Molecular design of two-dimensional graphdiyne membrane for selective transport of CO$_2$ and H$_2$ over CH$_4$, N$_2$, and CO

Quan Liu$^{a,*}$, Minggong Chen$^a$, Guining Chen$^{b,**}$, Xiaoyue Yao$^b$, Gongping Liu$^b$, Rong Xu$^c$, Wanqin Jin$^b$

$^a$ Analytical and Testing Center, School of Chemical Engineering, Anhui University of Science and Technology, Huainan, 232001, China
$^b$ State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 30 Puzhu Road (S), Nanjing, 211816, China
$^c$ Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Gehu Road, 213164, Changzhou, China

** Corresponding author. Analytical and Testing Center, School of Chemical Engineering, Anhui University of Science and Technology, Huainan, 232001, China.
** Corresponding author.
E-mail addresses: quanliu@aust.edu.cn (Q. Liu), gnchen@njtech.edu.cn (G. Chen).

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ABSTRACT

CO$_2$ capture and H$_2$ purification are the main challenges in syngas and flue gas processing. Two-dimensional graphdiyne (GDY) membrane, with intrinsic uniform pores, provides a promising candidate but lacks both a design strategy and an atomic understanding for these separations. In this study, for the first time, flexible GDYs are computationally designed with the engineering of various functional groups, namely GDY-H, GDY-F, GDY-OH and GDY-NH$_2$ to gain molecular-level insights into CO$_2$ capture and H$_2$ purification from binary mixtures of CO$_2$/CH$_4$, CO$_2$/CO, CO$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/CO and H$_2$/N$_2$. Gas separation performance is enhanced by the co-effect of size sieving and membrane-gas interactions. Both the hydroxylated GDY-OH and the aminated GDY-NH$_2$ membranes exhibit unprecedented performance for both CO$_2$ and H$_2$ separation. Despite processing a small-sized aperture, the GDY-NH$_2$ achieves the highest performance for CO$_2$ separations with permeance above $8.9 \times 10^8$ GPU and selectivities over CH$_4$, CO and N$_2$ up to 13935, 12356 and 809, respectively, which far surpass the 2008 upper bound. Structural and energetic analyses show that the flexible GDY-NH$_2$ tends to open its nanowindows and evoke concerted motions that enhance gas permeation, thereby promoting prompt diffusion. Additionally, the ultra-high H$_2$ separation performance of the functional GDY-NH$_2$ and GDY-OH is also several orders of magnitude higher than state-of-the-art membranes. This computational study reveals two dominant effects that govern the gas permeation process and suggests the great potential of hydroxylated and aminated GDYs for both CO$_2$ capture and H$_2$ purification.

1. Introduction

Gas separation has been an important subject in the industry, especially for CO$_2$ capture [1] and H$_2$ purification [2]. Without restraint on the combustion of fossil fuels, the massive emission of greenhouse gases such as CO$_2$ threatens the environment of the world. The capture and storage of CO$_2$ have been identified as one potential solution for natural gas sweetening, flue gas recycling, and greenhouse gas mitigation [3]. Meanwhile, wide attention has been aroused to search for clean energy resources as petroleum substitutes. Natural gas and syngas, as cleaner alternatives and renewable fuels, have shown tremendous potential in the future energy system, which are also the major sources for H$_2$ production [4]. In these processes, efficient separation technologies are required for both CO$_2$ capture and H$_2$ purification from industrial gas streams. Conventional industrial methods such as cryogenic distillation, pressure swing adsorption and amine scrubbing are energy-intensive processes [5]. Alternatively, membrane-based technology is more compact, energy-efficient, and possibly more economical than conventional technologies for gas separation [6,7]. Many membrane-based separations have been commercially applied, and their excellent performances have shown great potential in industrial practice.

