Functionalized α-GDY with different displacement distance for CO₂/CH₄ diffusion and separation

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Abstract. Functionalized α-GDY with −H, −F, and −N for different displacement distance were designed as promising membranes for separation CO₂ from CH₄ by using molecular dynamics simulations. The α-GDY were regulated to form suitable pore sizes by functionalization and displacement for separation CO₂ from CH₄. F-GDY membranes and displacement distance with 1/3 have ultralow CO₂ selectivity over N₂ of ~0, which indicate that no CO₂ pass through F-GDY membranes and CO₂ and CH₄ were separated efficiently. Among these membranes, N-GDY with 1/3 displacement distance has highest permeance of 5.97 × 10⁻⁵ mol m⁻² s⁻¹ Pa⁻¹ at 300 K. Relative concentrations distribution confirmed that almost CO₂ molecules adsorbed the pore wall of membrane, CH₄ distributed in the gas box and vacuum. The interaction energy between gas molecules and membrane was analyzed to elucidate the significant impact of functionalization on the selectivity of CO₂ over CH₄ and CH₄ permeances passing through porous BN membranes.

1. INTRODUCTION

The rapid economic development in recent decades has been accompanied by a growing demand for energy [1, 2]. Traditional fossil fuel have thus been rendered insufficient to meet the energy needs of the society development. Moreover, fossil fuel combustion produces multiple pollutants, which have serious effects on the natural environment and human health. Natural gas is a better choice owing to its abundant reserves, low price, and low levels of CO₂ emission from combustion. Natural gas is mainly composed of CH₄, CO₂, a small quantity of H₂S, CO, and N₂. Therefore, separation of CH₄ from natural gas is indispensable from the viewpoint of commercial value and practical application. Current separation technologies, such as pressure swing adsorption [3], cryogenic separation [4] and chemical scrubbing [5], are still suffering from their equipment investment, energy consumption, and environmental impact issues. In contrast, membrane separation has become a promising candidate for economical, efficient, and environmentally friendly gas separation [6]. During the development of membrane separation, various materials have been proposed to address the trade-off issue between permeability and selectivity, where the graphdiyne (GDY), a new two-dimensional carbon allotrope containing sp- and sp²- hybridized carbon atoms, is considered as the most promising membrane materials due to its promising electronic, optical, and mechanical properties [7, 8].
Recently, GDY as a potential gas separation membrane has been widely studied. Zhao et al. [9] studied GDY modified with H, F, and O atoms to separate CO$_2$/N$_2$/CH$_4$. The results showed the GDY-F and GDY-O membranes can excellently separate CO$_2$ and N$_2$ from CH$_4$ ($10^{4}$–$10^{5}$ at 298 K) and extremely high permeances for CO$_2$ and N$_2$ ($10^{-4}$–$10^{-2}$ mol/m$^2$ s Pa at 298 K). Zhang et al. [10] investigated single-layer porous graphene, α/α2/β-graphyne, and porous BN membrane with similar pore sizes to separate pentane isomers and found that graphynes with rigid –C≡C– triple bonds make the effective space of the pores smaller and harder to distort, so they have much higher barriers than for these of other membranes to effectively block the monobranched and dibranched pentane isomers. Cranford et al. [11] adopt GDY as nanomesh to achieve selective diffusion of H$_2$ amongst CO and CH$_4$. The results showed the mass flux of H$_2$ through a graphdiyne membrane to be on the order of 7 to 10 g cm$^{-2}$ s$^{-1}$ between 300 K and 500 K with CO and CH$_4$ remaining isolated. This results show GDY has the excellent performance in gas separation, studies on the multilayer GDY with different stack style and the effect of functionalization remain unclear.

In this work, we investigate the diffusion and separation of CH$_4$/CO$_2$ in functionalized α-GDY with –H, –F, and –N for different displacement distance. First, density functional theory is employed to optimize the geometry, build AA and AB stack membranes, and interlayer spacing, and structure characterization of functionalized α-GDY for different displacement distance are presented. Then, the selectivity and permeance are analyzed to evaluate the diffusion and separation capacity of the functionalized α-GDY for different displacement. Finally, diffusion process of CO$_2$/CH$_4$ are compared in terms of relative concentration and interaction energy. This work highlighted the potential of functionalized α-GDY membranes for CO$_2$ and CH$_4$ separation by functionalization and stack way.

