Modified approach to separate hydrogen from carbon dioxide using graphdiyne–like membrane

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Abstract

We propose a modified approach to separate a mixture of hydrogen (H\textsubscript{2}) and carbon dioxide (CO\textsubscript{2}) gases using the graphdiyne–like membrane (GDY–H) based on density functional theory (DFT) calculations and molecular dynamics (MD) simulations. This membrane is designed by substituting one-third diacetylenic linkages in the graphdiyne structure with hydrogen atoms. Our DFT calculations show poor selectivity and good permeances for H\textsubscript{2}/CO\textsubscript{2} gases passing through this monolayer membrane. To improve the performance of the GDY–H membrane for H\textsubscript{2}/CO\textsubscript{2} separation, we place two layers of GDY–H adjacent to each other which the distance between them is 2 nm. Then, we insert 1,3,5 three amine benzene between two layers. In this approach, the selectivity of H\textsubscript{2}/CO\textsubscript{2} is increased from 70% to 100%. Furthermore, GDY–H membrane shows excellent permeance, more than 10\textsuperscript{8} gas permeation unit (GPU), for H\textsubscript{2} molecule at temperatures above 20 K. The H\textsubscript{2} permeance is much higher than the value of the current industrial applications. Moreover, our proposed approach represents an appropriate balance between the selectivity and permeance factors for the gas separation which is a crucial parameter for H\textsubscript{2} purification and CO\textsubscript{2} capture processes in the industry.

Introduction

Nowadays, H\textsubscript{2} energy is considered as one of the most efficient substitutes instead of fossil fuels because of its high energy content, clean-burning product, zero pollutant emission, natural abundance and renewable nature.\textsuperscript{1–4} Therefore, it will be the most promising alternative energy source in the future. At the H\textsubscript{2} production processes, especially steam–methane reforming reaction, there are many byproducts such as CO, CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} which cause undesirable influences on the energy content and utilization of H\textsubscript{2}.\textsuperscript{5} Consequently, developing high-quality and low-cost technologies to separate H\textsubscript{2} from other impurity gases is very important in the industry.\textsuperscript{6}

Moreover, CO\textsubscript{2} is widely regarded as the main greenhouse gas. It is noteworthy that approximately 80% CO\textsubscript{2} emissions come from the combustion of the fossil fuels.\textsuperscript{4} It is predicted that the concentration of atmospheric CO\textsubscript{2} would increase up to 570 ppm in 2100 which leads to a global temperature rise of 1.9 °C.\textsuperscript{6} Therefore, CO\textsubscript{2} capture technology will play an important role in climate change and global warming phenomena.\textsuperscript{7} On the other hand, CO\textsubscript{2} capture is a very expensive technology. So, researchers focus on the developing of economical and efficient technologies.\textsuperscript{12}

Currently, H\textsubscript{2} separation from CO\textsubscript{2} and CO\textsubscript{2} capture processes have attracted wide attention especially in the industrial applications. The common traditional gas separation technologies are cryogenic distillation and pressure
swing adsorption. However, these technologies have disadvantages such as complicated operation and high energy consumption.

So far, many CO$_2$ capture technologies are used based on physisorption–chemisorption, amine dry scrubbing, metal-organic frameworks (MOFs) and ionic liquids. Recently, membrane-based separation technologies are widely used for H$_2$ purification and CO$_2$ capture because of low energy consumption, low investment cost, simplicity in operation and easy maintenance after installation. In this regard, various membrane materials such as polymeric membranes, MOFs and zeolite membranes, ranging from tens of nanometers to several micrometers in thickness, have been applied to the gas separation technology.

The selectivity and permeance are two important factors to evaluate the performance of the gas separation membranes. An ideal two-dimensional (2D) membrane for the gas separation would show a good balance between the selectivity and permeance factors. However, traditional membranes usually encounter the selectivity-permeance trade-off problem. The permeance is inversely proportional to the thickness of the membrane. Hence, one-atom-thick membrane may be an excellent candidate for the gas separation.

