Research Article

A new class of porous materials for efficient CO₂ separation: Ionic liquid/graphene aerogel composites

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ABSTRACT

Here, we report a new post-synthesis modification strategy for functionalizing reduced graphene aerogels (rGAs) towards an exceptional CO₂ separation performance. 1-*N*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) was impregnated on a rGA, prepared by reducing GA at 700 °C, at various ionic liquid (IL) loadings of 5, 10, 30, and 50 wt%. The resulting composites were characterized in deep detail by X-ray photoelectron spectroscopy, X-ray diffraction, N₂ physical adsorption measurements, scanning electron microscopy, Fourier transform infrared and Raman spectroscopies, and thermogravimetric analysis. Results indicated the presence of interactions between the rGA surface and the anion of the IL, potentially improving the CO₂ affinity. Volumetric gas adsorption measurements using these materials showed that the deposition of [BMIM][PF₆] on rGA surface at an IL loading of 50 wt% boosts the CO₂/CH₄ selectivity by more than 20-times, exceeding an absolute value of 120, a remarkably higher CO₂/CH₄ selectivity compared to that of other functionalized materials under similar operating conditions. Tunability of both the IL structure and the surface characteristics of rGA offer a tremendous degree of flexibility for the rational design of these IL/rGA composites towards high performance in gas separation applications.

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1. Introduction

Carbon dioxide (CO₂) is one of the essential impurities in natural gas stream. It decreases the overall energy content of the natural gas and leads to corrosion in the pipelines. Hence, capturing CO₂ from this vital energy source is a critical process for natural gas purification [1–3]. Adsorption-based gas separation processes are widely studied for CO₂ capture and separation because of their low energy consumption, environmental friendliness, and high efficiency nature compared to absorption and membrane-based

separation processes [4–6]. Various porous adsorbents, such as activated carbons, activated alumina, carbon nanotubes, zeolites, graphene-based porous materials, and metal organic frameworks (MOFs) have been intensively examined for CO₂ capture and separation [7–11]. Among these materials, graphene aerogels (GAs) are considered as a relatively new class of porous carbon materials considered in various applications, such as catalysis [12–14], supercapacitors [15,16], removal of water pollutants and dyes [17,18], gas sensing [19,20], energy storage [21], and gas separation [22–24]. They are composed of randomly stacked graphene layers and individual graphene layers have sp² hybridized honeycomb structure [25]. Owing to these structural properties, GAs possess mechanical flexibility and enhanced electrical properties as well as an advantage of being easily scalable compared to MOFs, zeolites, and silica gels, which are comparatively more fragile and involve complex synthesis processes [26].

In recent years, various functionalization strategies have been adopted to enhance the performance of GAs [27–30]; however, the

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number of studies considering such strategies on gas adsorption and separation applications is quite limited. For instance, Sui et al. [22] showed that CO₂ uptake was more than doubled from 0.93 to 2.45 mmol/g at 1000 mbar and 0 °C upon steam activation of a three-dimensional porous graphene-based material. Yun et al. [31], on the other hand, fabricated Si- and N-incorporated GAs through vapor deposition of (3-aminopropyl)triethoxysilane (APTES) and showed an increase in CO₂ uptake from 1.74 to 2.38 mmol/g at 10,000 mbar and 25 °C upon the deposition of APTES. Sui et al. [23] reported an enhancement in CO₂ uptake from 1.6 to 2.6 mmol/g at 1000 mbar and 0 °C, when GA was doped with nitrogen. Their results indicated that this increase in CO₂ uptake was accompanied by a slight increase in CO₂/CH₄ selectivity from 3.2 to 4. These results suggest that post-synthesis functionalization approach offers opportunities for improving gas separation performance. However, the strategies applied so far provided only a limited improvement in the separation performance of the material. Thus, it is crucial to explore novel post-synthesis functionalization strategies for GAs to make them promising for gas separation applications. In this regard, modifying them with ionic liquids (ILs) offers a broad potential. ILs are salts [32,33], generally exist as liquid below 100 °C with fascinating properties, such as negligible vapor pressure and non-volatility [34,35]. Additionally, the ILs offer tunable physical/chemical properties because of the presence of theoretically unlimited number of anion-cation combinations. Several studies reported improvements in the performance of various types of porous materials upon their combination with ILs. For instance, in the case of MOFs [36], they were either incorporated inside of a MOF to generate new adsorption sites [37,38] or were deposited on the external surfaces to act like a smart-gate deciding which molecule diffuses into the pores [39].

