Decoding Carbon-Based Materials’ Properties for High CO₂ Capture and Selectivity

Palak Mehra and Amit Paul *

Cite This: ACS Omega 2022, 7, 34538−34546

ACCESS Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Carbon-based materials are well established as low-cost, easily synthesizable, and low regeneration energy adsorbents against harmful greenhouse gases such as CO₂. However, the development of such materials with exceptional CO₂ uptake capacity needs well-described research, wherein various factors influencing CO₂ adsorption need to be investigated. Therefore, five cost-effective carbon-based materials that have similar textural properties, functional groups, and porous characteristics were selected. Among these materials, boidered ultramicroporous graphitic carbon had shown an excellent CO₂ capture capacity of 7.81 mmol/g at 273 K /1 bar with an excellent CO₂ vs N₂ selectivity of 15 owing to its ultramicroporous nature and unique boidered graphitic morphology. On the other hand, reduced graphene revealed a remarkable CO₂ vs N₂ selectivity of 57 with a CO₂ uptake of 2.36 mmol/g at 273 K/1 bar. In order to understand the high CO₂ capture capacity, important properties derived from adsorption/desorption, Raman spectroscopy, and X-ray photoelectron spectroscopy were correlated with CO₂ adsorption. This study revealed that an increase in ultramicropore volume and sp² carbon (graphitic) content of nanomaterials could enhance CO₂ capture significantly. FTIR studies revealed the importance of oxygen functionalities in improving CO₂ vs N₂ selectivity in reduced graphene due to higher quadruple−dipole interactions between CO₂ and oxygen functionalization of the material. Apart from high CO₂ adsorption capacity, boidered ultramicroporous graphitic carbon also offered low regeneration energy and excellent pressure swing regeneration ability for five consecutive cycles.

INTRODUCTION

Environmental deterioration and climate change brought considerable attention from researchers toward the emission of greenhouse gases. 1,2 The massive consumption of fossil fuels leading to carbon dioxide (CO₂) emission is the main cause of these problems. 3 Thus, developing CO₂ capture and storage methodologies demands the undivided attention of researchers. 4 Currently, the amine-scrubbing methodology is used for industrial CO₂ capture. 5 However, this approach has several drawbacks, such as high regeneration costs, solvent loss, toxicity, amine degradation, and a tendency to corrode the equipment. 5−8 In comparison, solid porous adsorbents are attractive as they offer easy handling, simple processing, and low regeneration costs. 9 In this category, porous materials having high surface areas, such as zeolites, metal−organic frameworks (MOFs), silica, nanocarbons, etc., are widely explored as CO₂ adsorbents. 10 Among these, carbon nanoma-
laminar morphology with functionalized surfaces, respectively. Recently, a simple yet innovative approach has emerged wherein graphene-based precursors (GO or rGO) and activated carbon materials are combined to obtain new materials that can enhance the CO\textsubscript{2} adsorption capacity. For example, poly(p-phenylenediamine) (PpFDA) as a carbon source and GO as a graphene source were used to prepare an N-doped porous carbon that provided a CO\textsubscript{2} uptake of 4.65 mmol/g at 298 K and 5 bar pressure. In another study, Yuan and co-workers reported nitrogen-doped porous carbon employing melamine-resorcinol-formaldehyde resin and graphene oxide. This material had shown a CO\textsubscript{2} adsorption capacity of 5.21 mmol/g at 298 K and 5 bar pressure. In other attempts, graphene-like morphology/graphene-based nanomaterials were also synthesized and explored for CO\textsubscript{2} adsorption.

For example, graphene-like multiscale microporous carbon nanosheets were synthesized by Shi et al., which provided a CO\textsubscript{2} adsorption capacity of 6.32 mmol/g at 273 K/1 bar. A novel three-dimensional B,N co-doped graphene-like carbon nanosheet material was developed, which showed 3.57 mmol/g CO\textsubscript{2} adsorption capacity (at 273 K and 1 bar). These materials have shown great potential for CO\textsubscript{2} adsorption application, which suggests that a detailed study to understand the impact of various structural features of these nanomaterials on CO\textsubscript{2} uptake is of great importance. In this context, Merchán and co-workers prepared hybrid hydrogels from graphene oxide and activated carbon fibers and focused on correlating various textural properties with CO\textsubscript{2} uptake. However, these materials had distinct domains of activated carbon fiber and GO, which resulted in difficulties correlating adsorption characteristics with graphene-like structures. The novel idea of investigating the relation between the properties of materials and CO\textsubscript{2} adsorption can help researchers to synthesize new materials that can achieve extraordinary CO\textsubscript{2} adsorption capacity and selectivity. Therefore, we opted for low-cost, easily synthesizable carbon materials to establish new insights in correlating the properties with CO\textsubscript{2} uptake capacity.

We recently reported a biordered ultramicroporous graphitic carbon (BUGC), which has a high surface area, ultramicropore/micropore volume, and unique graphitization ordering. Considering all the above examples, we envisioned that the BUGC’s properties should be beneficial for CO\textsubscript{2} uptake and can provide useful insights into the morphological effects on the adsorption properties of carbon nanomaterials. With this objective, we selected five nanomaterials, namely, non-porous carbon (NC), reduced graphene (RG), IMC (immense microporous carbon), BUGC (biordered ultramicroporous graphitic carbon), and MMC (microporous mesoporous carbon). These materials have distinct porous and functional group characteristics yet similar textures, which allowed us to understand the correlations of their properties with CO\textsubscript{2} capture capacity. In the following few sections, we discuss the syntheses, characterizations, and correlation plots for these materials with CO\textsubscript{2} uptake.

### Experimental Section

#### Materials and Chemicals.
Graphite (150 micron, cat#496588), non-porous carbon (untreated, granular, 4–8 mesh, cat#C2764) (NC), and commercial micro-mesoporous carbon (100 mesh, CMMC) were bought from Sigma-Aldrich. Potassium permanganate (K\textsubscript{2}MnO\textsubscript{4}), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), formic acid (HCOOH), potassium hydroxide (KOH), acetone, and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 50%) were also purchased from Sigma-Aldrich. Acetone and concentrated hydrochloric acid were supplied by Spectrochem and Pallav Chemicals, respectively. Milli-Q water (>18 M\text{Ω}) was used for all synthesis and solution preparation.