2. Model and method
Graphdiyne is synthesized via a C–C coupling reaction in solution at a mild temperature. The molecular design motif is outlined in Fig. 1. The hydrogen, fluorine, and nitrogen atoms are evenly distributed in the 2D molecular plane. Meanwhile, large pores are formed in the 2D molecule plane, which improves the efficiency of separation and diffusion. After building these three structures, DFT calculations are performed to optimize three structures with B3LYP/6-31+g(d,p) basis set in Gaussian 09 package. The original membranes of the functionalized GDYs are composed by six layers 2D molecular plane with AA stack. In order to adjust pore size and create the best separation performance, the six layer structure are divided equally into two parts. The lower three layer structures as an integral are moved about 1/5, 1/4, 1/3, and 1/2 distance of OA along the x direction. Next, the simulation box consists of three part: membranes, vacuums, and gas container. And the gas phase and vacuum phase are divided by the two membranes. The gas container is the mixture of CO$_2$ and CH$_4$ with 1:1 composition. MD calculations are completed using the Forcite code in Materials Studio. The interatomic interactions are described by the force field of a condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS). The Andersen thermostat method is used to control the temperature of the system at 300 K. MD simulations are carried out in the canonical (NVT) ensemble. During the simulations, the time steps are set to $1 \times 10^7$, with a fixed time step of 1 fs. Data was collected every 5 ps.

Fig. 1 Schematic model of three α-GDY membranes.

3. RESULTS AND DISCUSSION

3.1. Structure and stability
First, the interlayer distance is the critical factors to determine the thickness of membranes. The interlayer distances of GDYs membrane with the AA stack are also calculated by DFT method. The interlayer distances are 3.65 Å for H-GDY, 3.60 Å for F-GDY, and 3.63 Å for N-GDY, respectively. These values are compliant with experimental and theoretical results in Table 1, which prove rationality
of models and accuracy of calculation method. The two third and fourth layer membranes are employed to compute the relative energy for confirming the stability of the structures in Fig. 2 [12]. The relative energy is defined as:

$$ E = E_{\text{total}} - E_{x} - E_{y} $$

where $E$ is the relative energy, the $E_{\text{total}}$ is total energy of the two layer membranes, $E_{x}$ and $E_{y}$ is the individual energy of two layer membranes, respectively. So lower values of relative energy equate to better stability performance in GDY membranes. Clearly, the three GDY membranes with 1/2 displacement distance are the most stable structures. The results are similar to multilayer graphene [13], and consistent with pack way of multilayer GDY [8]. Because N and F atoms is strong electronegativity and electropositivity, the distance between N/F atoms of upper and lower two layers in AA stack is closer than these of AB stack, which leads to stronger electrostatic interaction. When two layers present AB stack with 1/2 displacement distance, the electrostatic interaction is weaker than those of AB stack, which is attributed that the distance between N/F atoms of upper and lower two layers is farthest than others.

Table 1 Comparison of interlayers of three α-GDY membranes with the experimental and theoretical value in previous literatures.

| Experiment | Theory | This work |
|------------|--------|-----------|
| H-GDY      | 3.65 Å | 3.64 Å    |
| F-GDY      | 3.73 Å | 3.60 Å    |
| N-GDY      | --     | --        | 3.63 Å    |

To investigate effectively the separation performance of the membrane, the selectivity is the critical indicator:

$$ S_{\text{CO}_2/\text{CH}_4} = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{y_{\text{CO}_2}/y_{\text{CH}_4}} $$

where $S$ is the selectivity of CO$_2$ over CH$_4$; $x_{\text{CO}_2}$ and $x_{\text{CH}_4}$ are the molar fractions of CO$_2$ and N$_2$ in their adsorbed phase; and $y_{\text{CO}_2}$ and $y_{\text{CH}_4}$ are the corresponding molar fractions of CO$_2$ and CH$_4$ in their bulk gas phases.

Table 2 shows number of gas molecules passing through the channel of GDYs and corresponding selectivity of CO$_2$ over CH$_4$. For the H-GDY’s, the membranes with displacement distance of 1 and 1/3, no CO$_2$ molecules pass through the membranes; the membranes with displacement distance of 1/2, 1/4, and 1/5, only 4, 2, and 1 molecules pass through the membranes, respectively. So, selectivities of CO$_2$ over CH$_4$ in five H-GDY is less than 0.2. For the F-GDYs the membranes with displacement distance of 1/5, 1/4, 1/3, and 1/2, no CO$_2$ molecules pass through the membranes; the membranes with displacement distance of 1, only 1 molecules pass through the membranes, respectively. So, selectivities of CO$_2$ over CH$_4$ in five H-GDY is less than 0.1. For the N-GDYs the membranes with displacement distance of 1/5 and 1/4, no CO$_2$ molecules pass through the membranes; the membranes with displacement distance of 1/3, 1/2, and 1, only 1, 3, and 1 molecules pass through the membranes, respectively. So, selectivities of CO$_2$ over CH$_4$ in five H-GDY is less than 0.2. These results present that only few CO$_2$ molecules pass through the membranes, so H-GDY,
F-GDY, and N-GDY show very low selectivity, namely, effective separation is achieved for the gas mixture.