Advanced membranes such as new polymers [8], metal-organic frameworks [9], mixed matrix [10] and graphene-based membranes [11] have sprung up for gas separation, reflecting that membrane technology is always in pursuit of higher performance. Therefore, it is crucial to explore and develop newly structured membranes. As an
allo tropes of graphene, the emerging graphdiyne (GDY), is proposed as an alternative option for gas separation in view of its well-endowed and high-density nanopolymers [12,13]. On the one hand, similar to other two-dimensional (2D) membranes, the atomic thickness of GDY substantially reduces molecular transfer resistance [14]. It was reported that monolayer GDY film could be thin to 0.6 nm by chemical vapor deposition [15], which would greatly facilitate molecular permeation. On the other hand, superior to other 2D membranes, the intrinsic uniform nanopolymers and tunable structures make the GDY controllable [12,16], as its functional derivatives have been facilely synthesized with variable precursors containing interesting electronic properties such as cyano (CN), amino (NH2) and methyl (Me) groups to further improve the surface activity and spatial structure. The successful synthesis of CN-GDY [16], NH2-GDY [17] and Me-GDY [18] for energy storage and fuel cells proves that the rational design of functional GDYs is feasible. However, no suitable functional derivatives have been reported yet for gas separation applications. In the past, only a few experiments have set foot in GDY membrane separation, primarily owing to many challenges that remain unsolved in practical membrane processes, especially with regard to scaling up integrated GDY membranes [19,20]. Excitingly, the latest experiment by Zhou et al. has proficiently implanted the GDY in gas separation and revealed its permeation mechanism, which represents a notable step forward in the application of GDY in the membrane process [21]. And a recent achievement of the GDY in membrane applications has been the enhancement of its long-term durability through an increase in surface hydrophilicity [22]. Although most studies on the GDY are currently limited to the theoretical realm, numerous theoretical studies have predicated the remarkable performance of GDY in the membrane process [19,20]. As reported in our previous simulation, the GDY derivatives showed a fantastic performance towards alcohol separations [23]. In water desalination, the predicted performance is also eye-catching. While in gas separation, most previous simulations about GDY membranes are targeted to separate the small-sized molecules, especially for H2 [24-26] or He [27,28]. Only a few reports were devoted to CO2 capture by tuning the tensile strain [29] and doping functional atoms [30] in the GDY.

It is also worth noting that most previous simulations regarded GDY as a rigid framework in the membrane process, with little consideration of its inherent flexibility, especially in gas separation. While Jiang et al. [31] and Hu et al. [32] demonstrated that structural flexibility should not be neglected and it has a decisive role in membrane separation performance. Additionally, the above simulations were based on density functional theory calculations [25,27,28], which might be hard to deliver precise data on the gas permeance of GDY membranes. Therefore, for the first time, considering the structural flexibility to reflect the realistic separation process, this study reveals the important role of concerted motions in facilitating gas permeation through GDYs by molecular dynamic (MD) simulations. Additionally, few attempts have been carried out on functional derivatives of GDYs for both CO2 and H2 separations. It should be known both the tunable apertures and active surfaces are the guarantee for high-performance membranes. Herein, the main objective of the work is to computationally design functional GDY membranes by structural modification for high-efficiency of both CO2 capture and H2 purification and provide new insights into the design of 2D-material membranes.

In this work, the aperture size and surface chemical property of pristine GDY are regulated with four functional groups (i.e., −H, −F, −OH and −NH2). Via MD simulations, the computationally designed GDY-Xs are applied to explore the separation of both CO2 and H2 over CH4, CO and N2. The proper aperture size and decorated group are essential for gas selective transport through functional GDY-Xs. The energetic analysis demonstrates that large molecules face a huge permeation barrier when crossing functional GDY-Xs, resulting in unprecedented gas selectivities. Then the separation mechanism is understood with structural analysis of membrane-gas interactions and concerted motions. The performance comparison is finally enclosed to evaluate the potential of the functional GDY-Xs towards both CO2 capture and H2 purification.

