDA][DES], the three samples 1.0[TMEDA][DES]@BN, 1.5[TMEDA][DES]@BN, and 2.0[TMEDA][DES]@BN also retained these two characteristics peaks. This shows that the introduction of sulfate IL does not destruct the skeleton of *h*-BN nanosheets. Moreover, it is showed that the XRD peaks had gradually broadened when the amount of sulfate ILs increased. This result implies that the  $\pi$ - $\pi$  stacking interaction in *h*-BN nanosheets was weakened because of the entry of sulfate ILs into the interlayer of *h*-BN. This similar phenomenon is well consistent with a previous literature reported by Huang K. et al [26].

Fig. 2 illustrates the FTIR spectra of *h*-BN nanosheets support, [TMEDA][DES] IL, and *x*[TMEDA][DES]@BN samples. The *h*-BN nanosheets support exhibited two typical peaks at 1380 and 800  $\text{cm}^{-1}$ , ascribing to the B-N in-plane vibration and B-N-B stretching vibration, respectively [26,27]. The peak around 3400  $\text{cm}^{-1}$  was also corresponding to the N-H vibration in *h*-BN nanosheets defect site [28,29]. The characteristics peaks of [TMEDA][DES] IL were found around 920, 1020, and 1240  $\text{cm}^{-1}$ , attributing to the S-O, S=O, and C-N vibrations, respectively [30]. Overall, all these six typical peaks were similarly observed in the *x*[TMEDA][DES]@BN samples. This demonstrates the successful impregnation of sulfate ILs monomer on the support material *h*-BN nanosheets.

Fig. 3 illustrates the SEM and TEM images of 1.5[TMEDA][DES]@BN and *h*-BN nanosheets, respectively. It is found that the support *h*-BN nanosheets displayed typical few-layered and folded structures (Fig. 3a, b, c and Fig. S5 in Supplementary data). After the introduction of [TMEDA][DES] IL, the size of *h*-BN nanosheets had no obvious change but *h*-BN nanosheets were gathered and stacked obviously due to the coating of viscous sulfate IL (Fig. 3d). All these results demonstrate that the sulfate IL [TMEDA][DES] was favorably coated on the surface layer