### Synthesis of Reduced Graphene (RG).
RG was synthesized by following a protocol previously reported by our group. Briefly, modified Hummer’s method was used wherein 2 g of graphite (150 µm) was dispersed in 46 mL of conc. H\textsubscript{2}SO\textsubscript{4} in a 250 mL round-bottom flask. This dispersion was kept in an ice bath (0 °C), and 6 g of KMnO\textsubscript{4} was added carefully. This addition was performed gradually by covering a time span of 20 min in order to keep the temperature of the dispersion below 20 °C. This mixture was stirred for 3 h at 35 °C using a reflux condenser. Thereafter, 92 mL of water was added cautiously over a period of 30 min. Next, in 280 mL of water, all of these contents were poured, and 10 mL of 30% H\textsubscript{2}O\textsubscript{2} was added to destroy excess KMnO\textsubscript{4} (the color changed from dark brown to yellow). Finally, this material was filtered and washed with water in a sintered glass filter until the sulfate was completely destroyed (checked with barium chloride addition), and it was named graphite oxide (GO). Then, GO was further washed with 20% formic acid solution to intercalate formic acid into the interlamellar regions of GO. Formic acid-intercalated GO was collected and dried at 60 °C. To obtain RG, 0.5 g of dried GO was exfoliated at 160 °C in a preheated oven.

### Synthesis of IMC and BUGC.
Both materials were prepared by a chemical activation method using KOH as a porogen, which was reported earlier by our group. For IMC, an optimized ratio of NC and KOH (1:5) was taken in an alumina boat. This mixture was kept in a temperature-controlled cylindrical tube furnace and ramped to a temperature of 750 °C with a ramp rate of 5 °C/min under a constant flow of N\textsubscript{2}. The sample was carbonized at 750 °C for 1 h, and then it was allowed to cool down under N\textsubscript{2} flow naturally. Thereafter, the obtained sample was washed with 5 M HCl to remove the mineral content. This procedure was followed by washing with distilled water to eliminate chloride ions. The carbon material procured by this procedure was named immense microporous carbon (IMC) since the material is mostly microporous in nature (vide infra). For BUGC, a similar procedure was utilized, except that the carbon precursor was NC and RG in a ratio of 8:2, a procedure reported previously by our group. The prepared materials were dried at 100 °C for 24 h in a hot air oven.

### Synthesis of MMC.
MMC was also synthesized by the procedure described above. Herein, instead of NC, CMMC was used as a precursor.

### Characterizations.
Scanning electron microscopy (SEM) morphological analysis was performed in a Carl ZEISS (Ultraplus) FE-SEM instrument at 20 kV. For SEM imaging, dried carbon materials were spread on carbon tape and coated with gold for 120 s. Transmission electron microscopy (TEM) experiments were conducted using a TEM FEI TALOS 200S under an accelerating voltage of 200 kV. For TEM sample preparation, sample dispersion was prepared in 2-propanol (0.5 mg in 15 mL), which was drop-casted on a carbon-coated copper grid. Before imaging, these samples were dried overnight at ambient temperature. A Lab RAM HR 800 (Horiba) instrument with an excitation wavelength of 532 nm laser was used to record Raman spectra. Fourier transform infrared (FTIR) spectroscopy experiments were carried out using a Perkin-Elmer Model UATR Spectrum Two Instrument.
in the range of 500 to 4000 cm\(^{-1}\). Degassed samples were directly used to capture the FTIR spectra. CO\(_2\) gas flowed at a rate of 100 mL/min for 12 h to capture the FTIR spectra of CO\(_2\)-rich samples. During the FTIR characterization, samples were exposed to air for <15 s. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Prob II, FEI Inc., with a scan time of 1 h per element for a core level scan (energy band of 20 eV, with pass setting of 23.5 eV, 0.025 eV step, 100 ms time per step, 5 cycles). N\(_2\) and CO\(_2\) adsorption/desorption experiments were carried out using a Quantachrome Autosorb QUA21011 instrument. Prior to the adsorption experiments, samples were degassed under vacuum at 80 °C for 20 h.

**RESULTS AND DISCUSSION**

**Morphological Analysis.** Morphological analyses of all nanomaterials were performed using SEM and TEM. The SEM image of NC showed a nonporous morphology (Figure S1a, SI), whereas RG revealed a layered structure (Figure S1b, SI).\(^{25,26}\) IMC, BUGC, and MMC showed porous characteristics (Figure S1c−S1e, SI).\(^{24,26}\) The magnified HRTEM images of BUGC revealed biordered characteristics wherein short-range graphitic orders were visible inside the grain boundary (Figure 1e), and along the grain boundaries, long-range graphitic order was present (Figure 1f).\(^{24}\) HRTEM images further exhibited narrow micropores in BUGC (Figure 1g). An in-depth analysis and discussion about the morphology of BUGC were provided by us previously.\(^{24}\) We proposed that the catalyzation of disordered NC with an ordered RG nanostructure might have occurred for the formation of BUGC, which resulted in the short-range ordered morphological pattern. These short-range ordered graphitic structures reorganize randomly, create a directionally disordered morphology, and generate micropores/ultramicropores. Moreover, the K\(^+\) ion from KOH intercalates between graphitic layers and facilitates the exfoliation of multilayered graphitic structure to form a single-layer graphene-like structure under heat treatment.\(^{24}\)

