Efficient separation of (C₁–C₂) alcohol solutions by graphyne membranes: A molecular simulation study

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ABSTRACT

With well-endowed nanopores, graphyne (GY) membranes have attracted considerable interest in alcohol purifications. However, the challenge lies in the rational design of GYs for efficient separation of (C₁–C₂) alcohol solutions. Herein, GYs are firstly developed for methanol recovery and ethanol dehydration by molecular simulations. Two design strategies including surface charge modification and functional group decoration are proposed in this study. For methanol-water separation, methanol is pre-selected due to the dominated mechanism of preferential adsorption and its flux increases with positive charges within a certain range. An excellent separation performance with 99.1 kg⋅m⁻²⋅h⁻¹ methanol flux and 15.2 separation factor is achieved by this GY-S membrane with +0.005 e/atom charged surface. This surface charge modification is also effective for methanol-ethanol separation, where the highest performance is harvested by the positively charged GY-M membrane. For water-ethanol separation, water is pre-selected owing to the size sieving effect. To reduce the blocking effect and permeation barrier, the GY-M is functionalized with polar groups so that water flux is promoted regardless of aperture sizes. The hydroxylated GY-M-OH fosters an exceptionally high dehydration performance with 225.8 kg⋅m⁻²⋅h⁻¹ water flux and 100 wt% water content in permeate. This theoretical study suggests that the GYs membranes might be promising for organic solvent recovery and dehydration.

1. Introduction

Bioalcohols as clean fuels are extremely important in many industries, which can be a petroleum substitute to alleviate the excessive greenhouse gas emission [1]. To date, among many bioalcohols, only methanol and ethanol fuels are technically workable for petrol engines. In view of the low toxicity of methanol, it is often necessary to further separate methanol from bioethanol as a by-product [2,3]. While methanol as renewable energy can also be used in many other applications such as fuel cells. The highly purified (C₁–C₂) alcohols can be produced by the fermentation of biomass [4]. Unfortunately, for these purification purposes, the conventional dehydration method such as distillation is an energy-intensive process [5] in that the formatted azeotropes have closely related volatility. Alternatively, membrane pervaporation (PV) with high permselectivity is an energy-efficient and environmentally friendly approach [6]. In this field, many membrane materials such as polymer [7,8], NaA zeolite [9,10] and graphene oxide [11,12] have been developed for alcohol purification. However, the separation factor of (C₁–C₂) alcohols is relatively low. Especially for methanol recovery, the reported separation factor of methanol over water is extremely low primarily owing to their similar molecular size and strong coupling effect [13,14]. Besides, for ethanol dehydration, the trade-off phenomenon limits the development of most water-premselective membranes of which the water flux can be further improved, including the potential NaA membranes (< 10 kg⋅m⁻²⋅h⁻¹) [9] and polymeric membranes (< 0.5 kg ⋅ m⁻² ⋅ h⁻¹) [15]. It is also noted that few reports are conducted for separating the mixture of methanol-ethanol. In general, it remains a challenge to obtain both high performances for methanol purification and ethanol dehydration.

Among diverse membranes that are available in separating alcohol solutions, the newly emerged graphynes (GYs) and their allotropes with uniform pores are promising candidates to achieve high separation performance on the basis of numerous theoretical studies [16,17]. The one-atom-thick nanosheet with a two-dimensional (2D) network dramatically promotes molecule transport [18,19]. As Zhou et al.

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reported that the ultrathin GY membranes presented an impressive water permeance that extended the state-of-the-art membranes by several orders of magnitude [20]. The intrinsic pores are uniformly arranged in GYs [21] and their aperture sizes are easily controllable via doping different atoms [22], which makes the apertures comparable towards guest molecules. With these standpoints, GYs are potential candidates for purifying alcohols. Yang et al. demonstrated that GYs could serve as an ethanol-selective GY membrane by utilizing their superhydrophobic surfaces [23,24].