Herein, we report a new post-synthesis modification strategy to functionalize reduced graphene aerogels (rGAs) using an IL to generate a unique class of composite materials with an exceptional CO₂ separation performance. 1-*N*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), one of the commercially available ILs was chosen because of its high thermal stability [40] and excellent affinity towards CO₂ with poor CH₄ solubility [41]. [BMIM][PF₆] was impregnated on a representative rGA sample and CO₂/CH₄ separation performance was investigated. The rGA was prepared by thermal reduction of GA at 700 °C [13] and the IL/rGA composites were prepared by incipient wetness at various IL loadings (5, 10, 30, and 50 wt%, named as IL_x/rGA, where *x* denotes the corresponding IL loading). Samples were characterized in detail by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), N₂ physical adsorption measurement, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and Raman spectroscopies, and thermogravimetric analysis (TGA) and tested for volumetric gas uptake measurements. Results showed that the high surface area of rGA allows impregnation of the IL at a significantly high loading amount, 50 wt%, leading to more than 20-times enhancement in the CO₂/CH₄ selectivity compared to that of the pristine rGA.

2. Materials and methods

2.1. Synthesis of reduced graphene aerogel

Graphite powder (natural, 99.9995%, Alfa Aesar) was oxidized by reacting with KMnO₄ (Merck Millipore) and NaNO₃ (99%, Alfa Aesar) in ice-cold concentrated sulfuric acid (95–97%, Sigma Aldrich) to obtain graphene oxide exfoliation solution via a modified Hummers' method [42], as explained in detail previously [43]. Briefly, NaNO₃ (3 g) and graphite (3 g) were dissolved in ice-cold concentrated sulfuric acid solution. Following dissolution, KMnO₄

(18 g) was introduced to the solution in small portions, while maintaining the solution temperature below 5 °C using an ice bath. Then, distilled water was added slowly to raise the temperature up to 75 °C and the temperature was kept constant for 30 min. The reaction was terminated with the addition of distilled water and 30% H₂O₂ (Sigma Aldrich). The obtained precipitate (graphite oxide) was washed with 5 wt% HCl followed by distilled water (DI). For the exfoliation of graphite oxide powder into single graphene oxide nanosheets, the powder was sonicated for 4 h in DI water. To eliminate the aggregated nanosheets, graphene oxide solutions were centrifuged for 30 min at 10,000 rpm. The supernatant solution was stored as graphene oxide (GO) exfoliation solution.

The GA was synthesized by the hydrothermal treatment of GO solution at 180 °C for 3 h, as previously reported [14]. 3.0 mg mL⁻¹ GO solution was placed in a Teflon-lined stainless-steel bomb, which was further placed in a drying oven. Following the hydrothermal treatment, the vessel was opened and monolithic black hydrogel was immersed into pure acetone for solvent exchange. After the solvent exchange process, the gel was dried via supercritical CO₂ (Speed SFE 15,000, Applied Separations, Inc) at 50 °C and 12.0 MPa for 2 h, resulting in formation of graphene aerogel (GA). Crushed GA powder was placed into a split-furnace and heated to 700 °C at a ramp of 20 °C/min in flowing Ar (100 mL/min) and held at this temperature for 1 min. Then, the furnace was allowed to cool down naturally in flowing Ar and the resulting sample was collected as rGA [13].

2.2. Synthesis of ionic liquid (IL)/rGA composites

IL/rGA composites were obtained via post-synthesis modification of pristine rGA using incipient wetness technique. For each IL loading amount (5, 10, 30, and 50 wt%), the stoichiometric IL amount was first added to 2 mL in anhydrous toluene (Merck, 99.8 vol%) and the mixture was stirred for 1 h to obtain a homogeneous solution. The resulting solution was added dropwise to the calculated amount of pristine rGA to obtain 5, 10, 30, and 50 wt% IL/rGA composites. The resulting composites were dried overnight at 135 °C under vacuum to completely evaporate the solvent. The samples obtained were labeled as IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA composites, where the subscript denotes the corresponding IL loading.