**Functional Group Analysis.** The FTIR spectra provided in Figure S2 revealed the presence of peaks corresponding to hydroxyl functionalities (C−O) (3300−3700 and 1030 cm\(^{-1}\)), alkene/alkane C−H bond (2980−3000 cm\(^{-1}\)), ketonic functionalities (C==O) (1695−1720 cm\(^{-1}\)), and alkene (C==C) bond (1540−1566 cm\(^{-1}\)).\(^{24,25}\) XPS was also performed to
Porosity of the Studied Materials. The defect ratio (\(d\)) and the respective percentages of carbon and oxygen are tabulated in Table S1. The highest percentage of oxygen was present in IMC and BUGC, in accordance with IUPAC classification, having an H3 type of hysteresis loop, indicating the mesoporous characteristics of the material (Figure 2e).\(^\text{29}\) MMC revealed a mixed type-I and type-IV isotherm, showing the microporous and mesoporous characteristics of the material (Figure 2e).\(^\text{29}\) BET surface areas (\(S_{\text{BET}}\)) were analyzed in the range of 0.05–0.2 \(P/P_0\) (relative pressure) and are tabulated in Table 1. The surface area of NC was only 37 \(\text{m}^2/\text{g}\), whereas RG exhibited a surface area of 732 \(\text{m}^2/\text{g}\) (Table 1). An increasing trend of surface areas in micropore-rich carbons (type-I isotherm) with the highest surface area for MMC (3090 \(\text{m}^2/\text{g}\)) followed by IMC (3030 \(\text{m}^2/\text{g}\)) and BUGC (2472 \(\text{m}^2/\text{g}\)) was obtained (Table 1). The porous characteristics of materials were analyzed using the non-local density functional theory (NLDFD) model. To probe the narrow micropores, \(\text{CO}_2\) adsorption isotherms were obtained at 273 K and were also analyzed by the NLDFD model (Figure 2 insets). The combined total pore volume and pore size distribution from \(\text{N}_2\) and \(\text{CO}_2\) isotherms are provided in Figure S6a–d and Figure S6e–h, respectively. RG was mesoporous in nature, having a sharp pore size distribution peak at 3.9 nm (Figure S6e, SI). On the other hand, IMC and BUGC exhibited completely ultramicroporous/microporous characteristics having pore size distribution in the ranges of 0.33–1.96 and 0.35–1.47 nm, respectively (Figure S6f,g, SI). MMC consisted of bimodal porous characteristics having microporous (0.34–1.32 nm) and mesoporous characteristics (2.56–5.25 nm) (Figure S6h, SI).

**Table 1.** Porous Characteristics of the Studied Materials Obtained from \(\text{N}_2\) Adsorption/Desorption Isotherms at 77 K (Superscript a) and \(\text{CO}_2\) Adsorption/Desorption Isotherms at 273 K (Superscript b)

| Material | \(S_{\text{BET}}\) (m\(^2\)/g) | Total pore volume (cm\(^3\)/g) | Ultramicropore volume (0.3–0.7 nm) (cm\(^3\)/g) | Micropore volume (0.7–20 nm) (cm\(^3\)/g) | \(CO_2\) uptake at 273 K (mmol/g) at 1 bar | \(CO_2\) uptake at 273 K (mmol/g) at 0.15 bar | \(CO_2\) uptake at 273 K (mmol/g) at 0.1 bar |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| NC       | 37               | 0.04             | 0.00             | 0.03             | 0.55             | 0.14             | 0.39             |
| RG       | 732              | 3.56             | 0.12             | 0.20             | 2.36             | 1.12             | 1.56             |
| IMC      | 3030             | 1.49             | 0.21             | 1.04             | 5.56             | 1.25             | 2.89             |
| BUGC     | 2472             | 1.07             | 0.31             | 0.84             | 7.81             | 1.98             | 4.29             |
| MMC      | 3090             | 2.30             | 0.20             | 0.77             | 4.00             | 1.06             | 2.82             |

**Figure 3.** \(\text{CO}_2\) adsorption isotherms at (a) 273 and (b) 298 K for different materials.

determine the surface functional groups of nanomaterials. All materials consisted of carbon and oxygen (Figure S3, SI), and the respective percentages of carbon and oxygen are tabulated in Table S1. The highest percentage of oxygen was present in RG followed by MMC, BUGC, and IMC. Next, the high-resolution C 1s spectra of these materials were deconvoluted to analyze carbon functionalization (Figure S4 and Table S2, SI). Except NC, all other materials had five types of functionalizations situated at 284.6 eV for C≡C (sp\(^3\) carbon), 285.1 eV for C−C/C−H (sp\(^3\) carbon), 286.3 eV for C−O (alcohol functionalities), 287.9 eV for C=O (ketonic functionalities), and 290 eV for O−C=O (carboxylic functionalities) (Figure S4, SI).\(^\text{24,28}\) Interestingly, a high percentage of sp\(^3\) carbon was present in BUGC followed by IMC and MMC, in accordance with the SEM and TEM analysis (vide supra) (Table S2, SI). A relatively low sp\(^2\) carbon content in RG does not indicate a low graphicitic content; rather, it was due to a higher percentage of oxygen content in comparison to other materials (Table S2, SI). Notably, the alcohol functionality (C−O) content was maximum in BUGC among all materials, whereas the percentage of ketonic functionality (C=O) content was maximum for RG (Table S2, SI).

**Raman Analysis.** The Raman spectra of all materials were fitted and analyzed (Figure S5, SI). Two major peaks at 1330 and 1590 cm\(^{-1}\) were observed due to defects (D-band) and stretching of sp\(^2\) carbons (G-band) in carbon lattice, respectively (Figure S5, SI).\(^\text{27,29}\) Moreover, D\(^*\) (~1110 cm\(^{-1}\)), D\(^\prime\) (1500–1540 cm\(^{-1}\)), and D\(^\prime\) (1680–1695 cm\(^{-1}\)) bands were also present, corresponding to the disordered graphitic lattice due to C\(_{\text{sp}}\) carbon centers, amorphous phases, and defects of the basal plane, respectively (Figure S5, SI).\(^\text{23}\)