2. Models and methods

Deriving from the experimentally synthesized GDY [12], membrane models used in this setup were constructed as per our previous works [23,33]. The aperture size of pristine GDY estimated by the diameter of an inscribed ball is about 5.4 Å, as pictured in Fig. S1a. With considering the structural flexibility, such a large aperture should allow the passage of most gases, like H2, CO2, N2, CO and CH4, thus resulting in poor gas selectivity. Additionally, the surface electronic structure of pristine GDY is relatively unattractive and insensitive to target molecules. Thus to enhance the preferential selectivity towards target molecules, both aperture diameter and surface sensitivity should be regulated through the engineering of functional groups. On this basis, four functional groups (i.e., −H, −F, −OH and −NH2) were proposed to modify the pristine structure of GDY. Indeed, these groups not only had variable steric hindrances but also differed in electron densities, thereby regulating the aperture size and surface electronic properties of GDYs. After optimization, the structural units of the functional GDY-Xs, labeled as GDY-H, GDY-F, GDY-OH and GDY-NH2, are presented in Fig. 1a-d. The aperture sizes of GDY-H, GDY-F, GDY-OH and GDY-NH2 were 3.7 Å, 3.1 Å, 2.9 Å and 2.5 Å, respectively. Although the pore diameters were smaller than the molecular sizes of investigated gases (Table S1), the flexible functional groups were allowed to swing freely during simulations so that they could switch their orientations and evolve concerted motions to give the green light for gas permeation. Electrostatic potential maps colored with van der Waals surfaces for functional GDY-Xs are shown in Fig. 1e-h. It can be observed that the −H groups only shrank the aperture size but hardly activated the surface as its surface electronic distribution was relatively even in Fig. 1e. On the contrary, the functional groups of −F, −OH and −NH2 had positive roles in tuning both aperture sizes and surface properties. In particular, the −OH and −NH2 groups endowed the GDY membranes with electron-rich surfaces, providing a strong ability to capture CO2 molecules.

In Fig. 2, the size of the simulation box for our sandwich-like model was determined by both the membrane dimensions and the total number of gases. In our present work, all membranes shared the same dimensions of 7.75 × 7.55 nm2 (Figs. S1b-f), while the length of the separation box along the z-direction was set as 25.00 nm. As shown in Fig. 2a, a functional GDY-X membrane was located in the box, dividing it into two individual parts where the left chamber was filled with 2000 gas molecules serving as the feed side and the right one set as a vacuum was the permeate side. Six different forms of gas mixtures (i.e., CO2/CH4, CO2/CO, CO2/N2, H2/CH4, H2/CO and H2/N2) among Fig. 2b-g, with the mixing mole ratio of 1000:1000 distributed randomly in the feed side. All separation systems shared the same simulation settings. To ensure low pressure in the permeate side and better collection of the permeated gases, we set the length of the permeate chamber along the z-direction to 16.00 nm, nearly double that of the feed chamber. Indeed, our simulation box and gas number were larger than most previous simulations [24,25,27,29], providing sufficient accuracy for simulation results. To mimic the infinite system, periodic boundary conditions were implanted in the x-y plane. While along the z-direction, two rigid graphene plates were fixed at both ends of the simulation box, serving as barriers to prevent gases from roaming between periodic systems. To prevent the out-of-plane displacement of the membrane, these neutral carbon atoms in functional GDY-Xs were position-restrained with a harmonic constraint of 1000 kJ/(mol nm2); while other atoms were highly flexible. The structure of membranes was mimicked by the popular all-atom optimized potential (OPLSAA) force field as per our previous works [23,33]. Gas molecules were described by Lennard-Jones (LJ) and electrostatic potentials, and their partial charge and electrostatic parameters are listed in Table S1. The cross-interaction LJ parameters among non-bonded atoms were calculated by...
Lorentz-Berthelot combination rules \cite{29}.

Initially, to remove unreasonable contacts among atoms, the system was subjected to geometry optimization and static minimization by performing the steepest descent approach with a maximum step size of 0.01 nm and a force tolerance of 1 kJ mol\(^{-1}\) nm\(^{-1}\). The Maxwell-Boltzmann distribution was adopted to assign an initial velocity to each particle. Then, simulations were conducted in an isothermal-isobaric ensemble for 2 ns to push the system to reach temperature equilibrium. By employing the velocity rescaling method \cite{34} with a relaxation constant of 0.5 ps, the temperature of the whole system was maintained at 300 K. Thereafter, the system was switched to the canonical ensemble, and another 30 ns MD simulations were performed for each particle.
production runs and further analysis, where the trajectories were stored every 2 ps. The equations of motion were integrated by the leap-frog algorithm with a time step of 1 fs. The long-ranged Coulomb interactions were determined by the particle-particle particle-mesh (PPPM) scheme [35], and the van der Waals interactions were computed with the cutoff for a real space of 1.2 nm. These state-of-the-art methodologies utilized in our present work have been commonly used by most researchers to simulate the membrane separation process, resulting in reliable and comparable simulation results [30, 36–38]. All MD simulations were performed in the Gromacs 5.1.5 [39]. The post-processing of animations and snapshots was made by Visual Molecular Dynamics (VMD) packages [40].

