Enhanced Selective Hydrogen Permeation through Graphdiyne Membrane: A Theoretical Study

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Abstract: Graphdiyne (GDY), with uniform pores and atomic thickness, is attracting widespread attention for application in H2 separation in recent years. However, the challenge lies in the rational design of GDYs for fast and selective H2 permeation. By MD and DFT calculations, several flexible GDYs were constructed to investigate the permeation properties of four pure gas (H2, N2, CO2, and CH4) and three equimolar binary mixtures (H2/N2, H2/CO2, and H2/CH4) in this study. When the pore size is smaller than 2.1 Å, the GDYs acted as an exceptional filter for H2 with an approximately infinite H2 selectivity. Beyond the size-sieving effect, in the separation process of binary mixtures, the blocking effect arising from the strong gas–membrane interaction was proven to greatly impede H2 permeation. After understanding the mechanism, the H2 permeance of the mixtures of H2/CO2 was further increased to 2.84 × 105 GPU by reducing the blocking effect with the addition of a tiny amount of surface charges, without sacrificing the selectivity. This theoretical study provides an additional atomic understanding of H2 permeation crossing GDYs, indicating that the GDY membrane could be a potential candidate for H2 purification.

Keywords: graphdiyne; molecular simulation; membrane separation; hydrogen purification

1. Introduction

As an attractive alternative fuel source, hydrogen (H2) could eliminate the use of polluting fossil fuels in industry and transport in the future [1]. So, the H2 energy is critical to reduce global greenhouse gases and promote sustainable development because of its natural abundance and high efficiency of combustion [2,3]. Today, in many industrial and drilling streams, H2 is mainly produced from natural gas, hydro-electrolysis, and the combustion of hydrides [4,5]. However, these processes release several million tonnes of by-products (such as carbon dioxide, nitrogen, and methane) per year [6]. How to separate the target product of H2 from the undesirable species is crucial to improve production efficiency and reduce the cost. Traditional separation techniques, such as pressure swing adsorption and cryogenic separation, would consume a considerable amount of energy to collect H2 [7]. With the improved performances and lower operating conditions, the advanced membrane-based separation is seen as an alternative to significantly improve energy efficiency [8,9]. At room temperature and low transmembrane pressure, it is more instructive for experiments to develop membranes with both good H2 permeance and selectivity [10].

Recently, two-dimensional (2D) carbon-based membranes have sparked global attention due to their atomic thickness [11]. Among various membranes, graphene-based materials are, assuredly, one of the powerful candidates for membrane separation according to our previous experimental [12,13] and simulation studies [14,15]. According to the separation mechanism of the size sieving effect, controllable pores in the 2D-material membrane are imperative for gas separation. However, it is
not cost-effective to drill uniform pores in graphene, and this process may introduce non-selective defects in the membrane [16]. Alternatively, newly emerged graphdiyne (GDY) allotropes that formed by the periodic combination of sp and sp² carbon atoms are proposed as alternative options for gas purification [16], because they process the well-distributed pores as well as the atomic membrane thickness [17]. Several studies have been reported to explore the gas permeation property through GDYs in recent years [18–20]. It is the comparable pores in GDYs that contribute to the outstanding gas separation properties, as Smith et al. first reported that the excellent H₂ separation performance was ascribed to the small triangular pores in the GDYs [21]. This later reports also showed that the various sized pores in diverse GDYs could be employed to distinguish the different sized molecules, such as He [18], O₂ [22], and CO₂ [23,24], concluding that the size sieving effect dominated the transport mechanism of GDYs for gas separation.