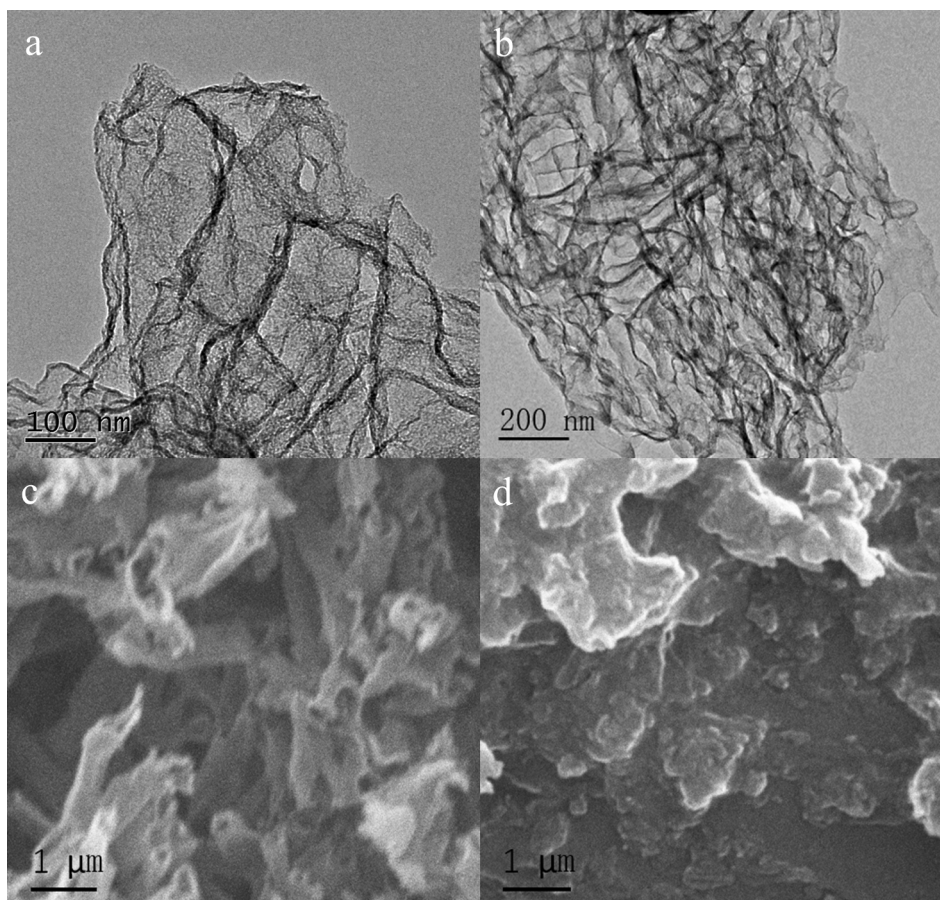


Fig. 3. TEM images of *h*-BN (a,b), and SEM images of *h*-BN (c) and 1.5[TMEDA][DES]@BN (d).

**Table 1**

Specific surface area, pore volume, and state of *h*-BN and [TMEDA][DES]@BN samples.

| Sample             | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | $V_t$ ( $\text{cm}^3 \text{g}^{-1}$ ) | State      |
|--------------------|-------------------------------------------------|---------------------------------------|------------|
| <i>h</i> -BN       | 264                                             | 0.62                                  | Dry powder |
| 0.5[TMEDA][DES]@BN | 44                                              | 0.27                                  | Dry powder |
| 1.0[TMEDA][DES]@BN | 32                                              | 0.17                                  | Dry powder |
| 1.5[TMEDA][DES]@BN | 18                                              | 0.09                                  | Dry powder |
| 2.0[TMEDA][DES]@BN | 10                                              | 0.03                                  | Dry powder |

of *h*-BN nanosheets.

Subsequently, the as-obtained  $x$ [TMEDA][DES]@BN and *h*-BN nanosheets were carried out by  $\text{N}_2$  adsorption–desorption analysis (Fig. S6–7, Supplementary data). Then, the pore volumes and specific surface areas of these samples are listed in Table 1. It is indicated that the *h*-BN nanosheets showed a typical type-IV isotherm with a specific surface area value of  $264 \text{ m}^2 \text{g}^{-1}$ . After impregnation with a certain amount of [TMEDA][DES] IL, the  $\text{N}_2$  sorption capacity of 1.5[TMEDA][DES]@BN was found to be very low. The surface area of 1.5[TMEDA][DES]@BN was calculated to be  $18 \text{ m}^2 \text{g}^{-1}$ , as well as its pore volume reached as small as  $0.09 \text{ cm}^3 \text{g}^{-1}$ . This finding implies that the pore volume of *h*-BN nanosheets was practically filled by the [TMEDA][DES] IL, contributing to a very low  $\text{N}_2$  uptake. In addition, thermogravimetric analysis of [TMEDA][DES] IL,  $x$ [TMEDA][DES]@BN, and *h*-BN nanosheets were further investigated. As shown in Fig. S8, the decomposition starting temperature of sulfate IL [TMEDA][DES] was higher than 450 K, demonstrating its good thermal stability. Also, the support *h*-BN nanosheets and four  $x$ [TMEDA][DES]@BN samples were found to be highly stable under the temperature below 480 K (Fig. S9, Supplementary data). In addition, the thermal stability of 1.5[TMEDA][DES]@BN after  $\text{SO}_2$  and  $\text{CO}_2$  adsorption–desorption cycles was studied. It is found

that compared with the fresh sample, the reused 1.5[TMEDA][DES]@BN remained good stability after undergoing the atmosphere with  $\text{SO}_2$  and  $\text{CO}_2$  (Figs. S10–11, Supplementary data). Although the sulfate anion ILs exhibited a relatively high stability under the condition of simulated flue gas in short runs, it should be noted that most industrial gas streams often contain various gases such as  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{N}_2$ . The stability for actual industrial scale would be indefinite and required to explore in longtime runs.