However, the reported GYs are limited to the ethanol-selective membranes, thereby not fully taking the inherent advantage of the well-defined nanopores for fast water permeation. Up to now, they have not been developed as water-preselective membranes for ethanol dehydration. Besides, none of them have targeted to methanol purifications from water and ethanol owing to their similar molecular size and polarity [3,25]. Additionally, the effect of GYs’ morphologies on the performance of ethanol dehydration and methanol purification is unexplored, and its permeation mechanism is elusive. Therefore, it is crucial to develop high-performance GY membranes for methanol purification and ethanol dehydration, and meanwhile give a systematic understanding of the separation mechanism.

In this study, GY membranes are theoretically explored for methanol purification and ethanol dehydration for the first time. By non-equilibrium molecular dynamics simulation (NEMD), pervaporation system is set up to separate methanol-water, methanol-ethanol and water-ethanol mixtures. In section 2, our computationally designed GYs and simulation methods are presented. In section 3, the separation performance of different GYs is examined. To further improve separation performance, two strategies for membrane design including surface charge modification and functional group decoration are proposed to precisely regulate aperture size and surface affinity. The effects of aperture sizes, surface charges and functional groups on PV performance are discussed in detail. By structural and energetic analyses via density contour maps, diffusion calculations and the potential of mean force (PMF), the separation mechanism is comprehensively understood. A comparison with the ever-reported membranes is enclosed to demonstrate the effectiveness of our designed GYs membranes in practical applications.

2. Models and methods

Based on the experimentally synthesized graphdiyne [26], several GY allotropes equipped with small (2.5 Å), middle (3.8 Å), large (4.6 Å) and extra-large (6.4 Å) apertures are constructed in the Material studio [27] and coded as GY-S, GY-M, GY-L and GY-XL, respectively, as shown in Fig. 1a-d. All GY membranes in the current study share the same dimensions of 7.75 × 7.55 nm², and each GY membrane has a high porosity, where the number of pores is about 144, 126, 63 and 53 in GY-S, GY-M, GY-L and GY-XL plates, respectively. The aperture sizes are determined by using Zeo++ code [28]. Given the kinetic diameters (Dk) of water (2.7 Å), methanol (3.6 Å) and ethanol (4.3 Å) [3], those GY membranes that have nanopores larger than 4.6 Å (i.e., GY-L and GY-XL) are hard to deliver good separations. Nevertheless, their apertures can be regulated by functional groups. On this basis, three functional groups (i.e., –H, –F and –OH) with variable steric hindrances and polarities are nominated to decorate the GY surface, which is also feasible in experiments by acid-oxidation treatment method [29]. Fig. 1f–h show the functionalized GY-M membranes where functional groups are closely bonded to pore edges, and their corresponding aperture sizes as shown in Fig. S1 decrease as GY-M > GY-M-H (3.5 Å) > GY-M-F (3.0 Å) > GY-M-OH (2.7 Å). Although the investigated molecules are larger than some apertures, flexible functional groups can dynamically switch orientations and raise concerted rotations to allow the passage of molecules [30]. Besides, to improve the polarity of GY membranes, but without sacrificing its aperture size, the surface charge modification is proposed based on our previous experimental study [31]. To avoid the local overcharging, the assigned charges on each atom in the whole GY plate should be better tiny [32], which ranges from −0.010 to +0.010 e/atom. Accordingly, the counter-charges are assigned on the right graphene plate where its potentials are set to have few interactions with the permeated molecules, thereby maintaining the whole system charge neutrality. Taking the GY-S membrane as an example, Fig. 1e depicts the charge distribution manner, where the positively charged atoms are highlighted with pink color. Our designed GY membranes have an atomic thickness of about 0.34 ~ 0.60 nm, which will minimize molecule transport resistance [19].