The defect ratio (\(I_D/I_G\)) was also determined for all samples and summarized in Table S3, SI. Importantly, the \(I_D/I_G\) ratio was lowest in BUGC, implying that the sp\(^2\) carbon character was the highest in BUGC, which validates the results obtained from XPS spectroscopy (vide supra).
CO₂ Capture. CO₂ uptake capacity of the materials was performed at two temperatures, i.e., 273 and 298 K (Figure 3). BUGC exhibited an exceptional CO₂ adsorption capacity of 7.81 mmol/g at 273 K and relative pressure of 1 bar (Figure 3a and Table 1). Under similar conditions, 5.56, 4.00, 2.63, and 0.55 mmol/g of CO₂ were adsorbed by IMC, MMC, RG, and NC, respectively (Figure 3a and Table 1). CO₂ adsorption measurements at 298 K and 1 bar relative pressure revealed a decrement in adsorption capacity in all materials (Figure 3b and Table 1). However, the order of uptake was similar, having the highest CO₂ uptake of 4.49 mmol/g for BUGC followed by IMC (2.90 mmol/g), MMC (2.81 mmol/g), RG (1.56 mmol/g), and NC (0.39 mmol/g). Uptake capacity at room temperature (298 K) was comparatively lower due to the high kinetic energy of CO₂ molecules at 298 K compared to 273 K. At higher temperatures, the adsorption energy decreases, which leads to reduced CO₂ adsorption.

Figure 4 presents the comparison of CO₂ and N₂ adsorption isotherms for different materials. To understand the adsorption mechanisms, all isotherms were fitted using either Langmuir single-site (eq S1, SI) or Langmuir-dual site adsorption models (eq S2, SI), and fitting parameters are provided in Table S4.

Except for RG (at 273 K), other isotherms were well fitted with a single-site model describing mostly monolayer adsorption. RG showed the highest accuracy with the Langmuir dual-site model describing two types of favorable sites for adsorption. The mechanism described for RG by the dual-site model presumably reflects the edges/defects as the first adsorption site and pores as second adsorption site. The decrement in “k” (Langmuir parameter) value with temperature signifies physical adsorption behavior between CO₂ and materials. Fitted isotherms were used to calculate the selectivity using ideal adsorbed solution theory (IAST). IAST provides ease of determining the selectivity in a gaseous mixture from equilibrium adsorption capacity obtained from the adsorption isotherm of the pure component at a particular pressure and temperature. The flue gas consists of more than 70% of N₂ in addition to other gases such as water or oxygen gas and only ~5~15% of CO₂. Therefore, the obtained molar loadings from fitted adsorption isotherms (0.15 bar for CO₂ and 0.85 bar for N₂) of pure component isotherms were used to calculate the selectivity using IAST.
Figure 6. FTIR spectral analysis of BUGC before and after purging CO₂ for 12 h: (a) full range spectra and (b) magnified regions of spectra. Respective spectral shifts are color matched for easy visibility.

to calculate CO₂ vs N₂ selectivity. IAST CO₂ vs N₂ selectivity for BUGC, IMC, and MMC were 15, 11, and 13, respectively (Figure 4d). Fascinatingly, RG displayed the highest selectivity of 57 (Figure 4a,d), which can be attributed to the extent of oxygen functionalities present and a detailed analysis has been provided in next few sections (vide infra).

Scientific Understanding of CO₂ Uptake. In order to understand the science behind the high CO₂ uptake of BUGC and high selectivity for RG, various materials' characteristics are analyzed with respect to CO₂ uptake (Figure 5). First, the porous characteristics of the materials are compared with uptake capacity in Figure 5a and Figure S8. The ultramicropore (<0.7 nm) volume showed an excellent correlation with CO₂ capture having a coefficient of determination (R²) value of 0.99 (Figure 5a). Ultramicropores offer a large adsorption potential due to adjacent pore walls (pore wall−wall interactions). The overlapping of these adsorption potentials generates van der Waals forces to attract CO₂ molecules.23,35 Next, the R² value of 0.73 was obtained upon analyzing the CO₂ adsorption capacity with micropore volume (0.7−2.0 nm) (Figure S7a, SI). However, the BET surface area and total pore volume of the materials had very poor correlations with the adsorption capacity and showed R² values of 0.45 and 0.01, respectively (Figure S7b,c, SI). Hence, these results firmly establish that the narrow micropores/ultramicropores (0.3−0.7 nm) are one of the major driving factors for the high CO₂ adsorption capacity of BUGC, which agrees well with the previous reports.26,36,37

The high adsorption capacity of BUGC compared to other materials also indicated the importance of unique graphitic regions. Therefore, to correlate sp² character, Raman spectroscopy inferences were utilized. In this context, the inverse of the defect ratio (I₆/I₀) calculated from Raman results correlated precisely with the CO₂ uptake capacity (R² = 0.99) (Figure 3b). The I₆/I₀ ratio is directly proportional to the G-band area, which signifies a higher sp² carbon content for a higher I₆/I₀ ratio. Thus, this analysis suggests that the higher sp² hybridized carbon content helps to improve CO₂ adsorption. To further verify this correlation, the percentage composition of various C 1s species derived from XPS spectra was also evaluated with CO₂ uptake at 1 bar (Figure 5c and Figure S8, SI). Fascinatingly, the percentage of sp² carbon (C≡C) correlated perfectly with the CO₂ adsorption capacity (R² = 0.99) (Figure 5c). A glimpse of this correlation was provided by Merchán and co-workers in their recent report, wherein they suggested that this structural property can improve the micropore volume and thus CO₂ uptake.23 Carbon in sp² hybridization states is considered to adsorb CO₂ through π−π interactions since sp² bonds (C≡C) are polarizable.38 Therefore, it can be concluded that the BUGC’s short- and long-range graphitic ordering, which is a polarizable π-electron system, has the potential to interact with CO₂ molecules effectively through dispersion forces. Additionally, this unique ordering created enormous ultramicropores (vide supra) in BUGC and thus high CO₂ uptake capacity was obtained for this material. Furthermore, oxygen-containing carbons such as hydroxyl/ester (C−O) and ketonic (C═O) functional groups had relatively poor correlations with R² values of 0.81 and 0.84, respectively (Figure S8b,c, SI).