3. Results and discussion

3.1. Gas permeance through GDY-Xs

Driven by a concentration gradient, gases energetically flow from the left chamber to the right chamber. To better visualize the permeation process, an animation of CO\(_2\) crossing the pristine GDY membrane is provided in Video 1. The gases in the feed side can promptly cross the pristine GDY. As the simulation time goes on, CO\(_2\) and N\(_2\) molecules are non-selectively concentrated in the permeate side. Figs. S2–S3 illustrate the net number of permeated gases (N) as a function of simulation time. For small molecules crossing large aperture, taking the cases in pristine GDY as examples, the N increases rapidly at the beginning, and then reaches a plateau over time, implying a net-zero permeation. The larger the slope of N ~ t curve is, the faster molecular permeation. Generally, CO\(_2\) and H\(_2\) exhibit faster permeations than other three gases (CH\(_4\), CO and N\(_2\)) primarily owing to their smaller molecular sizes. And all gases exhibit fast permeation when crossing the pristine GDY membrane, thus resulting in low gas selectivities. Interestingly, after engineering the pristine GDY with functional groups, the gas permeation gradually slows down, and the gap between two N ~ t curves in each figure is enlarged thanks to the narrowed aperture size. Especially for the hydroxylated GDY-OH and the aminated GDY-NH\(_2\) membranes, they can act as good barriers to effectively retain CH\(_4\), CO and N\(_2\) for perm-selective separation of both CO\(_2\) (Figs. S2d-e, i-j and n-o) and H\(_2\) (Figs. S3d-e, i-j and n-o). The gas permeance (S, mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)) is defined as the number of permeated gases per unit time per unit pressure and membrane area as Equation (1). Based on the time evolution of N, S can be quantitatively calculated by integrating Equations (1)–(3) [33], whereas \(A_{\text{mem}}\) is the membrane area, \(N_{\text{eq}}\) is the Avogadro constant, \(\Delta P\) represents the transmembrane pressure that is dependent on N, \(k\) is the Boltzmann constant, \((N_0 - N_{\text{eq}})\) refers to the number of gases with the exclusion of adsorbed parts, and \(L_i\) and \(L_o\) denote the lengths of the feed and permeate chambers along the z-axis. This work improves the significance of our results towards practical application by assuming a variable transmembrane pressure and fitting N ~ t curves with exponential functions, which differ from other calculations that assume a constant transmembrane pressure during the permeation process [26, 29, 30]. This approach is more appropriate for quantifying gas permeance, especially for fast permeation where N exhibits exponential growth with time [33].

For the reader’s convenience, the unit of S presented in this work is then converted to GPU (1 GPU = 3.35 × 10\(^{-10}\) mol m\(^{-2}\) s\(^{-1}\)Pa\(^{-1}\)) which is a typically reported unit in gas permeance.

\[
S = \frac{dN}{dN_{\text{eq}} A_{\text{mem}} \Delta P} \quad (1)
\]

\[
\Delta P = \frac{(N_0 - N_{\text{eq}}) kT}{A_{\text{f}}} - \frac{N_{\text{eq}} kT}{A_{\text{r}}} \quad (2)
\]

\[
N = \frac{(N_0 - N_{\text{eq}}) L_o}{(L_i + L_o)} \left( 1 - e^{-\frac{\Delta P}{R T}} \right) = \frac{2(N_0 - N_{\text{eq}})}{3} (1 - e^{-467.76}) \quad (3)
\]