### 3.2. $\text{SO}_2$ adsorption performance

Firstly, the  $\text{SO}_2$  adsorption capacities of  $x$ [TMEDA][DES]@BN were measured and the results are shown in Fig. 4a. It is indicated that  $\text{SO}_2$  uptake capacity increased sharply at low partial pressures, implying that  $\text{SO}_2$  has chemical adsorption in  $x$ [TMEDA][DES]@BN. Also, the  $\text{SO}_2$  adsorption capacity first increased significantly but then increased slightly with the increase of impregnation amount of sulfate ILs. For example, 0.5[TMEDA][DES]@BN and 1.5[TMEDA][DES]@BN exhibited  $\text{SO}_2$  uptakes of 3.5 and  $7.6 \text{ mg g}^{-1}$  at 293.2 K and 1.0 bar, respectively. Fig. 4b shows the effect of adsorption temperature on the performance of 1.5[TMEDA][DES]@BN. It is indicated that the  $\text{SO}_2$  uptake capacity decreased obviously with increasing temperature, enabling an exothermic adsorption process. According to the relationship between  $\text{SO}_2$  adsorption capacity and temperature, the isosteric heats were found to be  $-60$  to  $-40 \text{ kJ/mol}$  for  $\text{SO}_2$  adsorption on 1.5 [TMEDA][DES]@BN (Fig. S12, Supplementary data). This range of  $\text{SO}_2$  adsorption heat values reconfirms the chemical interaction between  $\text{SO}_2$  and 1.5[TMEDA][DES]@BN.

Subsequently, the FTIR spectra of load- $\text{SO}_2$  1.5[TMEDA][DES]@BN was further measured. It is seen from Fig. 4c that three new peaks at 765, 984, and  $1240 \text{ cm}^{-1}$  were observed for captured  $\text{SO}_2$ , which is ascribed