The optimized GY membranes were used to separate (C1–C2) alcohol solutions. The schematics of separation systems are illustrated in Fig. 2, where the feed and permeate chambers are separated by a GY membrane. The aqueous bath in the left chamber is filled with equimolar mixtures of methanol-water (or water-ethanol, or methanol-ethanol). Each separation system has the same settings in the number of solution molecules (5642) and the length of vacuum chambers (17 nm). The equimolar mixtures are helpful to improve statistical significance, which is generally adopted by previous studies [33,34]. Two graphene plates are placed at both ends of the chambers. An external driving force of about 300 bar along the z-direction is exerted on the left plate that is acted as a piston to drive the feed mixtures to cross the membrane and fall into the permeate chamber. To avoid the escape of molecules between periodic chambers, the right plate is fixed. Similar to previous studies [35–38], the intermolecular three-point potential model [39] was used to mimic the realistic water molecules, and membrane frameworks and other molecules were all described by the popular all-atom optimized potential (OPLSAA) force-field that is proper to describe the carbon-based materials [34,40]. For the interactions among non-bonded atoms, the Lorentz-Berthelot combination rules [41] were adopted to calculate their Lennard-Jones (LJ) and electrostatic potentials. To avoid the drift of membranes in the PV process, a position restriction was imposed on these carbon atoms that were randomly selected in GY plates, whereas other atoms were highly flexible. As per Video 3, the base plate of the membrane has a slight vibration while the decorated functional groups vibrate distinctly.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.memsci.2021.120139

After energy minimization by the steepest descent approach, the isobaric-isothermal ensemble with 2 ns was performed to further equilibrate the separation system. Then another 40 ns simulation was conducted in a canonical ensemble for production runs, in which the equations were integrated by the leap-frog algorithm with a time step of 1 fs and the trajectories were saved every 2 ps. The temperature in this setup was maintained at 300 K by using the velocity rescaling thermostat.
Although solvent evaporation might be difficult at this temperature, the applied high pressure serving as the driving force made a large contribution to its permeation. This high pressure together with a constant temperature of 300 K is commonly employed in NEMD simulations to improve computational efficiency and reduce time consumption [36, 43]. The initial velocities in each system were specified following the Maxwell-Boltzmann distribution. The electrostatic interactions were computed by the Ewald summation method, while van der Waals interactions were truncated at 1.2 nm. To mimic an infinite separation system, periodic boundary conditions were properly implemented in XYZ directions. All NEMD simulations were accomplished by using Gromacs v.4.5.5 [44]. For visualizing the separation process, an animation for methanol-water mixtures crossing the GY-S membrane produced with Visual Molecular Dynamics (VMD) packages [45] is provided as Video 1.

3. Results and discussion

With a pressure gradient between the entrance and exit of the membrane, feed solutions energetically flow from the left chamber to the right one. Fig. S2 illustrates the time evolution of the net number of permeated methanol molecules ($N_{\text{permeated}}$). The $N_{\text{permeated}}$ increases linearly with simulation time, which implies a steady flow [46]. By monitoring these flow curves, the fluxes that are normalized to the atmospheric pressure are calculated as presented in Fig. 3, where the calculation process is described in the supporting file. In Fig. S2, it is also observed that the $N_{\text{permeated}}$ increases with positive charges at first and then decreases at a given time. And the highest flow is fostered by the +0.005 e/atom charged GY-S membrane, insinuating the important effect of positive charges on methanol permeation, which will be discussed in detail below.

3.1. Methanol-water separation

First, the separation of methanol-water is examined by pristine GY membranes with the performance gauged on membrane flux and methanol separation factor ($S_{m/w}$). As seen in Fig. 3a, the fluxes of methanol are larger than water in all four GYs. This is ascribed to the higher affinity of pristine GYs towards methanol by virtue of Fig. S3a.

Apparantly, the size sieving effect is overwhelmed by the preferential adsorption of methanol that is the dominant mechanism in this separation process, which helps to preferentially capture the large molecules [24]. As a result, the methanol is pre-selected by these pristine GYs, although its D$_h$ is larger than water. High fluxes of methanol ($\sim$ 290.9 kg m$^{-2}$ h$^{-1}$) and water ($\sim$ 95.0 kg m$^{-2}$ h$^{-1}$) show up in those GYs that have pore sizes larger than or equal to 3.8 Å (i.e., GY-M, GY-L and GY-XL); unfortunately, the corresponding $S_{m/w}$ is extremely low ($\leq$ 1.7). It seems that an excellent $S_{m/w}$ is hard to be achieved by those methanol-selective GY membranes with large nanopores. Nevertheless, with a relatively small aperture (2.5 Å), the GY-S membrane exhibits a superior $S_{m/w}$ ($\sim$ 15.0) and an acceptable methanol flux of 86.2 kg m$^{-2}$ h$^{-1}$, which might be a promising candidate for separating methanol-water mixtures in practical applications.