2.3. Atomic force microscopy (AFM)

Bruker Dimension Icon in ScanAsyst mode was used to obtain AFM images of pristine GO thin films deposited onto clean Si wafers. Nanoscope analysis software was used to calculate the average root mean square (RMS) roughness of the obtained images.

2.4. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)

SEM images of pristine rGA and IL/rGA composites were obtained with a Zeiss Evo LS 15 with an accelerating voltage of 3 kV and a working distance of 3–3.3 mm under vacuum. The SEM images were taken at two different magnifications (10 k $\times$ and 100 k $\times$). To obtain map data of the samples, Energy-dispersive X-ray spectroscopy (EDX) imaging was performed by using a Bruker XFlash 5010 EDX detector with 123 eV resolution for pristine rGA and a representative sample (IL₃₀/rGA). EDX images were collected with an EHT of 5 kV and working distance of 6 mm.

2.5. X-ray diffraction (XRD)

A Bruker D8 Advance X-ray diffraction system with Cu K α 1

radiation source was used with a wavelength of 1.54 Å to obtain XRD pattern for pristine rGA and IL/rGA composites. X-ray generators power rating was 30 kV of voltage with the current of 10 mA. Lynxeye detector was used with 1 mm of slit size, and the diffraction patterns were obtained with a step size of 0.0204° in a range of 2θ of $5\text{--}50^\circ$.

2.6. N_2 physical adsorption measurements

The N_2 physical adsorption measurements for pristine rGA and IL/rGA composites were obtained by a Micromeritics ASAP 2020 physisorption analyzer. For each analysis, around 120 mg of the sample were loaded into the sample tube. The samples were first degassed overnight at 25°C for 12 h under vacuum. After activation of the samples, using He gas at liquid nitrogen temperature of -196°C , free space measurements were performed. Afterward, adsorption isotherm of N_2 gas was obtained between a pressure range of 10^{-6} and 1 bar. To estimate the surface area of the samples, the pressure steps between 0.05 and 0.3 bar were fit to Brunauer–Emmett–Teller (BET) equation, whereas pore size distribution (PSD) was calculated using Barrett–Joyner–Halenda (BJH) method from the N_2 adsorption isotherm.

2.7. Thermogravimetric analysis (TGA)

A TA Instruments Q500 model thermogravimetric analyzer with platinum pan was used to obtain thermal stability of pristine rGA and IL/rGA composites. First, to evaporate any physically adsorbed moisture content from the samples, a constant ramp of $5^\circ\text{C}/\text{min}$ up to 120°C was set, followed by isothermal treatment for 8 h at the corresponding temperature. Afterward, each measurement was conducted using very little sample amount (15 mg) and a very slow ramp rate ($2^\circ\text{C}/\text{min}$) to minimize the heat transfer limitations inside the rGA channels and to homogeneously distribute the heat inside the rGA pores. The temperature was raised up to 700°C at the corresponding ramp rate under N_2 flow of 40 mL/min and 60 mL/min of balance and purge gases, respectively. From the thermal decomposition temperatures results, the onset (T_{onset}) and derivative onset (T'_{onset}) temperatures were determined from thermogravimetry (TG) and derivative gravimetric (DTG) curves. As, (T_{onset}) values generally overestimate the thermal decomposition temperature [44,45] Therefore, for comparison the thermal stability limits of pristine rGA and IL/rGA composites, we considered to use the (T'_{onset}) values.

2.8. Fourier transform infrared (FTIR) spectroscopy

A Thermo Scientific Nicolet iS50 model FTIR spectrometer with an attenuated total reflection cell was used to obtain FTIR spectra of pristine rGA and IL/rGA composites. Transmission mode was used between the ranges of 3200 and 400 cm^{-1} . Scanning numbers of 64 and 512 for background and samples, respectively, and a resolution of 2 cm^{-1} were used for each measurement. Fityk software was used for the deconvolution of the FTIR spectra [46].