When crossing through the pristine GDY membrane, for each gas mixture, the pre-selected H\(_2\) and CO\(_2\) gases exhibit remarkably high permeances, above 2.9 × 10\(^6\) GPU, as presented in Fig. S4 for comparison purposes. Such a large aperture in pristine GDY also introduces high permeance (> 4.9 × 10\(^5\) GPU) to CH\(_4\), CO and N\(_2\), thus bringing about low selectivities (less than 10) for separating these binary mixtures. Fig. 3 shows the permeance of various gas mixtures through functional GDY-Xs. It can be observed that both aperture size and functional group play decisive roles in governing gas permeation. Generally, gas permeance increases as GDY-OH < GDY-F < GDY-H < pristine GDY, following the increasing trend of aperture size. Compared to CH\(_4\), CO and N\(_2\), both CO\(_2\) and H\(_2\) with smaller molecular sizes exhibit larger permeances, which indicates that these permeation processes were primarily dominated by the size-sieving effect. For the H-decorated GDY-H membrane of which the pores are slightly narrowed, the pre-selected species of CO\(_2\) has permeances up to 1.7 × 10\(^5\) GPU in CO\(_2\)/CH\(_4\) (Fig. 3a) and CO\(_2\)/N\(_2\) (Fig. 3c), and 2.1 × 10\(^5\) GPU in CO\(_2\)/CO (Fig. 3b). The reduced permeance in the mixture of CO\(_2\)/CO is primarily because the coupling effect between CO and CO\(_2\), which lags the CO\(_2\) transfer rate. Although the –F groups bring an activated surface, the pore size in GDY-F is still too large to effectively separate both CO\(_2\) and H\(_2\) over CH\(_4\), CO and N\(_2\). With a further reduction of pore size, the gas-sieving phenomenon is extremely prominent in the GDY-OH membrane as the permeances of the large molecules of CH\(_4\), CO and N\(_2\) are almost zero, signifying the infinity selectivities of both CO\(_2\) and H\(_2\) over CH\(_4\), CO and N\(_2\). Although in this condition the permeances of CO\(_2\) and H\(_2\) are largely reduced, they still have an obvious advantage when compared to the traditional membranes [41–44]. After incorporating the –NH\(_2\) groups, the GDY-NH\(_2\) has the smallest pore size. While interestingly, the CO\(_2\) permeance is actually improved, and meanwhile the CH\(_4\), CO and N\(_2\) are still completely retained as shown in Fig. 3a–c. More specifically, when separating the mixture of CO\(_2\)/CH\(_4\), the CO\(_2\) permeance of GDY-NH\(_2\) raises by 150% compared to that of the GDY-OH membrane (Fig. 3a). Therefore, the GDY-NH\(_2\) is the most suitable option for CO\(_2\) separation over CH\(_4\), CO and N\(_2\). The improved permeance of CO\(_2\) in the GDY-NH\(_2\) membrane, despite the smaller pore size, suggests that the permeation process in GDY-NH\(_2\) membranes is not only affected by the size-sieving effect but also governed by the energetic and dynamic properties of gas-membrane structures. The same case is also observed in H\(_2\) separations. As shown in Fig. 3d–f, the gas permeance of CH\(_4\), CO and N\(_2\) is almost zero when permeating through GDY-OH and GDY-NH\(_2\) membranes, while the H\(_2\) permeances through GDY-NH\(_2\) improve to 1.3 × 10\(^5\) GPU, 1.5 × 10\(^5\) GPU and 1.5 × 10\(^5\) GPU when separating the binary mixtures of H\(_2\)/CH\(_4\), H\(_2\)/CO and H\(_2\)/N\(_2\), respectively. Fig. 5 presents the equilibrium configurations of various separation systems. It is observed that all gases are non-selectively accumulated in the permeate side behind the GDY-H membrane, yielding high permeance but low gas selectivity. While crossing the GDY-OH and GDY-NH\(_2\) membranes, the pre-selected gases still show considerably high permeation, and meanwhile, the large molecule-sized gases are hard to be detected in the right chamber. The near-zero permeances of CH\(_4\), CO and N\(_2\) indicate that the hydroxylated GDY-OH and the aminated GDY-NH\(_2\) membranes possess almost infinite separation selectivities of both CO\(_2\) and H\(_2\) over CH\(_4\), CO and N\(_2\).