In the past decade, the design and synthesis of appropriate 2D membranes for gas separation have attracted wide attention. Recently, graphene and other carbon allotropes have been used as the gas separation membranes. These structures show many properties such as periodically distributed uniform pores and high chemical and mechanical stability which make them suitable candidates for the gas separation. Among various carbon allotropes, graphdiyne (GDY) is a new 2D carbon allotrope composed of sp and sp$^2$ hybridized carbon atoms which can be constructed by replacing some carbon–carbon bonds in a graphene with uniformly distributed diacetylenic linkages. This structure was firstly synthesized on the surface of copper substrates using a cross-coupling reaction. Theoretical and experimental studies show that the existence of sp and sp$^2$ hybridized carbon in GDY leads to high π-conjunction, wide interplanar spacing, excellent chemical stability, extreme hardness and high thermal resistance of this structure. Furthermore, the heat of formation of GDY is reported about 18.3 kcal per g–atom C, which makes it to be the most stable carbon allotrope containing diacetylenic linkages.

Recently, many studies have been done to investigate the gas separation process through the GDY monolayer membrane because of its abundant uniform pores, the size of pores and one-atom thickness. For example, Cranford and Buehler performed MD simulations to investigate the temperature and pressure dependence of H$_2$ purification from CO and CH$_4$ in the GDY membrane. Zhang et al. showed that GDY with larger pores demonstrates a high selectivity for H$_2$ over large gas molecules such as CH$_4$, but a relatively low selectivity over small molecules such as CO and N$_2$. Jiao et al. based on DFT calculations showed that the selectivity of H$_2$ toward CH$_4$ and CO in the GDY monolayer membrane is much higher than those of silica and carbon membranes.

It has been proved that changing the pore size of sp–sp$^2$ hybridized carbon in the GDY by substituting some diacetylenic linkages with heteroatoms could be a promising strategy to improve the performance of the GDY monolayer membrane in the gas separation process. In this regard, Desroches et al. synthesized the GDY–like nanoribbons (GDNR) in which one-third diacetylenic linkages of GDNR were replaced with H atoms which leads to form the rhomboidal pores instead of triangular pores. A nitrogen modified GDY is also investigated concerning its performance for H$_2$ purification from CH$_4$ and CO. This structure shows high performance for H$_2$ purification by decreasing H$_2$ diffusion energy barrier. Moreover, Zhao et al. designed three GDY–like monolayer membranes by substituting one-third diacetylenic linkages with different heteroatoms H, F and O (GDY–H, GDY–F and GDY–O membranes, respectively) to control the pore size of GDY for separating a mixture of CO$_2$/N$_2$/CH$_4$ gases. Then, they investigated the separation performance of these membranes using DFT calcula-
tions and MD simulations. Their study showed that the GDY–H membrane exhibits poor selectivity for CO$_2$/N$_2$/CH$_4$ gases, while the GDY–F and GDY–O membranes can excellently separate CO$_2$ and N$_2$ from CH$_4$ in a wide temperature range.

In the present study, we propose a modified approach to separate H$_2$ from CO$_2$ using GDY–H monolayer membrane which designed by Zhao et al. We calculate the energy barriers of H$_2$ and CO$_2$ gases passing through GDY–H monolayer membrane using DFT calculations. Then, we obtain the selectivity and permeance of the membrane for H$_2$ and CO$_2$ gases. Furthermore, we place two layers of GDY–H adjacent to each other which the distance between them is 2 nm. Then, we insert 1,3,5 three amine benzene (1,3,5 TAB) between two layers. The electron pair of N atoms in this structure can improve CO$_2$ capture process. We perform MD simulations to calculate the selectivity and excellent permeance for separating a mixture of H$_2$/CO$_2$ gases using the GDY–H membrane in the presence of 1,3,5 TAB at different temperatures.