Although the pore size is an important factor for gas separation membranes, other factors, particularly the surface properties, should not be neglected. Sang et al. [25] and Smith et al. [26] found that the functionalized surface of GDYs shown a better separation performance than that of the pristine one. Moreover, the adsorption phenomenon in GDYs also affected the permeation of gases, such as H₂S [27] and CO₂ [24,28]. It means, beyond the well-understood size sieving effect, there could be a more comprehensive mechanism to better describe gas transport through GDYs [19]. However, the main challenge is how such a mechanism determines the gas permeation properties, especially for selective H₂ permeation through GDYs, and how it contributes to further improvement of the H₂ permeance and selectivity of GDYs. In addition, most previous works focused on the first-principles calculations density functional theory (DFT) to study the selectivity of H₂ over CO₂, CO, N₂, and CH₄ [25,26,29]. A few studies calculated the H₂ permeance by performing molecular dynamic (MD) simulations, which however were based on a rigid framework of GDYs [20,23,30] and might be too idealized for actual GDYs for gas separation. Moreover, it is unclear what the ultimate size of nanopores in GDYs is allowed to transport H₂ molecules. Therefore, it is necessary to further understand the underlying separation mechanism of H₂ purification through a carefully designed flexible GDY membrane that possesses both high H₂ permeance and selectivity and find the ultimate diameter in GDYs for H₂ permeation.

In this work, a series of 2D GDYs are computationally constructed to examine the permeation of four pure gases (H₂, N₂, CO₂ and CH₄) and their equimolar binary mixtures (H₂/N₂, H₂/CO₂ and H₂/CH₄). Assuming that the separation performance of H₂ is affected by pore structures and surface charges, we systematically investigated these two effects by both MD and DFT calculations. Following the introduction, the atomic models of GDYs, as well as the separation systems, are illustrated in Section 2. In Section 3, the H₂ permeance is calculated by the time evolution of the permeated molecules according to the MD results, and the ideal selectivity is evaluated by DFT calculations. This separation mechanism of H₂ from binary mixtures is revealed by analyzing the diffusion coefficient, density contour, and energy barrier of the permeation. After that, the H₂ permeance of the mixture of H₂/CO₂ is further improved by reducing the blocking effect. Finally, the concluding remarks are summarized in Section 4.

2. Models and Methods

The GDYs were constructed in the Material studio [31] and then subjected to geometry optimization in the Forcite module with 5000 iterations. As presented in Figure 1a–d, the dimensions of the membranes were 7.75 × 7.55 nm² in this setup, and the investigated pore diameters were varied from 1.5 to 2.5 Å, which were measured according to the formula: \( D = 2 \sqrt{A/\pi} \) by inserting a van der Waals sphere, where \( A \) is the open pore area, as depicted in Figure 1e–h. We noted that the membrane in Figure 1b coded as GDY_1.5Å_p7% has the porosity of 7%, which is larger than that of 3% in Figure 1a (GDY_1.5Å_p3%), although both of these two membranes have a similar pore diameter of 1.5 Å. This above-mentioned porosity was calculated by the formula \( p = \frac{A_{\text{pore}}}{A_{\text{mem}}} \), where \( A_{\text{pore}} \) and \( A_{\text{mem}} \) denote to the areas of the totally unoccupied regions and the membrane surface, respectively.
Figure 1. Membrane models. Atomic structures of graphdiyne (GDY) membranes with different pore structures: (a) GDY_1.5Å_p3%; (b) GDY_1.5Å_p7%; (c) GDY_2.1Å; and (d) GDY_2.5Å. The first two membranes have different porosities of 3% and 7%, respectively. (e–h) The criterion for the definition of the pore diameter in each GDY membranes.

Based on the optimized membranes, MD calculations were performed to simulate the gas separation. Figure 2 shows the simulation system, where two chambers were isolated by the GDY membrane. The left chamber was a gas reservoir, comprising 2000 molecules of pure gases (or binary mixtures with the mixing ratio of 1000:1000, in volume ratio). The right one treated as a vacuum is the permeate side, which is the most common setting in MD simulations for collecting the permeated molecules. [20,23,30] At both ends of each chamber, rigid graphene was placed to prevent molecules from roaming between the periodic boxes. Considering that carbon-based membranes usually have good flexibility in experiments [32], all pores in GDYs were treated as flexible in our present work so that the atoms around pores could perform small displacements. Thus, the aperture would be enlarged to allow the passage of H₂ even though the molecular size is larger than the pore size. On the contrary, the atoms on the edge of membranes were imposed with a position restriction to ensure the uniform lattice of GDYs and decrease the impact on gas permeation [33]. Furthermore, no collapse appeared in our system, suggesting good stability of the flexible structures. This framework of GDYs was described by the all-atom optimized potential. This four gases were represented by Lennard–Jones (LJ) and electrostatic potentials originating from our previous work [14]. Between dissimilar atoms, the interactions were assembled by the Lorentz–Berthelot combination rule [34].
where \( N \) refers to the number of permeated molecules, \( N_A \) is the Avogadro constant, and \( \Delta P \) is the transmembrane gas partial pressure estimated by Equation (2):