2.9. X-ray photoelectron spectroscopy (XPS) analysis

To perform XPS measurements for pristine rGA and IL/rGA composites, a Thermo Scientific K-Alpha spectrometer with an aluminum anode (Al $K\alpha = 1468.3\text{ eV}$) was used. The electron take-off angle was set to 90° and the spectra were recorded using an Advantage 5.9 software. The calibration of the binding energies was performed by assigning the C 1s signal at 284.8 eV .

2.10. Raman spectroscopy

Raman spectra for pristine rGA and IL/rGA composites were obtained using Raman microscope (RENISHAW INVIA) between the wavelength range of $800\text{--}1800\text{ cm}^{-1}$. For each measurement, Raman microscope was equipped with a laser excitation wavelength of 532 nm and a $50\times$ objective.

2.11. CHNS/O organic elemental analysis

Organic CHNS/O elemental analysis was performed using Thermo Scientific Flash 2000 elemental analyzer.

2.12. Conductor-like screening model for realistic solvents (COSMO-RS) calculations

The CO_2 and CH_4 solubilities in [BMIM][PF₆] were estimated using COSMOThermX software, version C30_160. These calculations were performed using the TZVP parameterizations in a pressure range of $0.1\text{--}1\text{ bar}$.

2.13. Gas adsorption measurements

A Micromeritics (Particulate Systems) High-Pressure Volumetric Analyzer (HPVA II-200) was used to make gas adsorption measurements of pristine rGA and IL/rGA composites. Approximately 140 mg of the sample were used for each measurement. Each sample was degassed overnight under vacuum at 125°C until the pressure reached to 10^{-6} bar . To obtain the adsorption isotherm, the system was first purged with He gas to remove any residual gases from the previous experiment. The gas adsorption isotherms for CO_2 and CH_4 in pristine and IL/rGA composites were obtained at 25°C in the pressure range of $0.1\text{--}1\text{ bar}$.

3. Results and discussion

The heat treatment of GAs facilitates the partial removal of surface oxygen-containing groups and improves the available surface area by facilitating the formation of micropores [47], while improving the thermal and mechanical stability [48]. Thus, the GA was reduced at 700°C before the incorporation of the IL. Data indicated that an increase in the treatment temperature led to an increase in the surface area, for instance, from $499\text{ m}^2/\text{g}$ for a reduction temperature of 400°C to $625\text{ m}^2/\text{g}$ when the reduction temperature was 700°C . Accordingly, the reduction temperature was chosen as 700°C to boost the IL loading in the final IL/rGA composite.

The presence of graphene monolayers in pristine graphene oxide thin film was evident from the atomic force microscopy (AFM) images as presented in Fig. S1 of Supporting Information (SI). The images presented in Figs. S1(a–b) demonstrated the lateral heights of nanolayers as $3\text{ }\mu\text{m}$, whereas Figs. S1(c–e) images indicated the average thickness of the nanolayers as 1.1 nm , which is close to the theoretical thickness of a single graphene sheet. Furthermore, Fig. 1(a) presents a representative SEM image of the pristine rGA. It demonstrates the randomly oriented graphene layers forming an interconnected porous structure with the characteristic wrinkled-sheet structure [13]. The corresponding images obtained on the IL/rGA composites, given in Fig. 1(b–d), present that the wrinkled-sheet structure remains mostly intact upon the IL incorporation. In addition, EDX results mapped at different locations on each sample confirmed the uniform distribution of IL on rGA surface as presented in Fig. S2 for a representative sample of IL₃₀/rGA. Furthermore, we note here that although no clear differences were observed between the SEM images of pristine rGA and IL/rGA

Fig. 1. SEM images of (a) pristine rGA, (b) IL₁₀/rGA, (c) IL₃₀/rGA, and (d) IL₅₀/rGA at 100 k × magnification.

Fig. 2. XRD pattern of pristine rGA, IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA composites. (A colour version of this figure can be viewed online.)

composite, the EDX results revealed the presence of considerable amount of fluorine and phosphorus elements in the composite sample attributed to the anion ($[\text{PF}_6]^-$) of the IL.

XRD patterns of the as-prepared rGA and IL/rGA composites are presented in Fig. 2. Multiple peaks observed in a 2θ range of 16–28° on pristine rGA were associated with turbostratic disorder, which is associated with the translation or random rotation between adjacent layers of graphene [22,49]. Crystal structures of the IL/rGA composites were very similar to the as-synthesized pristine rGA with a slight increase in the intensity of the lower angle peaks indicating a possible change in the ratio of crystalline/amorphous domains. As the IL loading increases, one might expect an increase in the amount of the amorphous domain of the composite sample.