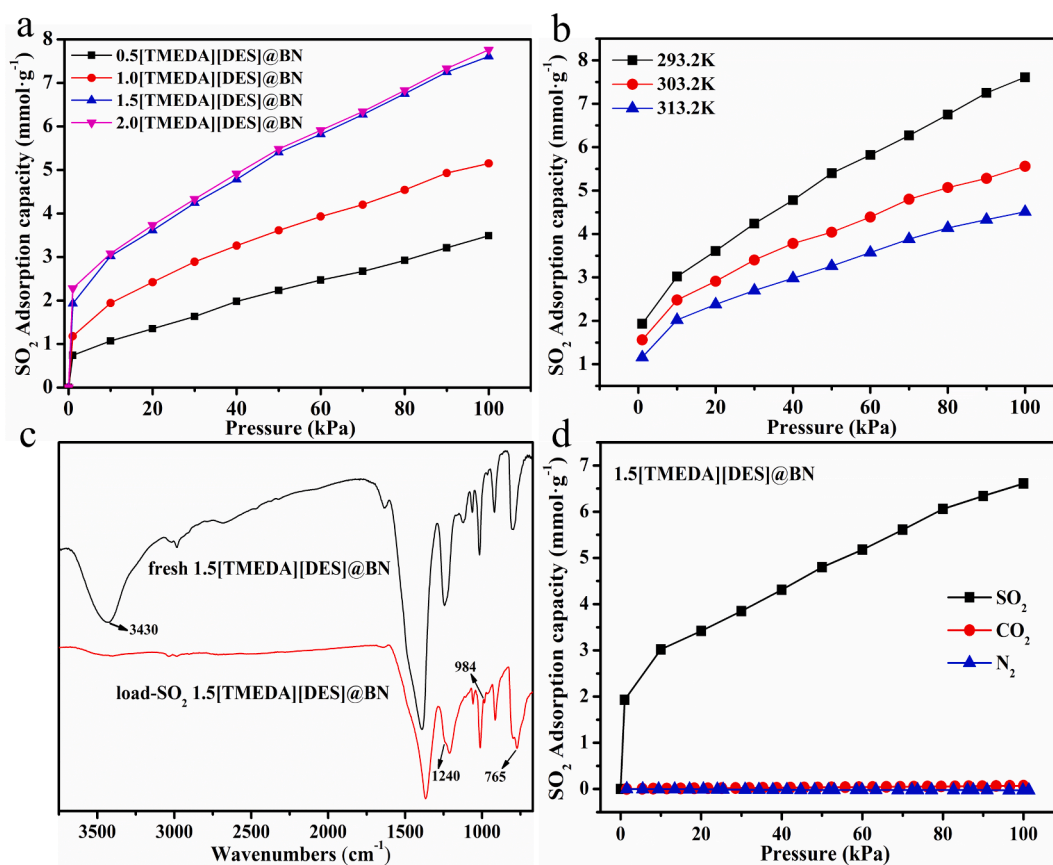


**Fig. 4.**  $\text{SO}_2$  adsorption isotherms of  $x$ [TMEDA][DES]@BN at 293.2 K (a);  $\text{SO}_2$  adsorption isotherms of 1.5[TMEDA][DES]@BN at different temperatures (b); FTIR spectra of fresh and  $\text{SO}_2$ -loaded 1.5[TMEDA][DES]@BN (c);  $\text{SO}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  adsorption isotherms of 1.5[TMEDA][DES]@BN at 293.2 K and 1.0 bar (d).

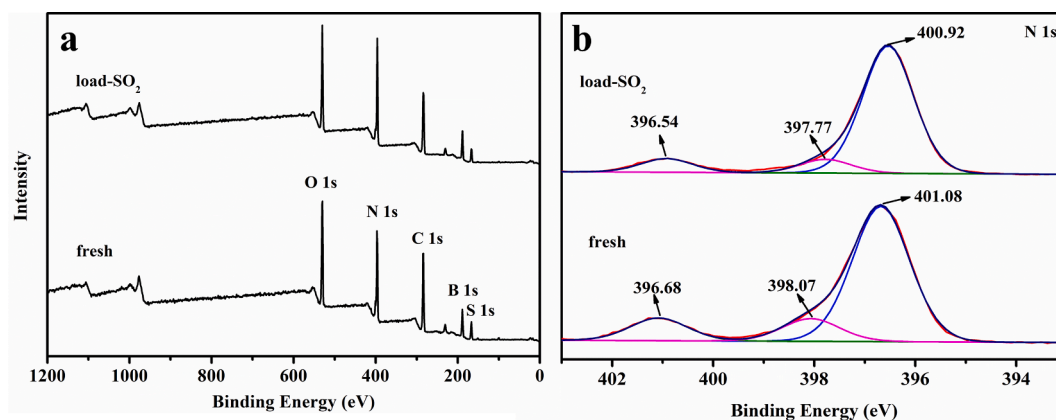


Fig. 5. XPS survey spectra (a) and N 1 s spectra (b) of 1.5[TMEDA][DES]@BN before and after SO<sub>2</sub> adsorption.