**Computational Methods**

A large 2D sheet 28.34 × 28.34 Å$^2$ in xy plane including 240 atoms of C and H is constructed to represent 2D GDY–H atomic layer to compute the energy barrier of the gases passing through it and describe the electron density isosurfaces for the gases interacting with porous GDY–H monolayer. Isoelectron density surfaces were obtained by the Gaussian 09 program at the B3LYP/6–31G(d) level with D3 correction and plotted at isovalues 0.0065 eÅ$^{-3}$ to determine the interaction between the electron density of the gas and the pore. Based on this method, we find the potential energy curves of a single H$_2$ and CO$_2$ particle when passing through the pore center of the membrane vertically and horizontally. In addition, the information of CO$_2$ capture by 1,3,5 TAB were obtained at the B3LYP/6–311++G(d,p) level with D3 correction.

MD simulations were performed to analyze H$_2$ purification using Forcite code in the Material Studio software under canonical (NVT) ensemble condition and the temperature range of 200–600 K was controlled by the Anderson thermostat. Periodic boundary conditions were applied in all three dimensions. The interatomic interactions were explained by a condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field, which has been widely used to compute the interactions between the gases and the carbon-based membranes. The cut-off distance of van der Waals interactions was set as 12.5 Å and the Ewald method used to calculate the electrostatic interactions. The cubic boxes with the dimensions of 37.55 × 37.55 × 37.55 Å$^3$ with 200 1,3,5 TAB molecules and 20 CO$_2$ molecules were performed in order to study radial distribution function (RDF) for carbon atoms in CO$_2$ and nitrogen atoms in 1,3,5 TAB.

The cubic boxes with the dimensions of 59.0 × 49.6 × 100 Å$^3$ for simulations were separate equally along the z-direction with pieces of the GDY–H membrane. Moreover, the cubic boxes with the dimensions of 59.0 × 49.6 × 120 Å$^3$ for simulations were trisected along the z-direction with two pieces of GDY–H membranes in the distance of 2 nm from each other which are placed at the middle of the box, forming one gas reservoir in the first part, 1,3,5 TAB in the middle and the vacuum region on the top side. During MD simulations, the carbon atoms on the edge of the membrane were always fixed, while all the other atoms in the system were fully relaxed. The total simulation time was 1000 ps, and Newtons equations were integrated using 1 fs time steps.

**Results and Discussion**

The stability of the designed membranes for the gas separation process is a crucial factor for their experimental applications. Zhao
et al. confirmed the stability of GDY–H monolayer membrane by calculating cohesive energy and phonon dispersion spectra. Their results showed that the cohesive energy of pristine GDY is 7.24 eV/atom, which is similar to the previous theoretical value 7.65 eV/atom. Moreover, the cohesive energy of GDY–H membrane is 6.73 eV/atom which is slightly smaller than the cohesive energy of pristine GDY, but is comparable with that of α–graphyne monolayer membrane 6.93 eV/atom and much higher than that of silicene 3.71 eV/atom. Therefore, the GDY–H monolayer membrane is strongly bonded structure and rather stable enough for its formation and application. Moreover, there is no imaginary frequency in the calculated phonon dispersion spectra for this membrane revealing that this structure is located at the minimum point on the relevant potential energy surfaces. This indicates that GDY–H membrane could be constructed in the experiments.

Figure 1 displays the most stable adsorption configurations of CO₂ molecule in the presence of 1,3,5 TAB molecule. For CO₂ molecule, the most stable adsorption sites occurred where C in CO₂ placed at the distance of 4.146 and 4.167 Å toward two nearest N atoms (Figure 1) with the binding energy of 0.52 eV and the C–O bond is parallel with C–H bond of the benzene ring in 1,3,5 TAB molecule. Taking account of the entropic penalty, it is expected that the binding energy should be greater than 0.5 eV to effectively capture gas molecule on solid surface. In the float environment of 1,3,5 TAB, we can demonstrate that these molecules show good behavior for the CO₂ capture.