The abovementioned correlations of uptake with respect to the percentage of hydroxyl/ketonic-type functionalities (C−O/C≡O) indicate that the presence of oxygen functionalities also affects the adsorption of CO₂ molecules. Therefore, in order to confirm the role of these functional groups with CO₂ uptake, FTIR experiments were carried out for BUGC (high adsorption capacity) and RG (high selectivity) after purging the materials with CO₂. Materials were degassed and purged with CO₂ continuously for 12 h, and thereafter, ex situ FTIR spectra were recorded and compared with those before purging (Figure 6 and Figure S9 and Table S5, SI). All the peaks for different functionalities were present after CO₂ purging, which indicates the unchanged identity of carbon materials and suggested non-covalent physisorption interactions between CO₂ and materials (BUGC and RG) (Figure 6a and Figure


S9a, S1). However, shifts in peak positions for different functionalities were observed (Figure 6b and Figure S9b, S1). These shifts can be correlated as quadrupole–dipole interactions wherein CO$_2$ acts as a quadrupole and dipoles are the ionic or polar sites of the adsorbent. Blue shifts in the wavenumber suggest the electron-donating nature of the functional groups of the materials, whereas red shifts highlight the electron-accepting nature. In the case of BUGC, the magnified spectra in Figure 6b suggest a blue shift in the wavenumber related to hydroxyl-type (C–O) (1030 cm$^{-1}$) and ketone-type (C=O) (1695 cm$^{-1}$) functionalities, suggesting the electron-donating nature of these oxygen-containing groups in the quadrupole–dipole interactions with CO$_2$ molecules. The peak located at 1564 cm$^{-1}$ for the graphitic (C=C) bond was also blue-shifted (Figure 6b), which highlights the participation of sp$^2$ hybridized carbon in the CO$_2$ adsorption mechanism in accordance with Raman and XPS correlations (vide supra). A COO$^-$ band situated at 2328 cm$^{-1}$ was red-shifted to 2315 cm$^{-1}$, indicating the electron-accepting nature of COO$^-$ functionalities (Figure 6b). Another shift of this band to a high wavenumber (2342 cm$^{-1}$, blue shift) was also observed, which corresponds to the electron-donating nature of the functional group (Figure 6b), and this shift symbolizes the interactions with the hydrogen atoms present at the edges of the carbon matrix. Apparently, a red shift in peak corresponding to the C–H bond (2988 cm$^{-1}$) was observed, indicating the electron-accepting nature of this bond (Figure 6b). Notably, similar shifts were observed in the case of RG, which are displayed in Figure S9a,b. However, the wavenumber shift was higher for RG compared to BUGC (Table S5, S1), which can be directly correlated to the relatively higher oxygen content in RG. Since the oxygen functionalities are electronegative in nature, they act as basic adsorption sites, which results in the attraction of CO$_2$ molecules toward themselves. Thus, it can be anticipated that the interactions between oxygen functionalities of RG and CO$_2$ molecules could be the major driving force for the high selectivity in RG. BUGC had a lower selectivity compared to RG due to a smaller percentage of oxygen (7.70% in BUGC vs 16.03% in RG, Table S1, S1), which is presumably a requirement for a higher selectivity. At this point, it can be concluded that the high CO$_2$ adsorption for BUGC was due to the ultramicroporous nature, unique sp$^2$ carbon-rich morphology, and presence of oxygen-containing functional groups. In IMC and MMC, a low ultramicroporous volume and undefined morphology lead to comparatively lower CO$_2$ uptakes. Interestingly, in the case of RG, the absence of ultramicropores limits the uptake capacity of the material; nevertheless, a greater amount of oxygen content was responsible for exceptional CO$_2$ vs N$_2$ selectivity.

**Thermodynamics and Recyclability of CO$_2$ Capture.**

In order to understand the thermodynamics of the adsorption, isosteric heat of adsorption ($Q_{ST}$) was determined using the Clausius–Clapeyron equation at 273 and 298 K (Figure 7a). $Q_{ST}$ reflects the interaction of adsorbate molecules with the adsorbent material. For all materials, $Q_{ST}$ values ranged between 18 and 35 kJ/mol, indicating a predominant physisorption phenomenon (<40 kJ/mol), in accordance with the above-fitted “k” (Langmuir parameter) values (vide supra). The smallest $Q_{ST}$ was in the range of 18–23 kJ/mol for IMC and MMC, which signifies their relatively weaker interactions with CO$_2$ molecules (Figure 7a). RG has shown high values of heat of adsorption, indicating strong interactions with CO$_2$ because of high concentrations of oxygen functional groups, as stated earlier, which validates the high selectivity (Figure 7a). An optimum $Q_{ST}$ in BUGC (30 kJ/mol) suggests a lower regeneration cost and low-energy desorption (Figure 7a). An ease of regeneration in BUGC was further verified by pressure swing regeneration experiments, wherein excellent cyclability after five consecutive cycles of CO$_2$ uptake was observed (Figure 7b). At this juncture, it is important to highlight that the BUGC had shown an excellent performance as a CO$_2$ adsorbent, and the adsorption capacity was significantly higher than that of recently reported carbon-based adsorbents (Table 2). Most importantly, the Table 2. Literature Comparison of the Latest Carbonaceous Materials Utilized for CO$_2$ Adsorption with BUGC

| nanomaterial                              | temperature (K)/pressure (bar) | CO$_2$ uptake (mmol/g) | references |
|------------------------------------------|--------------------------------|------------------------|------------|
| casein-derived porous carbon             | 273/1                          | 5.30                   | 1          |
| chemically activated carbon-S            | 273/1                          | 5.50                   | 34         |
| oxygen-functionalized mesoporous carbon  | 273/1                          | 4.16                   | 35         |
| asphaltene-derived activated carbon      | 273/1                          | 2.32                   |            |
| amine-functionalized mesoporous silica @ | 273/1                          | 3.64                   | 37         |
| corn husk oat hull kraft pulp            | 273/1                          | 2.33                   |            |
| soya-derived doped carbon (900,1000)     | 273/1                          | 0.90                   | 38         |
| hierarchical porous N-doped carbon       | 273/1                          | 1.27                   |            |
| nitrogen-doped activated porous carbon   | 273/1                          | 2.11                   |            |
| N-doped porous CNF (NiO/PCNF)            | 273/1                          | 2.7                    | 39         |
| N-containing pitch-based activated carbons | 273/1                          | 3.2                    |            |
| biorordered ultramicroporous graphite carbon (BUGC) | 273/1                          | 3.4                    | 40         |
|                                           | 273/1                          | 5.6                    | 41         |
|                                           | 273/1                          | 4.3                    |            |
|                                           | 273/1                          | 2.46                   | 42         |
|                                           | 273/1                          | 1.78                   |            |
|                                           | 273/1                          | 4.93                   | 43         |
|                                           | 273/1                          | 2.57                   |            |
|                                           | 273/1                          | 7.81                   | This work  |
|                                           | 273/1                          | 4.46                   |            |