Table 2 Number of gas passing through α-GDY membranes and corresponding selectivity of CO2/CH4.

| Distance | Parameters | CO2 | CH4 | Selectivity(CH4/CO2) |
|----------|------------|-----|-----|----------------------|
| 1/5      | H          | 1   | 0   | 0                    |
|          | F          | 22  | 12  | 13                   |
|          | N          | 13  | 13  |                       |
| 1/4      | H          | 2   | 0   | 0                    |
|          | F          | 20  | 14  | 12                   |
|          | N          | 12  | 12  |                       |
| 1/3      | H          | 0   | 0   | 1                    |
|          | F          | 27  | 15  | 13                   |
|          | N          | 13  | 13  |                       |
| 1/2      | H          | 4   | 0   | 3                    |
|          | F          | 25  | 18  | 16                   |
|          | N          | 16  | 16  |                       |
| 1        | H          | 0   | 1   | 1                    |
|          | F          | 26  | 13  | 12                   |
|          | N          | 12  | 12  |                       |

3.3. Permeance of CH4

Permeance, reflecting separation efficiency of gases, is an important indicator to evaluate performance of membrane. Only the process of CH4 molecules passing through the pores of the GDY’s membrane is investigated and estimate the He permeance, because few CO2 can pass through the GDY’s membrane. In these cases, the permeation process can be divided into three steps: gas molecules are firstly adsorbed to the membrane surface by the van der Waals interactions to reach the inlet of pore. Then, they linger on the surface for a few picoseconds before successfully crossing the membrane due to the existing of the gas concentration difference between the “gas reservoir” and the vacuum space. Finally, the gas molecules cross the membrane and reach the other side of the membrane. The system reaches equilibrium, there are some CH4 molecules passing through the different GDY membranes to the vacuum space at 300 K, while the other molecules cannot penetrate through GDY membranes. The permeability of CH4 in GDY membranes with different displacement distance are listed in Fig. 3. All permeability of CH4 in the GDY membranes with different displacement are larger than industrial production standard (6.7 × 10^-9 mol m^-2 s^-1 Pa^-1) [14]. This result indicates that the GDY membranes show excellent permeances of CH4 at a room temperature. N-GDY membranes with different displacement have the largest permeability of CH4. For the same displacement, the sequence of CH4 permeability follows N-GDY > H-GDY > F-GDY. Pore size of N-GDY with dangling bonds is larger than these of H-GDY with H atoms passivation and F-GDY with F atoms passivation, and H-C bond is shorter than F-C bond. For the same membrane with different displacement, the sequence of CH4 permeability follows 1/1 > 1/3 > 1/2 > 1/4. Because 1/1 with AA stack present the largest pore size; all small pore in 1/2 and 1/3 membranes, formed by displacement, allow CH4 to pass through; one of two small pore in 1/4 and 1/5 can allow CH4 to pass through, and the small pore of 1/5, allowing to CH4 to pass through, is larger than that of 1/4.
From the MD simulations, it can be concluded that the GDY membranes only allow CH$_4$ to penetrate and prevent CO$_2$ from passing through at 300 K. Furthermore, it is easier for CH$_4$ to pass through the N-GDY membrane than F-GYH and H-GDY due to pore sizes, revealing N-GDY has better permeance for CO$_2$/CH$_4$ separation.