Moreover, MD simulation was performed to confirm the DFT calculations. Liquid density is one of the available sources which can be used to validate a proposed force field. In this work, experimental data from the literature are compared with our results. The predicted density from our force field is in good agreement with the experimental data. The experimental value of the density of the 1,3,5 TAB is 1.279 cm³/ml at 298.15 K and 1 bar pressure, and the simulated density is 1.246 cm³/ml which is roughly ∼3% lower than the experimental value. This level of agreement is excellent considering that the calculations are purely predictive.

The RDF provides microstructure information into the nature of interactions as well as the arrangement of the molecules, which can be expressed as:

\[
g_{i,j}(r) = \frac{V}{N_i N_j} \sum_{i=1}^{N_i} \sum_{j=i+1}^{N_j} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_j(t)|) \rangle_t
\]

where \(\mathbf{r}_i\) and \(\mathbf{r}_j\) denote the position vectors of the \(i^{th}\) and the \(j^{th}\) particles and the bracket denotes the ensemble average on the distance between atoms \(i\) and \(j\). Moreover, \(N\) and \(V\) represent the number of the particles and vol-
Figure 3: Minimum energy pathways for H$_2$ and CO$_2$ gases passing horizontally (h) and vertically (v) through GDY–H membrane in the distance ±3 Å from the center of the pore.

In the gas separation membranes, the interaction energy between the gases and the membrane can be defined as

$$E_{\text{int}} = E_{\text{gas+sheet}} - (E_{\text{gas}} + E_{\text{sheet}})$$

(2)

where $E_{\text{gas+sheet}}$, $E_{\text{gas}}$ and $E_{\text{sheet}}$ are the total energy of the gas molecule adsorbed on the membrane, the energy of the isolated gas molecule and the energy of the membrane, respectively. In Figure 3, the minimum energy pathways for H$_2$ and CO$_2$ gases passing through GDY–H membrane are plotted in the distance ±3 Å from the center of the pore. Since the pore size of the membrane is large, we consider the gases passing horizontally and vertically through the membrane. As shown in Figure 3, the vertical and horizontal situations have minimum energy pathways for H$_2$ and CO$_2$ gases, respectively.

We also define the diffusion energy barrier for the gases to investigate the process in which the gases passing through the membrane as

$$E_{\text{barrier}} = E_{\text{TS}} - E_{\text{SS}}$$

(3)

where $E_{\text{barrier}}$, $E_{\text{TS}}$ and $E_{\text{SS}}$ denote the diffusion energy barrier, the total energy of the gas molecules and the pore center of the membrane at the transition state and the steady state, respectively. The kinetic diameters ($D_0$) of H$_2$ and CO$_2$ gases are 2.60 and 3.30 Å, respectively and the energy barriers of the gases passing through GDY–H membrane are 0.032 and 0.078 eV, respectively.

Furthermore, we plotted the isoelectron density surfaces at isovalue 0.0065 eÅ$^{-3}$ in Figure 4 to study the electron overlaps between H$_2$ and CO$_2$ molecules passing horizontally and vertically through GDY–H monolayer membrane. As shown in Figure 4, low electron overlap between H$_2$ and the membrane causes the energy barrier for H$_2$ to be very low. On the other hand, more electron overlap between CO$_2$ molecule and GDY–H membrane makes the...
higher energy barrier for CO$_2$ gas.

As is well known, the performance of the gas separation membranes is evaluated by two factors: selectivity and permeance. So, we investigate these parameters for H$_2$ and CO$_2$ gases passing through GDY–H membrane.

Based on the calculated diffusion energy barriers, we estimate the selectivity of H$_2$ toward CO$_2$ passing through GDY–H membrane using the Arrhenius equation which is defined as:

$$S_{x/gas} = \frac{r_x}{r_{gas}} = \frac{A_x e^{-E_x/RT}}{A_{gas} e^{-E_{gas}/RT}}$$

where $r$ is the diffusion rate and $A$ is the diffusion prefactor, which is assumed to be identical for all gases ($A=1 \times 10^{11}$ s$^{-1}$). Furthermore, $E$, $R$ and $T$ are the diffusion energy barrier, the molar gas constant and the temperature of the gases, respectively.