studied correlations of materials’ properties with CO$_2$ capture presented in this work will work as a strong foundation for the scientific community, which will help to further improve CO$_2$ capture by carbon-based materials.
CONCLUSIONS

In conclusion, five cost-effective carbon nanomaterials were selected for CO₂ capture. Among them, the BUGC nanomaterial prepared from simple KOH activation of two carbon resources (mechanically infused NC and RG) has shown the highest CO₂ uptake capacity of 7.81 mmol/g at 273 K and 1 bar pressure. This study revealed that a high ultramicroporous volume helps to improve CO₂ capture since the adjacent pore walls of ultramicropores develop a high adsorption potential to interact with CO₂ molecules. Next, the higher sp³ carbon content also promotes CO₂ adsorption as the polarizable π-electron cloud interacts with CO₂ molecules through dispersion forces. Thus, BUGC having high ultramicroporous volume, boidered morphology, and graphitic characteristics had a very high CO₂ adsorption capacity. In addition, BUGC revealed a high CO₂ vs N₂ selectivity of 15, low regeneration energy, and 100% CO₂ uptake retention for five consecutive pressure swing cycles. On the other hand, RG has shown a remarkable CO₂ vs N₂ selectivity of 57 due to the high percentage of different oxygen functionalities present in the nanomaterial, which act as basic adsorption sites due to their electonegative nature and attract CO₂ molecules toward themselves, employing a higher quadrupole–dipole interaction. Finally, it is important to highlight that the fundamental science developed herein will create a strong foundation for the further development of new materials to improve CO₂ uptake in the near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04269.

SEM, TEM, FTIR, XPS, Raman, N₂ adsorption, correlation plots, experimental details, and additional results (PDF)

AUTHOR INFORMATION

Corresponding Author

Amit Paul — Department of Chemistry, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal, MP 462066, India; orcid.org/0000-0002-8086-1606; Email: apaul@iiserb.ac.in

Author

Palak Mehra — Department of Chemistry, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal, MP 462066, India; orcid.org/0000-0002-4286-4777

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c04269

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.P. acknowledges financial support from DST-SERB New Delhi, (EMR/2016/005999, CRG/2020/002493), infrastructural support from IISER Bhopal, and the FIST supported TEM facility to the Dept. of Chemistry, IISER Bhopal. P.M. acknowledges IISER Bhopal for PhD fellowship. We sincerely thank Dr. Surajit Saha, Department of Physics, IISER Bhopal for Raman spectroscopy experiments and analysis. We thank Dr. Ravi Shankar Singh, Department of Physics, IISER Bhopal for assistance in XPS studies.

REFERENCES

(1) Singh, G.; Bahadur, R.; Ruban, A. M.; Davidraj, J. M.; Su, D.; Vinu, A. Synthesis of functionalized nanoporous biocarbons with high surface area for CO₂ capture and supercapacitor applications. Green Chem. 2021, 23, 5571–5583.
(2) Singh, G.; Lakhí, K. S.; Ramadass, K.; Sathish, C. I.; Vinu, A. High-Performance Biomass-Derived Activated Porous Biocarbons for Combined Pre- and Post-Combustion CO₂ Capture. ACS Sustainable Chem. Eng. 2019, 7, 7412–7420.
(3) Singh, G.; Lee, J.; Karakoti, A.; Bahadur, R.; Yi, J.; Zhao, D.; AlBahily, K.; Vinu, A. Emerging trends in porous materials for CO₂ capture and conversion. Chem. Soc. Rev. 2020, 49, 4360–4404.
(4) Zhi, J.; Wu, L.; Bu, Z.; Jie, S.; Li, B.-G. Polyethyleneimine-Grained HKUST-Type MOF/PolyHIPE Porous Composites (PEL@PGD-H) as Highly Efficient CO₂ Adsorbents. Ind. Eng. Chem. Res. 2019, 58, 4257–4266.
(5) Liang, W.; Liu, Z.; Peng, J.; Zhou, X.; Wang, X.; Li, Z. Enhanced CO₂ Adsorption and CO₂/N₂/CH₄ Selectivity of Novel Carbon Composites CPDA@A-Cs. Energy Fuels 2019, 33, 493–502.
(6) Kupgan, G.; Abbott, L. J.; Hart, K. E.; Colina, C. M. Modeling Amorphous Microporous Polymers for CO₂ Capture and Separations. Chem. Rev. 2018, 118, 5488–5538.
(7) Oschatz, M.; Antonietti, M. A search for selectivity to enable CO₂ capture with porous adsorbents. Energy Environ. Sci. 2018, 11, 57–70.
(8) Rodríguez-García, S.; Santiago, R.; López-Díaz, D.; Merchán, M. D.; Velázquez, M. M.; Fierro, J. L. G.; Palomar, J. Role of the Structure of Graphene Oxide Sheets on the CO₂ Adsorption Properties of Nanocomposites Based on Graphene Oxide and Polyyaniline or Fe₃O₄-Nanoparticles. ACS Sustainable Chem. Eng. 2019, 7, 12464–12473.
(9) Zhao, Y.; Liu, X.; Han, Y. Microporous carbonaceous adsorbents for CO₂ separation via selective adsorption. RSC Adv. 2015, 5, 30310–30330.
(10) Choi, S. W.; Tang, J.; Pol, V. G.; Lee, K. B. Pollen-derived porous carbon by KOH activation: Effect of physicochemical structure on CO₂ adsorption. J. CO2 Util. 2019, 29, 146–155.
(11) Creamer, A. E.; Gao, B. Carbon-Based Adsorbents for Postcombustion CO₂ Capture: A Critical Review. Environ. Sci. Technol. 2016, 50, 7276–7289.
(12) Pang, R.; Lu, T.; Shao, J.; Wang, L.; Wu, X.; Qian, X.; Hu, X. Highly Efficient Nitrogen-Doped Porous Carbonaceous CO₂ Adsorbents Derived from Biomass. Energy Fuels 2021, 35, 1620–1628.
(13) Raganati, F.; Miccio, F.; Ammendola, P. Adsorption of Carbon Dioxide for Post-combustion Capture: A Review. Energy Fuels 2021, 35, 12845–12868.
(14) Wang, Y.; Wang, H.; Zhang, T. C.; Yuan, S.; Liang, B. N-doped porous carbon derived from rGO-Incorporated polyphenylenediamine composites for CO₂ adsorption and supercapacitors. J. Power Sources 2020, 472, 228610.
(15) Ouyang, L.; Xiao, J.; Jiang, H.; Yuan, S. Nitrogen-Doped Porous Carbon Materials Derived from Graphene Oxide/Melamine Resin Composites for CO₂ Adsorption. Molecules 2021, 26, 5293.
(16) Balasubramanian, R.; Chowdhury, S. Recent advances and progress in the development of graphene-based adsorbents for CO₂ capture. J. Mater. Chem. A 2015, 3, 21968–21989.
(17) Shen, Z.; Liu, C.; Yin, C.; Kang, S.; Liu, Y.; Ge, Z.; Xia, Q.; Wang, Y.; Li, X. Facile large-scale synthesis of macroscopic 3D porous graphene-like carbon nanosheets architecture for efficient CO₂ adsorption. Carbon 2019, 145, 751–756.
(18) Gong, J.; Lin, H.; Antonietti, M.; Yuan, J. Nitrogen-doped porous carbon nanosheets derived from poly(ionic liquid): hierarchical pore structures for efficient CO₂ capture and dye removal. J. Mater. Chem. A 2016, 4, 7313–7321.
(19) Hao, G.-P.; Jin, Z.-Y.; Sun, Q.; Zhang, X.-Q.; Zhang, J.-T.; Lu, A.-H. Porous carbon nanosheets with precisely tunable thickness and selective CO$_2$ adsorption properties. Energy Environ. Sci. 2013, 6, 3740–3747.