To further enhance the methanol flux of the GY-S membrane, one effective strategy proposed for membrane design is surface charge modification. The separation performance versus surface charges is shown in Fig. 3b. With increasing charges from –0.010 to +0.005 e/atom, methanol flux rises significantly. In contrast, water flux remains essentially unchanged. As indicated, the highest methanol flux of 99.1 kg m$^{-2}$ h$^{-1}$ with a separation factor of 15.2 is achieved by this +0.005 e/atom charged GY-S membrane, of which the separation performance grows by 15%, compared to the pristine GY-S. Further increasing the charges has the membrane surface saturated with the methanol heaping up, so that the export transport flow becomes more difficult [47,48]. The methanol flux could not increase indefinitely, and a critical point (C = +0.005 e/atom) for the appearance of a charge inversion [49,50] is observed in Fig. 3b with a reduced methanol flux and separation factor. Therefore, the +0.005 e/atom charged surface is well-judged for methanol-water separation. As visualized by final snapshots in Figs. S4a–c, the largest methanol flow in permeate is stimulated by this positively charged GY-S membrane.

3.2. Methanol-ethanol separation

Unlike the above mixture, methanol and ethanol have similar polarity [25] so that they are harder to be separated from each other. The key to this separation goal is to screen a suitable aperture of GY membranes governed by a size-sieving mechanism. The methanol-ethanol
separation through different pristine GYs is investigated in Fig. 3c and d. A larger aperture usually exhibits a faster molecular permeation rate [37]. It shows that the ethanol permeation is materially impeded by GY-S and GY-M membranes of which the nanopores are far smaller than the ethanol molecular size, thus resulting in an infinite methanol separation factor over ethanol ($S_{\text{m/e}}$). In contrast, with large apertures, those GY-L and GY-XL membranes increase the fluxes, especially for ethanol owing to its slightly higher affinity to membranes according to Fig. S3a; however, the corresponding $S_{\text{m/e}}$ is compromised. Accordingly, in Fig. 3c, with a suitable aperture (3.8 Å), it is the GY-M membrane that exhibits superior performance with a methanol flux of 133.3 kg·m⁻²·h⁻¹ and an almost infinite $S_{\text{m/e}}$.

To develop a higher-performance GY-M membrane for methanol-ethanol separation and without sacrificing its separation factors, the strategy of surface charge modification is efficiently employed. As noted earlier, methanol flux in Fig. 3d has a positive correlation with surface charges varying from −0.010 to +0.008 e/atom. The turning points in Fig. 3b and d are slightly different because more attractions are needed for methanol to escape from the ethanol than the water. As visualized in Video 2, the highest separation performance of methanol-ethanol is harvested by this +0.008 e/atom charged GY-M membrane that not only maintains an infinite $S_{\text{m/e}}$ but also exhibits an astonishing methanol flux of 177.6 kg·m⁻²·h⁻¹, almost 33% higher than that of pristine GY-M.

Besides, the functionalized GY-M membranes proposed by the other design strategy are also examined to investigate how they can separate the mixtures of methanol-ethanol as well as methanol-water. However, it is found that the permeations are seriously impeded in that the functional groups naturally reduce the pore size and do little to the affinity between methanol and membranes as per Fig. S3b. Basically, methanol fluxes decrease as GY-M > GY-M-H > GY-M-F ≈ GY-M-OH, as shown in Fig. 4a and b. After comparing these two design strategies, it is believed that the surface charge modification is better than the

**Fig. 2.** Three simulation systems of equimolar (C₁–C₂) alcohol solutions crossing the GY membranes. (a) Methanol-water; (a) Methanol-ethanol; (c) Water-ethanol. Molecules: Ethanol (orange), methanol (purple), and water (green). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
functional group decoration to develop high-performance GY membranes for methanol-water and methanol-ethanol separation.