We plotted the calculated selectivity of GDY–H membrane for H$_2$ molecule toward CO$_2$ gas at a wide range of temperatures (100 K–600 K) in Figure 5. As is clear, the selectivity for H$_2$ molecule decreases with increasing temperature. Moreover, the calculated selectivities of H$_2$ toward CO$_2$ for GDY–H membrane and other proposed membranes at room temperature (300 K) are compared in Table 1. It can be concluded from Table 1 that GDY–H membrane exhibits poor selectivity for H$_2$ toward CO$_2$ among the other proposed membranes.

Besides the selectivity, the permeance parameter which indicates the separation efficiency, is another important factor to characterize the performance of a gas separation membrane. So, we study the permeance of GDY–H monolayer membrane for separating H$_2$ from CO$_2$.

We use the kinetic theory of the gases and the Maxwell–Boltzmann velocity distribution function to investigate the permeances of H$_2$ and CO$_2$ gas molecules passing through GDY–H membrane. The number of gas particles colliding with GDY–H sheet can be obtained as:

$$N = \frac{P}{\sqrt{2\pi MRT}}$$

where $P$, $M$, $R$ and $T$ are the pressure, molar mass, the molar gas constant and the temperature of the gases, respectively. The probability of a gas molecule overcoming the energy barrier and diffusing through the pore of the membrane is defined as:

$$f = \int_{v_B}^{\infty} f(v) \, dv$$

where $v_B$ and $f(v)$ denote the velocity and the Maxwell velocity distribution function of the membrane.

Table 1: Comparison of H$_2$/CO$_2$ selectivities for GDY–H membrane with other proposed membranes at room temperature (300 K).

| Membrane  | GDY–H | γ–GYN | γ–GYH | Graphenylene | g–C$_2$O |
|-----------|-------|-------|-------|--------------|---------|
| (This work) |       |       |       |              |         |
| Selectivity | 5.90  | 2 × 10$^{13}$ | 9 × 10$^{17}$ | 1 × 10$^{14}$ | 3 × 10$^3$ |
gas particles, respectively. The flux of the particles can be expressed as \( F = N \times f \). We assume that pressure drop \( \Delta P \) is \( 1 \times 10^5 \) Pa. Then, we can obtain the permeance factor of the gas molecules passing through the membrane by \( p = F / \Delta P \). 

In Figure 5, we plotted the permeance of the \( \text{H}_2 \) and \( \text{CO}_2 \) gases passing through the GDY–H membrane as a function of temperature. The red dotted plot exhibits the industrial permeance limit (IPL) for the gas separation. As shown in Figure 5, with increasing temperature, the permeance of each gas increases largely, while the divergence of permeances between two gases decreases. On the other hand, when the temperature becomes higher, the kinetic energies \( E = 3k_B T / 2 \) of the gases become larger. So, the influence of the energy barrier decreases and the gases pass through GDY–H membrane more easily. Moreover, we conclude that GDY–H membrane shows the permeance of \( \text{H}_2 \) and \( \text{CO}_2 \) gas molecules are much higher than the value of them in the current industrial applications at temperatures above 20 K and 80 K, respectively. However, GDY–H membrane does not show an appropriate balance between the selectivity and permeance factors. Therefore, the performance of GDY–H membrane in the separation of \( \text{H}_2 \) and \( \text{CO}_2 \) gases is unsuitable.

We now present a modified approach to improve the performance of GDY–H membrane for separating a mixture of \( \text{H}_2 \) and \( \text{CO}_2 \) gases. We place two layers of GDY–H adjacent to each other which the distance between them is 2 nm. Then, we insert 1,3,5 TAB between two layers which has a lot of N atoms. The electron pair of N atoms in this structure can improve \( \text{CO}_2 \) capture process. We use MD simulations to estimate selectivities and permeances of \( \text{H}_2 \) and \( \text{CO}_2 \) gases passing through monolayer of membrane, two layers of membrane and two layers of membrane in the presence of 1,3,5 TAB at the temperature range of 200–600 K.