Surface areas of pristine rGA and IL/rGA composites were calculated from the N_2 adsorption isotherms as presented in Fig. 3. The pristine rGA had a BET surface area of 625 m^2/g and it decreased upon IL impregnation to 447, 142, 86, and 17 m^2/g for IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA, respectively. These results indicate the successful deposition of IL on rGA surface, leading to a decrease in the overall surface area. Furthermore, pore size distribution (PSD) of pristine rGA was obtained by Barrett–Joyner–Halenda (BJH) method from N_2 physical adsorption isotherm as presented in Fig. S3. The data revealed that most of the pore volume was present in the pores in the range of 2–10 nm.

The TGA profile of pristine rGA demonstrated almost no weight loss up to 700 °C, while the bulk IL was completely disappearing at temperatures below 450 °C (Fig. 4). Consistently, the IL/rGA composites showed weight losses in accordance with their corresponding IL loadings as shown in Fig. 4. Accordingly, the T_{onset} of the bulk IL was 298 °C, consistent with previous reports [38]. It decreased to approximately 176 ± 4 °C for IL₅/rGA and IL₁₀/rGA (Table S1). On the basis of these results, we inferred that the IL molecules interact with the surface of rGA at these relatively low loadings and these interactions significantly affect the thermal decomposition mechanisms [44]. When the IL loading increases, the T_{onset} values increase as well but they still remain lower than 298 °C, T_{onset} of the bulk IL. The corresponding values were 240 and 263 °C for IL₃₀/rGA and IL₅₀/rGA, respectively. Hence, we infer that even at considerably high IL loadings, interactions were still present as evidenced by the changes in the decomposition

Fig. 3. N_2 adsorption (filled symbols)-desorption (empty symbols) isotherms at -196°C for pristine rGA, IL_5/rGA , IL_{10}/rGA , IL_{30}/rGA , and IL_{50}/rGA composites. (A colour version of this figure can be viewed online.)

Fig. 4. (a) TGA and (b) DTG curves of pristine rGA, bulk $[BMIM][PF_6]$, IL_5/rGA , IL_{10}/rGA , IL_{30}/rGA , and IL_{50}/rGA composites. (A colour version of this figure can be viewed online.)

Fig. 5. FTIR spectra of pristine rGA, bulk $[BMIM][PF_6]$, IL_5/rGA , IL_{10}/rGA , IL_{30}/rGA , and IL_{50}/rGA composites between 1300 and 500 cm^{-1} and 3200 – 2800 cm^{-1} . (A colour version of this figure can be viewed online.)

temperatures.

To identify these interactions present between the surface of rGA and the IL molecules, infrared (IR) spectra of the pristine rGA, bulk IL, and IL/rGA composites were compared in Fig. 5.

Data showed that intensity of the features associated with $[BMIM][PF_6]$ increases with an increase in IL loading. They further indicated that positions of some of these IL-related features shifted in the IL/rGA composites. The major shift was observed on the peak located at 815 cm^{-1} assigned to PF_6 asymmetric stretching. In the IL/rGA composites, this peak shifted to 848 , 852 , 854 , 857 cm^{-1} when the corresponding IL loading was 5 , 10 , 30 , and $50\text{ wt\%}$, respectively. These shifts indicate that interactions between the rGA surface and the IL molecules involve mostly interplay between the surface and the anion of the IL. This inference was further supported by the XPS data. The XP spectra given in Fig. 6 illustrated that the features mostly related with F1s and P2p of the $[PF_6]^-$ anion shifted to lower energies when the IL was interacting with the rGA, while those of the cation-related features were not presenting any significant shifts. As the IL loading increases, these anion-related features grow, well-correlated with the IL amount, and the spectra showed bulk-like IL presence on the surface of rGA. Furthermore, CHNS/O elemental analysis results presented in Table S2 confirm the presence of oxygen, which indicates the presence of oxygen-containing functional groups on rGA surface such as, carbonyl, carboxyl, epoxy and hydroxyl groups [14]. Consistently, $(C=O)$ and $(C=O)$ functional groups, and $\pi-\pi^*$ shakeup satellite peaks were characterized from XP C1s spectrum of the pristine rGA at the binding energies of 285.9 , 288.4 , and 290.4 eV , respectively [50,51]. Thus, we inferred that anion of IL is interacting with oxygenated groups on rGA surface consistent with the blue-shifts observed in the corresponding positions of the FTIR and XPS features of the IL.