\[
\Delta P = \frac{\left( N_0 - N_{ad} - N \right) kT}{V_l} - \frac{NkT}{V_r}
\]

in which \( N_{ad} \) refers to the number of gases adsorbed on the membrane surface, \( V_l \) and \( V_r \) are the volumes of the left and right chambers, respectively, and \( k \) represents the Boltzmann constant. Therefore, the time evolution of the number of permeated molecules is integrated as Equation (3), where \( R \) is the gas constant,

\[
N = \frac{(N_0 - N_{ad}) L_r}{(L_l + L_r)} \left( 1 - e^{-\frac{RT(S_l + S_r)}{\Delta P t}} \right) = \frac{2(N_0 - N_{ad})}{3} \left( 1 - e^{-467.75t} \right).
\]
As presented in Figure 3a, the number of permeated H2 is increased exponentially with the simulation time, which agrees well with the above mathematical analysis. This permeance of pure H2 is shown in Figure 3b. Obviously, it is remarkably enhanced with the increase of porosity and pore size. With the smallest pore of 1.5 Å, the porosity of 0.03 and 0.07 have the H2 permeance of 1.34 × 105 and 2.55 × 105 GPU (1 GPU = 3.35 × 10−10 mol·m−2·s−1·Pa−1), respectively. This permeation of other gases (i.e., CO2, N2 and CH4) through the GDYs was also simulated. It was shown that only the biggest pore with 2.5 Å allowed the passage of N2, CO2, and CH4, as presented in Figure 3c. This incompatibility of the kinetic diameter of gases (i.e., H2, 2.89 Å; N2, 3.64 Å; CO2, 3.30 Å; CH4, 3.8 Å) [39], and the pore size is ascribed to the flexible structures, implying that the membrane of GDY_2.5Å is not suitable for H2 purification. Moreover, the comparable pore with 2.1 Å diameter can not only completely block the other three gases but also process the good H2 permeance of 5.94 × 108, which implies that the selectivities of H2 over CO2, N2, and CH4 can be extremely high in the membrane of GDY_2.1Å. We noted that the molecules of N2, CO2, and CH4 can not be detected in the permeation side as long as the pore diameter was smaller than 2.1 Å, indicating the infinitely low permeance of N2, CO2, and CH4.

![Figure 3. Pure gas permeation. (a) The time evolution of permeated H2 molecules; (b) The permeance of H2 through different GDYs; (c) The permeance of four gases in GDY_2.5Å.](image)

To evaluate the ideal selectivities of H2 over other three gases in GDY_2.1 Å, the DFT calculations were performed to calculate permeation barriers as per our previous study [15]. Figure 4a illustrates the minimum energy pathway (MEP) of four gases crossing the membrane. This inset configurations are the energetically stable states of CO2 permeation at different locations. By searching the saddle point in MEPs, the energy barriers of permeation can be calculated. Evidently, the permeation barrier of H2 crossing the flexible GDY_2.1 Å is drastically reduced to 1.55 kJ/mol (Figure 4a, inset), which results in extraordinary H2 permeance. On the contrary, the permeation barriers of CO2, N2, and CH4 are all extremely high. In Figure 4b, the temperature-dependent H2 selectivity has an inverse correlation with the temperature according to the Arrhenius Equation (4), whereas Pi is the permeation rate, A is the permeation prefactor that can be assumed as 1011 s−1 [38], and T is the temperature. For H2/CO2 and H2/N2, the ideal selectivities of H2 can be up to 1017 at 300 K, which is the same order with the modified GDYs [25]. It remains very high (>108) even at 600 K, further suggesting the extraordinary H2 separation performance through GDY_2.1 Å.