The MD simulated configurations of the gas particles passing through the porous GDY–H membrane at different temperatures are shown in Figure 6. The gases adsorbed on the surface of the membrane by van der Waals interaction. Then, they linger on the surface for a few
Table 3: Number of the gas molecules passing through the GDY–H membrane in the range of 200-600 K.

| Temperature (K) | Monolayer | Two layers | Two layers with 1,3,5 TAB |
|----------------|-----------|------------|--------------------------|
|                | H₂ CO₂    | H₂ CO₂     | H₂ CO₂                   |
| 200            | 94 13     | 79 1       | 75 0                     |
| 300            | 96 17     | 92 2       | 84 0                     |
| 400            | 98 23     | 96 4       | 88 0                     |
| 500            | 106 30    | 98 5       | 89 0                     |
| 600            | 106 31    | 101 7      | 90 1                     |

picoseconds before passing through the monolayer membrane, since the gas concentration is different between the gas reservoir (containing H₂ and CO₂) and the vacuum space.

Based on the MD simulations, one can obtain the numbers of gas molecules passing through the membranes after 1 ns by counting the number of molecules in the vacuum regions. In this regard, the selectivity of gas A toward gas B can be defined as

\[
S_{A/B} \% = \frac{x_A / x_B}{(x_A / x_B) + (y_A / y_B)} \times 100
\]

\[
= \frac{N_A / N_{0,A}}{(N_A / N_{0,A}) + (N_B / N_{0,B})} \times 100 \quad (7)
\]

where \(x_A(x_B)\) and \(y_A(y_B)\) are the mole fractions of component A (B) in the vacuum regions and the gas reservoir, respectively and \(N_A(N_B)\) and \(N_{0,A}(N_{0,B})\) are the corresponding number of molecules A (B).

Furthermore, we can define the permeance of the gases passing through the membrane as

\[
p = \frac{\nu}{S \times t \times \Delta P} \quad (8)
\]

where \(\nu\) and \(S\) denote the mole of the gases which permeated through the membrane and the area of the membrane, respectively. Also, \(t\) is the time duration of the simulations (1 ns) and the pressure drop (\(\Delta P\)) is set to 1 bar across the pore of GDY–H membrane.

The selectivity of H₂ toward CO₂ and permeance of H₂ and CO₂ gases passing through monolayer, two layers and two layers in the presence of 1,3,5 TAB are plotted in Figure 7.

It can be seen that the selectivity of H₂/CO₂ is increased to 100% in the presence of 1,3,5 TAB and the permeance of H₂ and CO₂ gases passing through GDY–H membrane is very high (more than 10⁸ GPU). Moreover, the permeance of H₂ and CO₂ molecules enhances with increasing temperature.

The calculated permeances of H₂ for GDY–H membrane in our approach together with that of the previously proposed membrane at room temperature are summarized in Table 2.

As is clear, our approach shows an appropriate H₂

Table 2: Comparison of H₂ permeance for the GDY–H membrane in our approach with other proposed membranes at room temperature (300 K).

| Membrane       | Monolayer (This work) | Two layers (This work) | Two layers with 1,3,5 TAB (This work) | Graphenylene–GYN | γ–GYN | γ–GYH | g–C₂O |
|----------------|-----------------------|------------------------|--------------------------------------|------------------|-------|-------|-------|
| Permeance      | 2.1 × 10⁸             | 2.0 × 10⁸              | 1.9 × 10⁸                            | 2.6 × 10⁷        | 3.4 × 10⁷ | 1.5 × 10⁷ | 9.4 × 10⁶ |
permeance for GDY–H membrane in comparison of the other proposed membrane. The size of the pores in the GDY–H membrane is large in comparison to the other carbon allotrope membranes which causes weaker electrostatic and Lennard–Jones interactions between the membrane and the gas particles that will make the gas separation process harder. However, the presence of 1,3,5 TAB in our approach facilitated the CO$_2$ capture process which leads to improve the selectivity and permeance of GDY–H membrane. Consequently, our approach shows an appropriate balance between selectivity and permeance factors for the separation of H$_2$ and CO$_2$ gases.