(20) Zhang, Z.; Cano, Z. P.; Luo, D.; Dou, H.; Yu, A.; Chen, Z. Rational design of tailored porous carbon-based materials for CO$_2$ capture. J. Mater. Chem. A 2019, 7, 20985–21003.

(21) Shi, W.; Zhang, Q.; Liu, S.; Su, S.; Chang, B.; Yang, B. Copper ions-assisted inorganic dynamic porogen of graphene-like multiscale microporous carbon nanosheets for effective carbon dioxide capture. J. Colloid Interface Sci. 2021, 600, 670–680.

(22) Shen, Z.; Song, Y.; Yin, C.; Luo, X.; Wang, Y.; Li, X. Construction of hierarchically porous 3D graphene-like carbon material by N co-doping for enhanced CO$_2$ capture. Microporous Mesoporous Mater. 2021, 322, 111158.

(23) Ye, Y.; Vega Martín, L.; Sánchez Montero, M. J.; López-Díaz, D.; Velázquez, M. M.; Merchán, M. D. Optimizing the Properties of Hybrids Based on Graphene Oxide for Carbon Dioxide Capture. Ind. Eng. Chem. Res. 2022, 61, 1332–1343.

(24) Mehra, P.; Singh, C.; Cherian, I.; Giri, A.; Paul, A. Deciphering the Incredible Supercapacitor Performance of Conducting Borided Ultramicroporous Graphitic Carbon. ACS Appl. Energy Mater. 2021, 4, 4416–4427.

(25) Singh, C.; Mishra, A. K.; Paul, A. Highly conducting reduced graphene oxide synthesis via low temperature chemically assisted exfoliation and energy storage application. J. Mater. Chem. A 2015, 3, 18557–18563.

(26) Singh, C.; Paul, A. Immense Microporous Carbon@Hydroquinone Metamorphosed from Nonporous Carbon As a Supercapacitor with Remarkable Energy Density and Cyclic Stability. ACS Sustainable Chem. Eng. 2018, 6, 11367–11379.

(27) Mehra, P.; Paul, A. Covalently Functionalized Hydroxyl-Rich Few-Layer Graphene for Solid-State Proton Conduction and Supercapacitor Applications. J. Phys. Chem. C 2022, 126, 6135–6146.

(28) Mehra, P.; Wilson, M.; Paul, A. Acid-Base Synergism in Nitrogen- and Oxygen-Functionalized Few-Layer Graphene for Low-Activation Barrier Solid-State Proton Conduction. J. Phys. Chem. C 2022, 126, 10534–10545.

(29) Barua, A.; Paul, A. Synergistic Effect of Oxygen and Nitrogen Co-doping in Metal–Organic Framework-Derived Ultramicroporous Carbon for an Exceptionally Stable Solid-State Supercapacitor via a “Proton Trap” Mechanism. Energy Fuels 2021, 35, 10262–10273.

(30) Singh, G.; Lakhi, K. S.; Sathish, C. I.; Ramadass, K.; Yang, J.-H.; Vinu, A. Oxygen-Functionalized Mesoporous Activated Carbons Derived from Casein and Their Superior CO$_2$ Adsorption Capacity at Both Low- and High-Pressure Regimes. ACS Appl. Nano Mater. 2019, 2, 1604–1613.

(31) Al-Ghoufi, M. A.; Da’ana, D. A. Guidelines for the use and interpretation of adsorption isotherm models: A review. J. Hazard. Mater. 2020, 393, 122383.