\[
S_{i/j} = \frac{P_i}{P_j} = \frac{A_i \exp\left(\frac{-E_{\text{barrier}, i}}{RT}\right)}{A_j \exp\left(\frac{-E_{\text{barrier}, j}}{RT}\right)} \quad (4)
\]
3.2. Transport Mechanism: Blocking Effect

For binary gas mixtures, the MD calculations were also performed to simulate the separation process. To visualize H$_2$ purification properties through the membrane of GDY$_{2.1\text{Å}}$, the equilibrium configurations of final frames are presented in Figure 5a–c. As seen, the GDY$_{2.1\text{Å}}$ membrane acts as an effective filter for H$_2$ separation while completely blocking the passage of CO$_2$, N$_2$, and CH$_4$, so that the H$_2$ is largely gathering in the vacuum chamber. This corresponding H$_2$ permeance of the three binary mixtures is presented in Figure 5d. Interestingly, the mixture of H$_2$/N$_2$ exhibits the highest H$_2$ permeance of 4.71 × 10$^5$ GPU, which is a little higher than that of H$_2$/CH$_4$ and almost twice as many as the mixture of H$_2$/CO$_2$. The primary reason is that on the membrane surface, the strongly interacting gas (CO$_2$) preferentially adsorbs, blocking the transport pores of H$_2$ molecules, thus resulting in a relatively low H$_2$ permeance.

**Figure 4.** DFT calculations of gases crossing the membrane of GDY$_{2.1\text{Å}}$. (a) Minimum energy pathways of four gases. (b) Ideal selectivities of H$_2$ over N$_2$, CO$_2$, and CH$_4$ as functions of temperature.

**Figure 5.** H$_2$ permeation of three equimolar binary mixtures crossing the GDY$_{2.1\text{Å}}$. This final snapshots: (a) H$_2$/N$_2$, (b) H$_2$/CH$_4$, and (c) H$_2$/CO$_2$. Blue: N; cyan: C; red: O; white: H. (d) The H$_2$ permeance of different binary mixtures.
Further analyses are carried out to understand this blocking effect. This radial distribution function (RDF) was calculated to present the affinity of GDY_2.1Å to four gases by using Equation (5):

$$g_{ij}(r) = \frac{N_{ij}(r, r + \Delta r)V}{4\pi r^2 \Delta r N_i N_j}$$

(5)

where $N_{ij}(r, r + \Delta r)$ is the number of species $j$ around $i$ within a shell from $r$ to $r + \Delta r$, $r$ is the distance between two species, and $N_i$ and $N_j$ refer to the numbers of atom types $i$ and $j$, respectively. As presented in Figure 6a, there is an increasing trend of the gas–membrane interaction as $H_2 < N_2 < CH_4 < CO_2$. This weakest interaction together with the smallest molecular size endows $H_2$ with exceptional permeance. Meanwhile, the strong interaction promotes the gases, particularly $CO_2$ to preferentially adsorb on the membrane surface. To offer more intuitionistic information, the density contours of the distribution of $N_2$, $CH_4$, and $CO_2$ were plotted on the GDY_2.1Å surface. This general distribution behavior of the three gases is similar as shown in Figure 6b–d, where the pores that are largely clogged by these gases are larger than the pore diameters. Nevertheless, the intensity of gas accumulation is quite different. As seen in Figure 6d, the pores are the most clogged, with the number of adsorbed $CO_2$ molecules exceeding $6.5 N_w/uc$ in every pore. Similar to the affinity analysis in Figure 6a, the extent of the blocking effect follows the increasing trend of $N_2 < CH_4 < CO_2$, decreasing the placeholders of $H_2$ on the membrane surface in Figure 7a.