3.2. Energetic properties and gas selectivities

The energetic properties of gases crossing membranes are evaluated by the free energy profile based on Boltzmann sampling (i.e., \(G = -R T \ln \frac{\rho(s)}{\rho(bulk)}\)), where \(R\) is the gas constant, \(\rho(s)\) and \(\rho(bulk)\) respectively refer to the gas density perpendicular to the interface and in the feed chamber, as presented in Fig. 4. Different from other methods [38, 45] used in free energy calculations, this method is relatively convenient to deliver the molecular permeation barrier [36, 37]. In this calculation, the position of the membrane is set to 8.5 nm, so the regions below and above this location correspond to the molecular approaching and
detaching process, respectively. As seen, all energy profiles show only one saddle point where the gas is unlikely to reside. The permeation barrier is calculated by $\Delta E_{\text{barrier}} = E_{\text{high}} - E_{\text{valley}}$, where $E_{\text{high}}$ and $E_{\text{valley}}$ denote the highest and lowest energy values in the molecular approaching process. Generally, gas permeation barriers decrease with the expansion of pore sizes, thus leading to the increase of gas permeance in Fig. 3. Small-sized molecules like CO$_2$ and H$_2$ are facing relatively low energy barriers (< 19.4 kJ/mol) even when crossing the GDY-OH and GDY-NH$_2$ membranes. Also note that the energy profile of CO$_2$ shows an obvious valley at $z = 8.2$ nm before CO$_2$ approaches the membrane’s upper surface, indicating that there is an intermolecular attraction between CO$_2$ and membranes. While as to CH$_4$, CO and N$_2$, they are facing an extremely high energy barrier (> 35.3 kJ/mol) when passing through the GDY-OH and GDY-NH$_2$. The corresponding energy profiles are even cut off before CH$_4$ and CO approach the membrane’s upper surface. As a result, no large-sized gases are detected in the permeate chamber. For better visualization, the animations for CO$_2$ separation over CH$_4$, CO and N$_2$: (a) CO$_2$/CH$_4$; (b) CO$_2$/CO and (c) CO$_2$/N$_2$; H$_2$ separation over CH$_4$, CO and N$_2$: (d) H$_2$/CH$_4$; (e) H$_2$/CO and (f) H$_2$/N$_2$.

Fig. 3. Gas permeance of various binary mixtures through functional GDY-Xs. CO$_2$ separation over CH$_4$, CO and N$_2$: (a) CO$_2$/CH$_4$; (b) CO$_2$/CO and (c) CO$_2$/N$_2$. H$_2$ separation over CH$_4$, CO and N$_2$: (d) H$_2$/CH$_4$; (e) H$_2$/CO and (f) H$_2$/N$_2$.

Fig. 4. Energy profiles of five gases crossing various functional GDY-X membranes. (a) H$_2$; (b) CO$_2$; (c) CH$_4$; (d) CO; (e) N$_2$. The membrane is located at $Z = 8.5$ nm.

The membrane selectivity, $\alpha_{ij}$, is another important metric in characterizing separation performance. While for the cases in GDY-NH$_2$ and GDY-OH, the permeances of CH$_4$, CO and N$_2$ are almost undetectable owing to such large permeation barriers. Consequently, the corresponding $\alpha_{ij}$ approaches an infinite level. To evaluate the $\alpha_{ij}$ in this scenario, the Arrhenius equation can be used by the formula of $\alpha_{ij} = S_i / S_j = (A_i / A_j) \exp (\Delta E_{ij} / RT)$, where $A$ is the pre-exponential factor and
ΔE_i/\text{j} refers to the difference of energy barriers between species \text{j} and \text{i}. For the investigated gases, their pre-exponential factors are considered equal [24,28,29]. Based on the above energy profiles, the separation selectivities for these binary mixtures are presented in Fig. 5, where the selectivity is basically risen with reducing the aperture size. For CO_2/CH_4 separation as shown in Fig. 5a, the infinite selectivities of CO_2 over CH_4 possessed by GDY-NH_2 and GDY-OH membranes should be at least as high as 13935 and 8510, respectively. For CO_2/CO and CO_2/N_2 separations, the highest CO_2 selectivities over CO and N_2 can be accordingly estimated as 12356 and 809. Owing to the low permeation barriers of H_2 crossing membranes, it is observed that the H_2 selectivities over CH_4, CO and N_2 in the GDY-NH_2 membrane are extremely high, which can be respectively up to 79076, 70115 and 4590. These unexpected selectivities forebode the potential application of functional GDY-OH and GDY-NH_2 membranes in both CO_2 capture and H_2 purification.