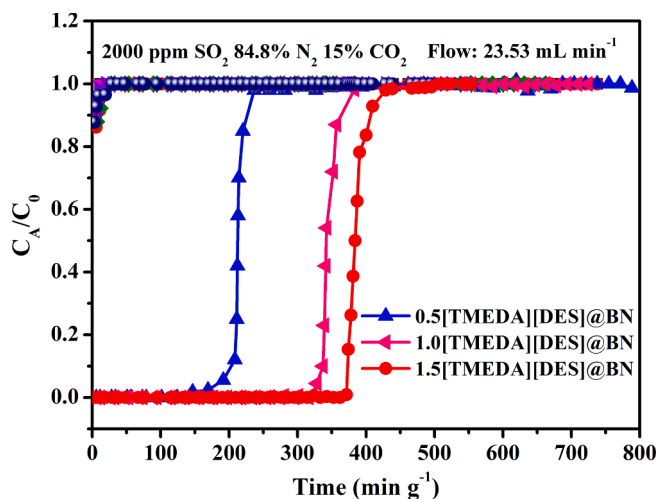


Fig. 6. Experimental column breakthrough curves for trace 2000 ppm SO<sub>2</sub> separation with *x*[TMEDA][DES]@BN adsorbents at 303.2 K and 1.0 bar.

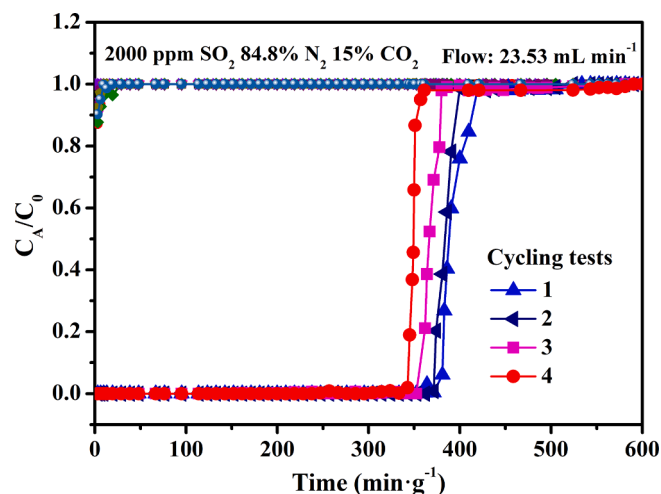


Fig. 7. Cycling column breakthrough tests for SO<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub> (2000 ppm SO<sub>2</sub>) separations with 1.5[TMEDA][DES]@BN at 303.2 K and 1.0 bar.

to the S–O vibration, the S=O symmetric and asymmetrical vibrations, respectively [31]. Moreover, XPS characterization for 1.5[TMEDA][DES]@BN before and after SO<sub>2</sub> adsorption was performed to clarify the adsorption active site (Fig. 5). For fresh 1.5[TMEDA][DES]@BN, the N 1 s XPS spectra were deconvoluted into three peaks and the peaks at the binding energies of 396.68 eV, 398.07 eV, and 401.08 eV can be assigned to N–B of *h*-BN, N–C of tertiary amine, and quaternary N, respectively. For SO<sub>2</sub>-loaded 1.5[TMEDA][DES]@BN, it is found that the binding energy of tertiary N decreased to 397.77 eV (a reduction of 0.3 eV) after SO<sub>2</sub> adsorption. However, the binding energies of N–B and quaternary N only decreased by 0.14 and 0.16 eV, respectively. This finding shows that N–C of tertiary amine is much more likely to be the key adsorption site on 1.5[TMEDA][DES]@BN for SO<sub>2</sub> capture. In addition, Fig. 4d shows the N<sub>2</sub> and CO<sub>2</sub> uptakes by 1.5[TMEDA][DES]@BN at 293.2 K and 1.0 bar. It is demonstrated that 1.5[TMEDA][DES]@BN almost excluded the adsorption of N<sub>2</sub> and CO<sub>2</sub>. CO<sub>2</sub> and N<sub>2</sub> uptakes only reached 0.07 and 0.005 mmol g<sup>−1</sup>, respectively, which is a result of weak acidity of CO<sub>2</sub> and inertia of N<sub>2</sub>. Then the SO<sub>2</sub>/CO<sub>2</sub> selectivity of 1.5[TMEDA][DES]@BN was calculated on the basis of the ideal adsorbed solution theory (IAST) [24,25]. As shown in Fig. S13 in the Supplementary data, 1.5[TMEDA][DES]@BN displayed excellent IAST selectivities of SO<sub>2</sub>/CO<sub>2</sub> (2714–109) in the SO<sub>2</sub> molar fraction range 0.01–0.9. An ultrahigh SO<sub>2</sub>/CO<sub>2</sub> selectivity for 0.01 bar SO<sub>2</sub> was found to be 2714 at 293.2 K and 1.0 bar. Therefore, 1.5[TMEDA][DES]@BN has a good potential for highly selective trace SO<sub>2</sub> capture in the FGD process.