Figure 6. Blocking effect on the surface of GDY_2.1Å. (a) Radial distribution function (RDF) of gases around the membrane. Density contours of the impermeable gases on the surface: (b) $N_2$ ($H_2/N_2$); (c) $CH_4$ ($H_2/CH_4$); (d) $CO_2$ ($H_2/CO_2$). This unit of density ($N_w/uc$) is $1/(1.25Å^3)$. 
which favors the permeation of small-sized molecules of H$_2$. While beyond the size sieving effect, the separation process of binary mixtures, the blocking effect greatly impedes H$_2$ permeation. This above understanding of the separation mechanism is beneficial to further guide the improvement of H$_2$ permeance particularly for the mixture of H$_2$/CO$_2$ without sacrificing its selectivity. An effective way proposed here is to reduce the most severe blocking effect of CO$_2$ by surface charge modification. As depicted in the inset figure in Figure 8a, the positive and negative charges are uniformly imposed on the network of GDY$_{2.1\AA}$ from ±0.00001 to ±0.35 e/atom, whereas the net charge of the whole membrane is zero. This CO$_2$ molecules still cannot cross the membrane regardless of surface charges. Compared to the pristine GDY membrane, the increased H$_2$ permeance of the binary mixture of H$_2$/CO$_2$ was observed when surface charges are lower than ±0.1 e/atom in Figure 8b. It can be up to $2.84 \times 10^5$ GPU by imposing a tiny amount of surface charge of ±0.035–0.050 e/atom. This exceptionally high permeance is several orders of magnitude greater than the existed experiments [40–42], which is ascribed to the ultimate pore size and atomic thickness of GDYs. The following decreasing trend in Figure 8b was ascribed to the surface overcharge, where the existed experiments [40–42], which is ascribed to the ultimate pore size and atomic thickness of GDYs. The following decreasing trend in Figure 8b was ascribed to the surface overcharge, where the existed experiments [40–42], which is ascribed to the ultimate pore size and atomic thickness of GDYs. 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high permeance is several orders of magnitude greater than the existed experiments [40–42], which is ascribed to the ultimate pore size and atomic thickness of GDYs. This following decreasing trend in Figure 8b was ascribed to the surface overcharge, where the generated strong electrostatic repels not only CO₂ but also H₂ from approaching. Thus, achieving the perfect balance between these two mechanisms, a tiny amount of surface charges is qualified to maximize the H₂ permeance by reducing the blocking effect of strong interlaced molecules of CO₂, meanwhile ensuring the placeholders of small-sized molecules of H₂ as well.

![Figure 8](http://www.mdpi.com/xxx/s1)

Figure 8. The effect of the surface charges on gas permeation. (a) The distribution of charges on the network of GDY_2.1Å; (b) H₂ permeance of the binary mixture of H₂/CO₂ as a function of surface charges. (Inset) The time evolution of permeated H₂ molecules through the charged GDYs.

4. Conclusions

In summary, a multiscale study combining MD and DFT calculations was performed to investigate the gas permeation through carefully designed flexible GDY membranes with different pore structures and surface charges. Four single gases and three equimolar binary mixtures (H₂/other gas) were simulated to study the selective gas permeation through GDYs. Approximately infinite selectivities of H₂ over N₂, CO₂, and CH₄ in GDY_2.1Å membranes were demonstrated by DFT calculations. This underlying mechanism indicated that the blocking effect impeded H₂ permeation and the GDY_2.1Å is prone to separate H₂ from such binary mixtures in which the other species has a weak gas–membrane interaction. Moreover, by imposing a tiny amount of surface charges, the H₂ permeance of the binary H₂/CO₂ mixture was further enhanced up to 2.84 × 10⁵ GPU without sacrificing the selectivity. These excellent transport properties make the GDYs a promising candidate for efficient H₂ purification. Although the present work is a theoretical study, it is believable that the GDYs can be elaborately designed for realistic separations with the improvement of a well-controlled synthesis strategy.

Supplementary Materials: The following are available online at [http://www.mdpi.com/2077-0375/10/10/286/s1](http://www.mdpi.com/2077-0375/10/10/286/s1), Video S1: The separation process of the binary mixture of H₂/CO₂ through GDY_2.1Å.

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