Furthermore, the probability density distributions of CO$_2$ gases as a function of distance to GDY–H membrane plane at different temperature are plotted in Figure 8. As shown in Figure 8, in the monolayer case, we conclude that there is physical adsorption of CO$_2$ gases on the near of the membrane. In two layers case, CO$_2$ gases which passed through the first layer approach to the second layer and adsorb physically in the near of it. In the distance between two layers of the third case, the probability density of CO$_2$ gases is increased which shows that CO$_2$ gases are captured by 1,3,5 TAB. It means that there is no physical adsorption for CO$_2$ gases (except a single peak at 600 K). The probability density distribution plots show high adsorption for the gases in the range of 2-3 Å from the sheets at low temperatures. This result is in good agreement with the adsorption height obtained by DFT calculations. As the temperature increases, the kinetic energy of the gas particles enhances. Consequently, they overcome the adsorption energy and easily desorbed from GDY–H membrane. Therefore, at high temperatures, the probability distribution for each CO$_2$ gas decreases.

**Conclusion**

Recent advances in the gas separation technology provide new perspectives for the use of carbon allotropes for the development of gas separation membranes. However, one of the

**Figure 8:** Probability density distribution of the CO$_2$ molecules passing through GDY–H membrane at different temperatures as a function of distance in a) monolayer, b) two layers and c) two layers of the membrane in the presence of 1,3,5 TAB.
main challenges of the most designed carbon membranes is the selectivity-permeance trade-off challenge. Therefore, developing new approaches for the gas separation process based on carbon allotrope membranes seems essential.

In this work, we proposed a modified approach to improve the performance of a GDY-like membrane (GDY–H) to separate a mixture of H\textsubscript{2} and CO\textsubscript{2} gases. This membrane is designed by substituting one-third diacetylenic linkages in GDY structure with hydrogen atoms and the stability of it confirmed by Zhao et al.\textsuperscript{49}

First, regarding the calculated energy barriers for the gases, we investigated the performance of GDY–H monolayer membrane for H\textsubscript{2} and CO\textsubscript{2} separation based on DFT calculations. Our results show poor selectivity and good permeance for H\textsubscript{2} and CO\textsubscript{2} gases passing through the membrane. The permeance for H\textsubscript{2} and CO\textsubscript{2} gases are much higher than the value of them in the current industrial applications specially at temperatures above 20 K and 80 K, respectively. However, this monolayer membrane does not show a good balance between the selectivity and permeance factors.

To improve the performance of GDY–H membrane, we placed two layers of GDY–H adjacent to each other which the distance between them is 2 nm. Then, we insert 1,3,5 TAB between two layers which the electron pair of N atoms in this structure can improve CO\textsubscript{2} capture process. We performed MD simulations to analyze the selectivity and permeance of GDY–H membrane in three cases: monolayer of the membrane, two layers of the membrane and two layers of the membrane in the presence of 1,3,5 TAB. Our results show that the selectivity of H\textsubscript{2}/CO\textsubscript{2} is increased from 70% to 100% in the presence of 1,3,5 TAB. Moreover, GDY–H membrane exhibits excellent permeances, more than 10\textsuperscript{8} GPU, for H\textsubscript{2} and CO\textsubscript{2} gases. Consequently, this proposed approach represented an appropriate balance between the selectivity and permeance factors for H\textsubscript{2} and CO\textsubscript{2} separation.

We believe that our proposed approach can be considered as a good experimental target for H\textsubscript{2} purification and CO\textsubscript{2} capture processes, which are very crucial technologies in the industry.

**Acknowledgment**

The authors acknowledge the Computational Spectroscopy Laboratory of Department of Chemistry at Sharif University of Technology for providing the computer facilities.

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