### 3.3. Trace SO<sub>2</sub> capture performance

It is known that the concentration of SO<sub>2</sub> in industrial flue gas (e.g. coal burning flue gas) ranges from 500 to 3000 ppm [32]. To evaluate the practical capability of *x*[TMEDA][DES]@BN for trace SO<sub>2</sub> capture, breakthrough experiments were conducted from a simulated flue gas containing 2000 ppm SO<sub>2</sub> at 303.2 K and 1.0 bar. Fig. 6 shows 2000 ppm SO<sub>2</sub> separation performance of *x*[TMEDA][DES]@BN samples. It is found that the breakthrough performance of SO<sub>2</sub> on 1.5[TMEDA][DES]@BN exceeded that on 0.5[TMEDA][DES]@BN and 1.0[TMEDA][DES]@BN, which agrees with the higher saturated SO<sub>2</sub> adsorption capacities of 1.5[TMEDA][DES]@BN (1.9 mmol g<sup>−1</sup>) than 0.5[TMEDA][DES]@BN (1.2 mmol g<sup>−1</sup>) and 1.0[TMEDA][DES]@BN (0.8 mmol g<sup>−1</sup>) at 293.2 K and 0.01 bar (Fig. 4a). Moreover, the breakthrough of 2000 ppm SO<sub>2</sub> on 1.5[TMEDA][DES]@BN was found to be very slow and the retention time was ~390 min g<sup>−1</sup>. By contrast, the breakthrough of N<sub>2</sub> and CO<sub>2</sub> rapidly eluted with 20 min g<sup>−1</sup>. Therefore, 1.5[TMEDA][DES]@BN enables highly selective adsorption of 2000 ppm SO<sub>2</sub> with clean CO<sub>2</sub> and N<sub>2</sub> eluted from the column bed.

Furthermore, cycling breakthrough tests were conducted to evaluate the recyclability of 1.5[TMEDA][DES]@BN for 2000 ppm SO<sub>2</sub> capture. The results are shown in Fig. 7. It is indicated that the breakthrough performance of 1.5[TMEDA][DES]@BN for 2000 ppm SO<sub>2</sub> did not reduce obviously, and the retention time still retained ~350 min g<sup>−1</sup> after four cycles. It is because little parts of SO<sub>2</sub> uptake by chemical interaction would hard to desorb at 323.2 K for releasing SO<sub>2</sub> under

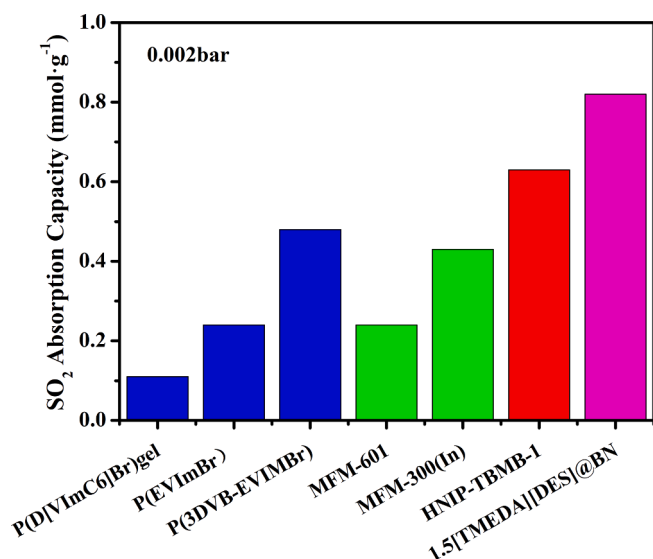


Fig. 8. SO<sub>2</sub> adsorption performance of various adsorbents at 0.002 bar SO<sub>2</sub> partial pressure.