Possible changes in the surface characteristics of rGA upon IL impregnation were investigated by comparing the Raman spectra of rGA with those of the IL/rGA composites focusing on the intensity ratios of two bands at 1322 and 1593 cm^{-1} associated with D and G bands, quantifying the degree of disorder and the density of defects on the surface, respectively. The intensity ratio of I_D/I_G of pristine rGA and IL/rGA composites calculated from Raman spectra given in Fig. 7 are presented in Table S3. Data showed that as the IL loading increases, the I_D/I_G ratio tends to decrease. This decrease is

Fig. 6. XPS spectra of (a) survey spectra, (b) F 1s, (c) P 2p, (d) O 1s, and (e) N 1s regions of pristine rGA, IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA composites. (A colour version of this figure can be viewed online.)

Fig. 7. Raman spectra of pristine rGA, IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA composites between 1800 and 870 cm⁻¹. (A colour version of this figure can be viewed online.)

Fig. 8. (a) CO₂ and (b) CH₄ uptakes of pristine rGA, IL₅/rGA, IL₁₀/rGA, IL₃₀/rGA, and IL₅₀/rGA at 25 °C. Filled symbols represent experimental data whereas solid lines represent the fitted data of models. (A colour version of this figure can be viewed online.)

originated from the interactions between the intercalated IL molecules and the wrinkled rGA layers.

To investigate the consequences of these IL-rGA interactions on the performance of the composite for gas adsorption and separation, volumetric gas adsorption measurements were performed for CO₂ and CH₄ in a pressure range of 1–1000 mbar and at 25 °C separately on pristine rGA and the corresponding IL/rGA composites (Fig. 8). Experimentally obtained gas adsorption isotherms were fitted to the dual-site Langmuir, Langmuir-Freundlich, and dual-site Langmuir-Freundlich models to obtain gas uptakes as a function of pressure at specified values. The fit parameters for each model are presented in Table S4.

The results illustrated that upon the impregnation of IL on the rGA, CO₂ and CH₄ adsorption capacities decreased depending on the corresponding IL loading. Because the extent of these decreases in uptakes were dependent on the type of gas and IL loading, one can expect that the impregnation of IL on rGA influences the separation performance of the pristine rGA. Thus, the ideal selectivities of pristine rGA and IL/rGA composites were determined using the data presented in Fig. 9.

Fig. 9 represents the improvement in CO₂/CH₄ ideal selectivity of pristine rGA upon IL impregnation with IL loading. Accordingly, the ideal CO₂/CH₄ selectivity at 1 mbar improved from 5.9 on pristine rGA to 27.6, when the IL loading was 5 wt%. The corresponding CO₂/CH₄ ideal selectivities for IL₁₀/rGA and IL₃₀/rGA composites at the same pressure were 41.6 and 116.2, respectively. The highest improvement in CO₂/CH₄ ideal selectivity was observed for IL₅₀/rGA composite, 20.5-times of the selectivity of pristine rGA, exceeding 120. This improvement in separation performance of IL₅₀/rGA composite can be attributed to the high solubility of CO₂ accompanied with a poor solubility of CH₄ in the IL as confirmed by the COSMO-RS calculations presented in Fig. S4 [41].

Fig. 9. CO_2/CH_4 ideal selectivities of pristine rGA and the IL/rGA composites as a function of pressure. (A colour version of this figure can be viewed online.)