3.3. Gas-membrane interactions

In most cases, gas permeation through functional GDY-Xs is governed by the gas-sieving mechanism. While through the GDY-OH and GDY-NH_2 membranes, the strong host-guest interactions deriving from functional groups come to dominate the separation process. Fig. 6 illustrates the positive effect of gas-membrane interactions in promoting CO_2 permeation. The data were taken from the cases in GDY-OH and GDY-NH_2. As seen, the GDY-OH and GDY-NH_2 membranes show the strongest interaction towards CO_2 molecules than other gases, which is supported by radial distribution function (RDF) analysis in Fig. 6a-b. These intermolecular attractions help the membrane to preferentially capture CO_2 from the feed tank to approach the membrane surface. Within the various types of interactions, the Coulombic effect is found to play a crucial role in attracting CO_2 molecules, leading to a lower energy pathway for CO_2 permeation. This effect is particularly pronounced in the GDY-NH_2 membrane, as shown in Fig. 5c. This observation is consistent with prior experimental findings [45–47]. Owing to these favorable interactions, the membrane surface is fully occupied by CO_2 molecules as visualized by the snapshots in Fig. 5S. While comparing these two polar membranes, CO_2 interacts more strongly with GDY-NH_2 than with GDY-OH, as indicated by the more favorable Coulombic attractions of GDY-NH_2 with CO_2 gases and the larger RDF value of the CO_2 curve in Fig. 6b compared to Fig. 6a. This is primarily because –NH_2 is more nucleophilic than –OH. That is, the CO_2 molecule, as one type of sour gas, prefers to be captured by these alkaline amino groups. As a result, the probability density distributions of CO_2 are higher on both sides of the GDY-NH_2 surface than on the GDY-OH surface as per Fig. 6c, and the total number of the adsorbed CO_2 molecules is more prominent on the GDY-NH_2 membrane (Fig. 6d). All of these factors increase the chances of CO_2 passing through the GDY-NH_2 membrane. That is why the CO_2 permeance of GDY-NH_2 is higher than that of GDY-OH. To give a deeper insight into molecular distribution on the membrane surface, molecular density contour maps are analyzed in Fig. 6e–f. As seen, three red clouds adjacent to –NH_2 groups are formed in Fig. 6f. The red-colored region signals the fertility of CO_2, while the blue region implies a sterile area for CO_2. As a result, the average capacity of CO_2 accumulation is somewhat higher in the pores of GDY-NH_2 than that of GDY-OH. In a word, the decorated amino groups help to capture more CO_2 molecules surrounding themselves and improve the pass rate of CO_2.

3.4. Concerted motions

Reliable membrane separation requires careful consideration of both the aperture size and shape [48]. During the process of molecules crossing the membrane, the aperture shape changes due to the flexible functional groups that dynamically switch their orientation [32], evoking concerted rotations of pores. These are visualized in Fig. 7a–b by the distances between the opposing center atoms of functional groups. Taking CO_2 permeation as an example, the rotations of hydroxy and amino groups create open and closed nanowindows before and after CO_2 passes through pores, thus forming two different dynamical states: (1) an open nanowindow that is determined by the atom distance among O1–O3 and N1–N3, where functional groups flap away from the membrane skeleton when CO_2 approaches the nanopores, and (2) a closed nanowindow that can be referred to the atom distance among O4–O6 and N4–N6, where the retroflex dihedral angles are recovered. This open aperture shape enlarges the effective pore size for efficient gas passage. It is observed that the concerted motions between CO_2 and amino groups are more pronounced as the open nanowindow’s effective size in GDY-NH_2 (Fig. 7b) is larger than that in GDY-OH (Fig. 7a), thus fostering a faster CO_2 diffusivity (≈5.2 × 10^{-4} cm^2/s) in GDY-NH_2. The detailed diffusivities of gases crossing different-sized pores are presented in Fig. 7c, where all diffusion coefficients generally increase with aperture sizes, except in GDY-NH_2 due to the above-discussed concerted motions. Once CO_2 passes through the pore, the nanowindows in GDY-NH_2 lock tightly from the inside to prevent the passage of large molecules. Thereafter, as to N_2, CO and CH_4, their diffusion rates are restricted by these closed pores, almost undetectable behind the GDY-NH_2 and GDY-OH membranes, as seen in Fig. 7c. While with the smallest molecular size, the diffusivities of H_2 are unimpeded and all above 14.0 × 10^{-4} cm^2/s.