flowing He purge. However, it is indicated that the FTIR spectra of regenerated 1.5[TMEDA][DES]@BN were nearly the same as the fresh and no characteristic peaks for captured SO<sub>2</sub> was found in the recycled 1.5 [TMEDA][DES]@BN (Fig. S14, Supplementary data). There were also no changes in the morphology and structure of *h*-BN before and after SO<sub>2</sub> adsorption-desorption cycle, further showing the good stability of *h*-BN structure (Fig. S15, Supplementary data). All these above results demonstrate that the 1.5[TMEDA][DES]@BN material has excellent stability and recyclability for 2000 ppm SO<sub>2</sub> adsorption. However, the simulated flue gas, after all, is a little different from the actual industrial flue gas. The industrial scale performance in longtime runs should be further studied to resolve the potential limitations and more investigations are underway in our laboratory.

### 3.4. Comparison of SO<sub>2</sub> adsorption capacity and rate

The comparison of 2000 ppm SO<sub>2</sub> adsorption capacity of 1.5 [TMEDA][DES]@BN and other materials adsorbents in literature were summarized and shown in Fig. 8. It can be seen that 1.5[TMEDA][DES]@BN exhibited considerable SO<sub>2</sub> uptake as high as 0.82 mmol g<sup>-1</sup> even at a very low SO<sub>2</sub> pressure of 0.002 bar, outperforming most of the reported ionic polymers such as P(DVImC6Br) gel, P(EVImBr), P(3DVB-EVImBr), and HNIP-TBMB-1 [33,34]. Moreover, the 2000 ppm SO<sub>2</sub> uptake capacity of 1.5[TMEDA][DES]@BN also exceeded the adsorption

capacity of MOFs materials MFM-601 (0.24 mmol g<sup>-1</sup>) [35] and MFM-300(In) (0.43 mmol g<sup>-1</sup>) [36], and were analogous to the benchmarking materials P(Ph-2MVIm-Br) (1.13 mmol g<sup>-1</sup>) and P(Ph-3MVIm-Br) (1.20 mmol g<sup>-1</sup>) [37]. The uniform dispersion of sulfate IL on the support *h*-BN nanosheets affords the abundant ionic sites and thus results in the superior SO<sub>2</sub> uptake capacity even at 0.002 bar SO<sub>2</sub> partial pressure.

Fig. 9 shows the SO<sub>2</sub> adsorption rate on *h*-BN nanosheets, [TMEDA][DES] IL, and x[TMEDA][DES]@BN at 293.2 K and 1.0 bar. It is seen from Fig. 9a that pure *h*-BN nanosheets support showed a SO<sub>2</sub> uptake capacity of only 2.4 mmol g<sup>-1</sup> but had a rapid SO<sub>2</sub> capture rate within 1 min, indicating that the 2D architecture can effectively promote the adsorption rate of SO<sub>2</sub>. Thereafter, *h*-BN nanosheets supported sulfate ILs 1.5[TMEDA][DES]@BN not only showed an adsorption saturation capacity of 7.6 mmol g<sup>-1</sup>, but also had a fast SO<sub>2</sub> uptake rate less than 5 min at 293.2 K and 1.0 bar. In particular, the SO<sub>2</sub> uptake of 1.5 [TMEDA][DES]@BN could reach ~85% of saturated capacity after a short time of 1 min. Thus, the outstanding SO<sub>2</sub> adsorption rate of 1.5 [TMEDA][DES]@BN is much faster than many reported porous materials such as P(Ph-4MVIm-Br) (10 min) [37], PI-COF-m60 (20 min) [17], and NPC-1-900 (30 min) [38]. However, the neat [TMEDA][DES] IL possessing high viscosity led to an extremely slow absorption rate with a saturation time of >200 min, though the adsorption saturation capacity was 11.5 mmol g<sup>-1</sup> at 293.2 K and 1.0 bar (Fig. 9b). Therefore, it is demonstrated that 1.5[TMEDA][DES]@BN possessed both 2D architecture from *h*-BN nanosheets and abundant ionic sites from [TMEDA][DES] IL, and thereby exhibited both large SO<sub>2</sub> uptake and fast adsorption rate.