Structural modifications of the IL by the interactions with the surface also help to improve the separation performance. For example, incorporation of [BMIM][PF₆] in ZIF-8 was shown to be very effective in improving CO_2/CH_4 separation performance of ZIF-8 [38]. The CO_2/CH_4 ideal selectivity of ZIF-8 increased with an increase in IL loading, however, the IL amount that could be incorporated into ZIF-8 was limited with approximately 24 wt%. At this loading the selectivity was approximately four-times of that of the pristine ZIF-8 at 1 mbar, providing an ideal selectivity of approximately 10.6. The rGA support that we considered in this study, on the other hand, allowed us to impregnate the same IL up to 50 wt% owing to the porosity and three-dimensional macro-structure of rGA, facilitating the access of IL molecules into the wrinkled-sheet structure. Such high loading of IL provided an improvement of more than 20-times in CO_2/CH_4 selectivity (>120). Furthermore, we also compared the ideal CO_2/CH_4 selectivity results of IL/rGA composites with various different adsorbents including porous carbons, zeolites, MOFs, and IL functionalized MOFs in Table S5. Accordingly, our IL₅₀/rGA composite exhibited remarkably higher CO_2/CH_4 selectivities at especially low pressures (<100 mbar) compared to other pristine and functionalized materials under similar operating conditions.

Moreover, to show the reproducibility and reusability of the composite samples, we prepared a second batch of the IL₅₀/rGA composite following the same synthesis procedure and performed cyclic CO_2 and CH_4 adsorption measurements. The adsorption data presented in Fig. S5 confirm the reproducibility of the composite. Moreover, Fig. S6 represents the cyclic performance for CO_2 adsorption cycles on this second batch of IL₅₀/rGA. The results indicate that the IL leaching, if any, is negligible and the composite is reusable for at least ten CO_2 adsorption cycles. In addition, we note that the oxygenated functional groups present on the surface of rGA offer surface sites for immobilizing the IL on the surface, as confirmed by the interactions identified by the FTIR and XPS results. Thus, these interactions protect IL molecules from leaching and offer a high degree of reusability of the composites as demonstrated in Fig. S6.

These results are the first to demonstrate a broad potential of depositing an IL on a three-dimensional form of graphene for reaching an exceptional CO_2 separation performance. It is also noted that the rGA surface can be tuned by adjusting the pre-treatment conditions and by adding various functional groups or doping with heteroatoms as reported in the literature [52–54]. Thus, we anticipate that the interactions between the IL molecules and the surface can be tuned simply by adjusting the surface

characteristics of the rGA and by changing the IL structure. Thus, combining the ease of tunability of the surface characteristics of GAs with the availability of almost unlimited number of possible ILs offers great flexibility for the rational design of these IL/rGA composites towards high performance in different gas separation applications.

4. Conclusions

[BMIM][PF₆] was impregnated onto a rGA, prepared by reducing GA at 700 °C, at various IL loadings. The characterization data demonstrated that the IL molecules interact with the surface of rGA through their anion. The volumetric uptake measurements were performed on each material for CO_2 and CH_4 . Results showed that the CO_2/CH_4 separation performance of rGA, improved by more than 20-times, exceeding 120, upon the impregnation of [BMIM][PF₆] at a loading of 50 wt%. Data indicated that such increase in selectivity is directly associated with the exceptionally high loading of IL and the molecular interactions improving the CO_2 affinity. These results are the first to illustrate a post-synthesis functionalization approach resulting in a record high improvement in the separation performance of three-dimensional graphene. A comparison of this CO_2 separation performance with those of other pristine and functionalized materials under similar operating conditions demonstrated the broad potential of these IL/rGA composites for gas separation applications. Tunability of both the rGA surface and the IL's structure offer great flexibility for rational design.

CRedit authorship contribution statement

Muhammad Zeeshan: Conceptualization, Investigation, Methodology, Writing - original draft. **Kaan Yalcin:** Investigation, Methodology, Writing - original draft. **F. Eylul Sarac Oztuna:** Investigation, Methodology, Writing - original draft. **Ugur Unal:** Supervision, Conceptualization, Methodology, Writing - review & editing. **Seda Keskin:** Supervision, Conceptualization, Methodology, Writing - review & editing. **Alper Uzun:** Supervision, Conceptualization, Methodology, Writing - review & editing.

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 data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2020.08.079>.

Supporting Information

Gas adsorption fitting parameters, EDX images, gas solubilities,

T_{onset} values of samples, and comparison of ideal CO₂/CH₄ selectivity values with literature.

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