(32) Nováček, M.; Jankovský, O.; Luxa, J.; Sedmidubský, D.; Pumera, M.; Filas, V.; Lhotka, M.; Klímová, K.; Maťáčková, S.; Sofer, Z. Tuning of graphene oxide composition by multiple oxidations for carbon dioxide storage and capture of toxic metals. J. Mater. Chem. A 2017, 5, 2739–2748.

(33) Wang, Y.; Hu, X.; Hao, J.; Ma, R.; Guo, Q.; Gao, H.; Bai, H. Nitrogen and Oxygen Codoped Porous Carbon with Superior CO$_2$ Adsorption Performance: A Combined Experimental and DFT Calculation Study. Ind. Eng. Chem. Res. 2019, 58, 13390–13400.

(34) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. AIChE J. 1965, 11, 121–127.

(35) Liu, Y.; Wilcox, J. Effects of Surface Heterogeneity on the Adsorption of CO$_2$ in Microporous Carbons. Environ. Sci. Technol. 2012, 46, 1940–1947.

(36) Zhang, Z.; Zhou, J.; Xing, W.; Xue, Q.; Yan, Z.; Zhuo, S.; Qiao, S. Z. Critical role of small micropores in high CO$_2$ uptake. Phys. Chem. Chem. Phys. 2013, 15, 2523–2529.

(37) Presser, V.; McDonough, J.; Yeon, S.-H.; Gogotsi, Y. Effect of pore size on carbon dioxide sorption by carbide derived carbon. Energy Environ. Sci. 2011, 4, 3059–3066.

(38) Molavi, H.; Eskandari, A.; Shojaei, A.; Mousavi, S. A. Enhancing CO$_2$/N$_2$ adsorption selectivity via post-synthetic modification of NH$_2$-UiO-66(Zr). Microporous Mesoporous Mater. 2018, 257, 193–201.

(39) Lee, J. H.; Lee, H. J.; Choi, J. W. Unveiling anomalous CO$_2$-to-N$_2$ selectivity of graphene oxide. Phys. Chem. Chem. Phys. 2017, 19, 22743–22748.

(40) Casco, M. E.; Morelos-Gómez, A.; Vega-Díaz, S. M.; Cruz-Silva, R.; Tristán-López, F.; Muramatsu, H.; Hayashi, T.; Martínez-Escandell, M.; Terrones, M.; Endo, M.; Rodríguez-Reinoso, F.; Silvestre-Albero, J. CO$_2$ adsorption on crystalline graphitic nanostructures. J. CO2 Util. 2014, 5, 60–65.

(41) Anas, M.; Gönel, A. G.; Bozbag, S. E.; Erkey, C. Thermodynamics of Adsorption of Carbon Dioxide on Various Aerogels. J. CO2 Util. 2017, 21, 82–88.

(42) Chen, J.; Yang, J.; Hu, G.; Hu, X.; Li, Z.; Shen, S.; Radosz, M.; Fan, M. Enhanced CO$_2$ Capture Capacity of Nitrogen-Doped Biomass-Derived Porous Carbons. ACS Sustainable Chem. Eng. 2016, 4, 1439–1445.

(43) Guo, Y.; Tan, C.; Sun, J.; Li, W.; Zhang, J.; Zhao, C. Porous activated carbons derived from waste sugarcane bagasse for CO$_2$ adsorption. Chem. Eng. J. 2020, 381, 122736.

(44) Kush, B.; Kapsi, M.; Veziri, C. M.; Athanasekou, C.; Pilatos, G.; Reddy, K. S. K.; Raj, A.; Karanikolos, G. N. Asphaltenes-Derived Activated Carbon and Carbon Nanotube Membranes for CO$_2$ Separation. Energy Fuels 2018, 32, 11718–11730.

(45) Liu, L.; Zou, G.; Yang, B.; Luo, X.; Xu, S. Amine-Functionalized Mesoporous Silica @ Reduced Graphene Sandwichlike Structure Composites for CO$_2$ Adsorption. ACS Appl. Nano Mater. 2018, 1, 4695–4702.

(46) Valdebenito, F.; García, R.; Cruces, K.; Ciudad, G.; Chinga-Carrasco, G.; Habibi, Y. CO$_2$ Adsorption of Surface-Modified Cellulose Nanofibril Films Derived from Agricultural Wastes. ACS Sustainable Chem. Eng. 2018, 6, 12603–12612.

(47) Rana, M.; Subramani, K.; Sathish, M.; Gautam, U. K. Soya derived heteroatom doped carbon as a promising platform for oxygen reduction, supercapacitor and CO$_2$ capture. Carbon 2017, 114, 679–689.

(48) Li, J.; Tian, L.; Liang, F.; Wang, J.; Han, L.; Zhang, J.; Ge, S.; Dong, L.; Zhang, H.; Zhang, S. Molten salt synthesis of hierarchical porous N-doped carbon submicrospheres for multifunctional applications: High performance supercapacitor, dye removal and CO$_2$ capture. Carbon 2019, 141, 739–747.

(49) Wei, H.; Chen, H.; Fu, N.; Chen, J.; Lan, G.; Qian, W.; Liu, Y.; Lin, H.; Han, S. Excellent electrochemical properties and large CO$_2$ capture of nitrogen-doped activated porous carbon synthesized from waste longan shells. Electrochim. Acta 2017, 231, 403–411.

(50) Li, Q.; Guo, J.; Xu, D.; Guo, J.; Ou, X.; Hu, Y.; Qi, H.; Yan, F. Electrosynp N-Doped Porous Carbon Nanofibers Incorporated with NiO Nanoparticles as Free-Standing Film Electrodes for High-Performance Supercapacitors and CO$_2$ Capture. Small 2018, 14, 1704203.

(51) Lee, M.-S.; Park, M.; Kim, H. Y.; Park, S.-J. Effects of Microporosity and Surface Chemistry on Separation Performances of N-Containing Pitch-Based Activated Carbons for CO$_2$/N$_2$ Binary Mixture. Sci. Rep. 2016, 6, 23224.