## 4. Conclusions

In summary, the *h*-BN nanosheets supported sulfate functionalized ILs were prepared, characterized, and served as highly efficient adsorbents for trace SO<sub>2</sub> capture. It is found that the 1.5[TMEDA][DES]@BN displayed considerably high SO<sub>2</sub> capacity, with the amount of 2.3 mmol g<sup>-1</sup> at 293.2 K and 0.01 bar, and 0.82 mmol g<sup>-1</sup> at 293.2 K and 0.002 bar, which is much better than most of known adsorbents reported in the literature. Moreover, the 1.5[TMEDA][DES]@BN showed a very fast SO<sub>2</sub> adsorption rate with a saturation time of less than 5 min, as well as reached a superior SO<sub>2</sub>/CO<sub>2</sub> selectivity (2714) for the mixture of 1% SO<sub>2</sub> and 99% CO<sub>2</sub>. In addition, dynamic column breakthrough tests further confirmed the excellent separation performance and good reversibility of 1.5[TMEDA][DES]@BN in deeply removing 2000 ppm SO<sub>2</sub> in the mixture of SO<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub>. Therefore, it is believed that the impregnation of ILs on 2D *h*-BN nanosheets to produce new adsorbents is an operative strategy for highly efficient separation and purification of trace SO<sub>2</sub>.

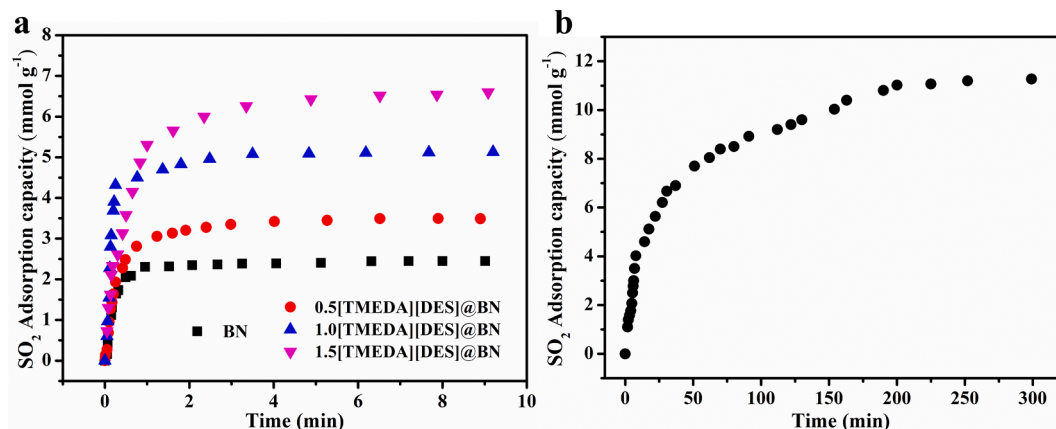


Fig. 9. SO<sub>2</sub> adsorption rate for *h*-BN and x[TMEDA][DES]@BN (a); [TMEDA][DES] (b) at 293.2 K and 1.0 bar.

## CRediT authorship contribution statement

**Wen-Qiang Gong:** Writing - review & editing. **Xian-Lu Wu:** Writing - review & editing. **Zhang-Min Li:** Writing - review & editing. **Yan Zhou:** Writing - review & editing, Supervision. **Wenshuai Zhu:** Writing - review & editing, Supervision. **Duan-Jian Tao:** Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2021.118824>.

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