3.5. Comparisons of separation performance

Although functional GDYs have not yet been practically utilized due to several technological challenges, the experiments on their allotropes have demonstrated the potential of introducing amine groups into 2D membranes to significantly enhance CO_2 separation performance [49, 50]. Note that the gas permeances in this work are mostly around ~10^{-5} GPU, consistent with the latest experimental value [21]. This high gas permeance is partly owing to the atomic thickness of GDYs of about 0.6 nm [15] as per the density distributions in Fig. 6c. Most other membranes are unable to match this high value. While to make a fair comparison with other potential membranes, the gas permeance in this setup is further converted to permeability (Barrer) by multiplying the membrane thickness. Data points marked by the triangle and square symbols from previous references are summarized in Tables S2–S3. On the one hand, the permeabilities of pre-selected gases (i.e., CO_2 and H_2) through the GDY-NH_2 membranes can be up to 87.5 Barrer and 925.3 Barrer, respectively, which are comparable to other membranes reported up to date [41–44]. On the other hand, the separation selectivities of the hydroxylated GDY-OH and the aminated GDY-NH_2 membranes for the binary mixtures of CO_2/CH_4, CO_2/N_2, H_2/CH_4 and H_2/N_2 are all exceptionally high. Typically, the selectivities of CO_2 over both CH_4 and N_2 through the GDY-NH_2 membrane not only far exceed the 2008 Robeson upper bound [35], but also are several orders of magnitude higher than most commercial membranes (Fig. 8a). These two functional membranes, especially GDY-NH_2, also possess unprecedented performances for H_2 separation as shown in Fig. 8b. Overall, the...
performances of functional GDY-OH and GDY-NH$_2$ show bright future for both CO$_2$ and H$_2$ separation over CH$_4$ and N$_2$, suggesting their great potential in processing raw natural gas, flue gas and syngas.

4. Conclusion

By molecular simulation, the pristine GDY is computationally functionalized through the engineering of variable groups to design the GDY-H, GDY-F, GDY-OH and GDY-NH$_2$ membranes, and to examine how they perform in separating different binary mixtures of CO$_2$/CH$_4$, CO$_2$/CO, CO$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/CO and H$_2$/N$_2$. Typically, the larger the aperture is, the higher the gas permeance is achieved. Despite having the narrowest aperture, the GDY-NH$_2$ exhibits higher CO$_2$ permeance than GDY-OH, which is primarily because its higher gas-membrane interactions and greater concerted motions generate a CO$_2$-friendly surface and higher diffusion coefficients, thereby facilitating CO$_2$ passage. With the smallest molecular size, H$_2$ is unimpeded through these functional pores. The perm-selective gases of both CO$_2$ and H$_2$ have a permeance on the order of magnitude $10^5$ GPU through the functional GDY-Xs. The energetic analysis demonstrates that the grafted hydroxy and amino groups erect a huge permeation barrier to effectively block CH$_4$, CO and N$_2$ molecules, thus yielding unprecedented selectivities for both CO$_2$ and H$_2$ separations. After taking the atomic thickness of GDY-Xs into account, the gas permeabilities of the hydroxylated GDY-OH and the aminated GDY-NH$_2$ membranes are comparable to the commercial membranes, while the observed gas selectivities substantially exceed most previous reports by several orders of magnitude. Our work brings a bright future for the viable design of GDY membranes at the atomic level towards gas separation such as post-combustion carbon capture, natural gas/biogas sweetening, and H$_2$ purification.

Author statement

Quan Liu: Methodology, Software, Data curation, Writing-original
Fig. 8. Separation performances of GDY-OH and GDY-NH$_2$ membranes versus other classical membranes for (a) CO$_2$ and (b) H$_2$ separation over CH$_4$ and N$_2$. Black and red lines in each figure represent the 2008 Robeson upper bounds versus 0.1 μm membrane thickness. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2023.121557.

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