3.4. Diffusion process

**Relative concentration.** To illuminate distribution of CO$_2$/CH$_4$ in the boxes, the relative concentration as a function of the distance along the z direction at the equilibrium state in Fig. 4. $z = 0$ is located at one side of the vacuum box away from the membrane. The relative concentration profile indicates CH$_4$ molecules are distributed in the whole box, and CO$_2$ molecules are adsorbed mainly in inner wall of membrane. The black lines represent the membranes. For the H-GDYs, when the displacement distance is 1/5, almost all of the CO$_2$ molecules and some CH$_4$ molecules are adsorbed in inner wall of membrane, so gas phase and vacuum phase boxes are fills with only CH$_4$ molecules. With the displacement distance increasing, the relative concentration of CO$_2$/CH$_4$ have similar characteristics, but relative concentration of CO$_2$ molecules adsorbed in inner wall of membrane increase. The results show more CO$_2$ can be blocked by membranes, displacement is conducive to CO$_2$ and CH$_4$ separation. For the F-GDYs and N-GDYs, the distributions of CO$_2$ and N$_2$ are similar to these of H-GDY, almost all of the CO$_2$ molecules are adsorbed in inner wall of membrane. And the relative concentrations of adsorbed CO$_2$ molecules in the F-GDYs and N-GDYs are higher than these of H-GDY, more CH$_4$ are concentrated in inner pore and surface of membrane. Because the F and N atoms with electropositivity/electronegativity have the stronger interaction with CO$_2$/CH$_4$ than these of H atom. A number of adsorbed CO$_2$ in the pore wall can prevent CH$_4$ from entering the pore, so that membrane surface have good CH$_4$ adsorption.

**Interaction energy.** To elucidate the priority of CH$_4$ over CO$_2$ passing through the GDYs, the interaction energies between all CH$_4$/CO$_2$ and GDYs membranes are calculated, as shown in Fig. 5. The interaction energy is defined as:

$$E_{\text{inter}} = E_{\text{total}} - E_{\text{membrane}} - E_{\text{gas}}$$  \hspace{1cm} (3)

where $E_{\text{inter}}$ is the interaction energy, $E_{\text{total}}$ is the total energy of gas molecules and membrane, $E_{\text{membrane}}$ is the energy of separation membrane, and $E_{\text{gas}}$ is the energy of gas molecules. According to this definition, the larger negative value indicates the stronger interaction between the gas molecules and the membrane. The results show that the interaction energy decreases gradually at beginning and then stabilizes with simulation time increasing. Because only gas molecules in both side of gas box contact...
with the membrane at the initial stage, then gas molecules move and diffuse, the increasing gas molecules appear around the separation membrane. The interaction energy between the CO2 and GDY membranes is relatively stronger than that of CH4, which is related to their quadruple moment (4.30 × 10^{-26} esu cm² for CO2 vs 0 esu cm² for CH4) [15]. The stronger interaction energy renders CO2 prior to CH4 to adsorb on the separation membrane, especially for F and N atoms decorating the inner wall of GDY membranes. In Fig. 5a, for the given gas molecules, both interaction energies between the CO2/CH4 and GDY membranes follow the order of N-GDY > F-GDY > H-GDY, due to the effect of functionalization in the membranes. And the interaction energy between the CO2 and GDY membranes is stronger than that of CH4, due to their quadruple moment. The interaction energy between the CH4 and GDY membranes preferentially reaches equilibrium than that of CO2. The interaction energy between the CO2/CH4 and GDY membranes for AA stack is smaller than these of displacement structures, because displacement structures not only change the pore size of membranes, but also enlarge the contact area with gases, which enhance the interaction between the gases and GDY membranes.

![Interaction energy between the gas molecule and α-GDY membranes.](image)

**Fig. 5** The interaction energy between the gas molecule and α-GDY membranes.

### 4. CONCLUSIONS

In summary, diffusion and separation of CO2/CH4 in functionalized GDYs membranes with different displacement have been investigated by MD simulation. GDYs membranes create the favorable environment for the separation of CO2 from CH4 due to the cooperative effect of pore topological characteristics for different displacement and functionalization. For the same functionalization, F-GDY membranes show ultralow selectivity of CO2 over CH4; for the same displacement, the 1/3 displacement present the ultralow selectivity of CO2 over CH4. This results illustrate no CO2 passing through the membranes, the CO2 and CH4 mixtures can achieve complete separation. Furthermore, the CH4 passing through 1/3 displacement is highest permeance of 2.77 × 10^{-5} to 5.98 × 10^{-5}. Diffusion process shows that functionalized GDYs membranes lead to the stronger interaction energy with CO2/CH4, especially for CO2, thus facilitating CO2 to absorb on the pore wall of GDYs prior to CH4. So, CO2 molecules don’t pass through the GDY membrane, CH4 molecules process high permeance. CH4 is more conducive to reach an equilibrium state in functionalized GDYs membranes with different displacement with a larger diffusion coefficient than CO2. Results suggest that the functionalized GDYs membranes with different displacement exhibit complete separation of CO2 over CH4 and good permeance of CH4 and emphasize the effect of the cooperative effect of displacement and functionalization toward the outstanding gas separation.

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