



Full Length Article

Tunable gas adsorption in graphene oxide framework

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ABSTRACT

Effect of length of linker inter-space was studied on the adsorption capacity of CO₂ by graphene oxide framework (GOF). Effect of linker inter-space of 14, 11, and 8 Å was studied here. The linker inter-space of 11 Å showed the highest CO₂ adsorption capacity. A dual-site Langmuir model was observed for adsorption of CO₂ and CH₄ into the GOF. According to radial distribution function (RDF), facial and central atoms of linker are the dual-site predicted by Langmuir model. Two distinguishable sites of adsorption and parallel orientation of CO₂ are the main reasons of high adsorption capacity in 11 Å linker inter-space. Gas-adsorbent affinity obtains the orientation of CO₂ near the linker. The affinity in the 11 Å linker inter-space is the highest. Thus, it forces the CO₂ to lay parallel and orient more localized than the other GOFs. In addition, CH₄ resulted higher working capacity than CO₂ in 14 Å. This occurs because of the change in gas-adsorbent affinity by changing pressure. An entrance adsorption occurs out of the pore of the GOF. This adsorption is not as stable as deep adsorption.

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1. Introduction

Carbon capture has been introduced as a critical technology for reducing the released CO₂ in the atmosphere. Although considerable renewable energy generation methods have been developed to eliminate carbon emissions, no technology can effectively scaled to replace fossil fuels in the near future. In addition, applying any technologies to reduce carbon emissions have to include some forms of carbon capture [1,2]. The most traditional industrial method for eliminating CO₂ from gas streams involves absorption of CO₂ with concentrated solvent containing amines typically monoethanolamine [3]. However, the energy consumption of this process is high and alternative processes have been suggested, *i.e.* advanced solvents, membranes, and adsorption.

Graphene has arisen to become a wonderful two-dimensional planar material with unique properties [1,2]. In addition to its unusual electronic properties, it is associated with high-surface area, the predicted value being about 2600 m²/g [4]. To synthesis graphene sheet, layers of graphite material should be separated by oxidation or intercalation [5].

Under standard conditions, different functional groups of graphene oxide, GO, do not allow the available sp² carbons and inter-layer spaces be accessible for gas capturing or storage. Changing the

interlayer spacing to generate novel porous graphene based materials would be of valuable for gas storage and capturing related.

In recent investigations, fullerene intercalated graphene sheets demonstrated enhanced CO₂ adsorption with increasing fullerene concentration [6,7]. At low pressures, the optimum CO₂ adsorption occurs in the pores with an effective diameter of 5 Å because of the energetically favorable surface interaction [8]. In a relatively large interlayer spacing 10–24 Å, the considerable amount of CO₂ adsorption occurs at relatively high pressures due to multilayer molecular adsorption. Besides, a molecular simulation of multilayer graphene with and without Li-doping was carried out for the CH₄ adsorption. In addition, effect of interlayer distance was studied [9]. At an interlayer distance of 3.4–5.1 Å, it was observed that CH₄ adsorption was not occurred due to steric effect of the adsorption space in graphene and Li-graphene. However, an interlayer space between 6.8–20.4 Å results a good CH₄ adsorption. Accordingly, changing the interlayer spacing can be used for selective gas adsorption.

Modification of GO layers through intercalation or pillaring with linkers is an effective method to increase the interlayer space [10]. Graphene oxide frameworks (GOFs) are new interesting porous materials prepared by separating the GO layers with various pillaring units. The chemical bonding between the GOF monolayers suggests greater mechanical stability compared to GO.

Theoretically, constructed graphene networks pillared by carbon nanotubes are predicted to exhibit high gas storage capacity [11,12]. In the past few years, pillared GO frameworks making

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use of boronate ester as the linker have received tremendous attention as versatile building blocks for the construction of porous material [5].

Chan et al. [13] studied the H₂ adsorption on 1,4-phenyldiboronic acid linker and reported adsorption of 1.85 wt%. Burrell et al. [10] studied GOF by simulation and predicted H₂ adsorption of 6.1 wt%. Reunchan et al. [14] and Lan et al. [15] investigated adsorption of H₂ on the metal decoration of host material. They reported that decorated metal prefers to form cluster which decreases H₂ uptake. Other studies in this field [16–18] also verified this result.

Many studies have been focused on the adsorption of gases (most of them focus on H₂) on the intercalated GO and rarely investigated the pillared GO. In the current study, CO₂ adsorption on boronic acid GOF was studied by means of molecular dynamics simulation. Totally, the main objective of this study can be summarized as investigating the effect of linker density, comparing adsorption of CO₂ and CH₄ on one of the studied GOFs, studying the structural behavior of the gases in the interlayer, and investigating dynamics behavior of the gases in GOF.

2. Simulation method

Three linkers with different interspaces have been selected to explore the effect of linker density in adsorption of CO₂ on GOF. In the present work, we consider idealized GOF materials with different linker inter space as shown in Fig. 1a. We assigned High (H-GOF), Medium (M-GOF), and, Low (L-GOF) to the GOFs to show the different spaces between the linkers. High, Medium, and Low correspond to linker inter space of 14, 11, and 8 Å.

In order to evaluate adsorption isotherm, the method reported in Ref. [19] was applied. In addition, instead of ideal gas equation of state, the data reported by NIST database [20] were selected to calculate gas pressure. To fix the GOF at its position and prevent translation of the system, SHAKE algorithm [21] by the tolerance of 1×10^{-5} was applied to the graphene and linkers. Simulations were performed under constant temperature, 298 K, and volume (NVT ensemble) using Nose-Hoover thermostat [22,23]. Orthorhombic three-dimensional periodic boundary conditions, with a simulation box measuring 78 Å in the z-direction and x-y plane of $43 \times 28 \text{ Å}^2$, was considered as an initial system, see Fig. 1b. First, all systems were equilibrated for 1.5 ns under a constant pressure of 1 atm and temperature of 298 K. Production step was followed by 4.0 ns MD run with a time step of 1.0 fs while the coordinates were saved every 0.1 ps for further analysis. We used the force field parameter reported in Ref. [24] for GOFs and DREIDING force field parameter [25] for the gas molecules.

Adsorption energy of the gases, E_{ad} , was obtained by [26]:

$$E_{ad} = E_{GOF-gas} - E_{GOF} - E_{gas} \quad (1)$$

where $E_{GOF-gas}$ is total energy of GOF-gas system at equilibrium geometry, E_{GOF} is total energy of GOF, and E_{gas} is total energy of gas molecule.

Potential of mean force (PMF) for the particles was calculated by means of the average densities in x-y plane using the fact that [26]:

$$PMF(z) = -kT \ln \left(\int \frac{\rho(z,r)}{\rho} dr \right) \quad (2)$$

where k is Boltzmann constant, T is temperature, and ρ is the number density. The rolling average stack to 20,000 time steps was conducted between Δz slabs of 0.01 Å. First, the number of time steps used for the collection of the $\rho(z)$ histograms was stated. Then, each function was given in turn. The Simpson method was applied to calculate the integral.

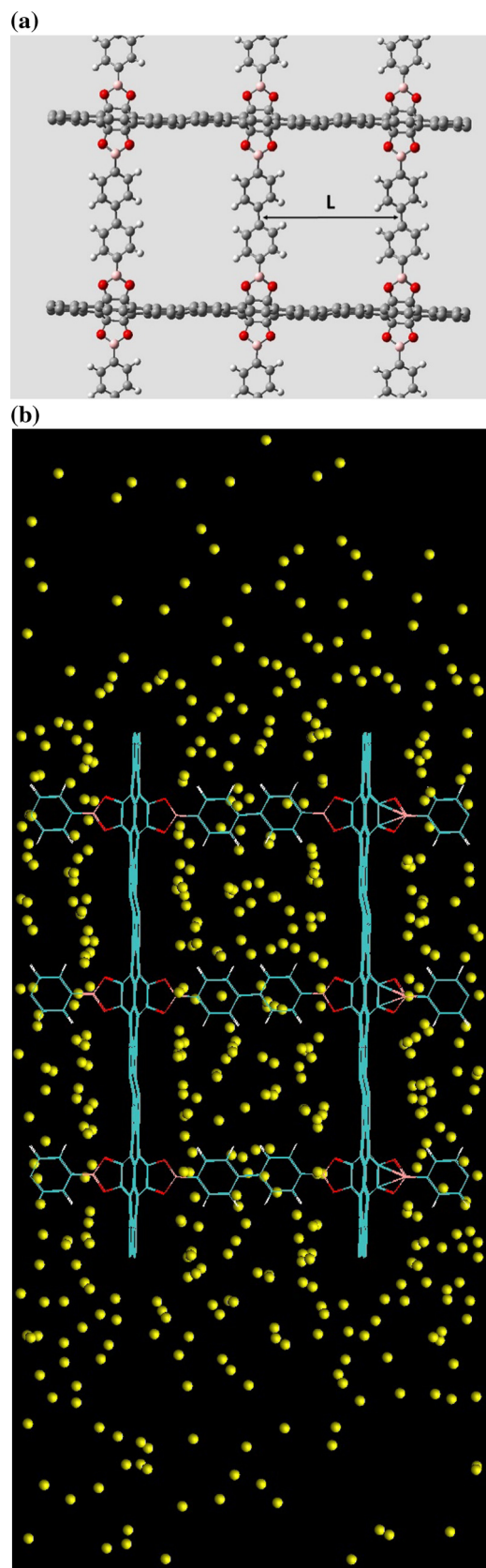


Fig. 1. Introducing (a) Inter space of L between the linkers, (b) simulation box.

Analyzing atomic correlation is performed by radial distribution function (RDF). RDF shows the probability of finding a particle in a certain distance to another particle [27]:

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