3.3. Microscopic insight into the methanol purification process

As demonstrated, surface charge modification is an effective strategy to improve the performance of methanol purification from water and ethanol. The microscopic insight into the effect of surface charges on methanol permeation is illustrated in Fig. 5. On the one hand, the affinity of methanol to GYs is notably strengthened by positively charged membranes as evidenced by Fig. 5a. On the other hand, the surface charge also affects the molecular permeation barrier and transport rate [34]. As seen in Fig. S5, with increasing surface charges from $-0.010$ to $+0.008$ e/atom, the permeation barrier of methanol crossing GY-M membranes is drastically reduced to 6.5 kJ/mol. As a result, the corresponding methanol mobility is accelerated nearly three times, as seen in Fig. S6a. Particularly in the range of $-0.005$ to $+0.005$ e/atom, its diffusion coefficient almost increases linearly with surface charges, as illustrated in Fig. 5b. The fastest diffusion ($7.34 \times 10^{-6}$ cm$^2$/s) is evoked by this $+0.008$ e/atom charged membrane, thus resulting in the largest methanol flux in Fig. 3d. These two actions synergistically promote methanol flow, which is the primary reason why the methanol flux is facilitated by positively charged surfaces in Fig. 3b and d. However, the overcharging surfaces hinder the methanol diffusion primarily owing to the natural properties of molecules that cause the appearance of the charge inversion [49,50].

Structural analysis is further conducted by final snapshots at the membrane interface. For methanol-water separation as visualized in Figs. S4a–c, the GY-S membrane surface is preferentially adsorbed by methanol, and this adsorption is improved by a positively charged surface, thus resulting in the largest methanol flux in Fig. 3d. These two actions synergistically promote methanol flow, which is the primary reason why the methanol flux is facilitated by positively charged surfaces in Fig. 3b and d. However, the overcharging surfaces hinder the methanol diffusion primarily owing to the natural properties of molecules that cause the appearance of the charge inversion [49,50].

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aperture (4.6 Å) in the GY-L membrane allows the passage of ethanol as shown in Fig. S4f. As visualized, the suitable candidate for methanol-ethanol separation is the GY-M membrane that not only shows a higher ethanol rejection than the GY-L membrane but also a higher methanol flow than the GY-S membrane.

3.4. Water-ethanol separation

Fig. 3e shows the permeation fluxes of water-ethanol mixtures through different GYS with various aperture sizes. Obviously, water molecules are pre-selected by GY-S and GY-M membranes, while the ethanol is fully rejected. This is because the D_v of water is smaller than ethanol and their separation in those small-sized nanopores is dominated by the size-sieving effect. As a result, the corresponding water content in permeate is 100 wt%, epitomizing an infinite water separation factor; however, its fluxes in pristine GY-S and GY-M are relatively low (≤ 1.7 kg m^{-2} h^{-1}). While crossing large-sized nanopores, the ethanol molecules instead of water preferentially enter those GY-L and GY-XL membranes through which the ethanol flux is higher than water. This is because the experimentally confirmed superhydrophobicity of pristine GYS [51] shows a greater affinity towards ethanol learning from the affinity analysis in Fig. S3a, and the size-sieving effect is overwhelmed by ethanol preferential adsorption, which is similar to the separation of methanol-water mixtures.

To further enhance the PV performance for ethanol dehydration, the other design strategy that is about functional group decoration is alternatively adopted. Fig. 3f illustrates the influence of functional groups on water flux through the GY-M membranes. The water flux increases astonishingly in the order of GY-M < GY-M-H < GY-M-F < GY-M-OH regardless of the aperture size, simply following the trend of the polarity of functional groups. While ethanol is always completely rejected. Unlike the methanol permeation, the water is highly attracted by these polar groups (i.e., –F and –OH) in that the affinity of GY-M-OH towards water molecules is strengthened by hydroxyl groups according to Fig. S3b, which greatly facilitates water permeation. As a result, with the help of the decorated –OH groups, water permeation is dominated by the synergistic mechanisms of size-sieving effect and water preferential adsorption, thus promoting water flux to 225.8 kg m^{-2} h^{-1}, over 130 times higher than the pristine GY-M membrane. Note that an infinite separation factor of water is always remained by this GY-M-OH membrane, as visualized in Video 3. This flabbergasting performance of GY-M-OH for water-ethanol separation far exceeds the existing membranes [9, 52–54].

3.5. Microscopic insight into ethanol dehydration

To provide microscopic insight into the ethanol dehydration process, structural and energetic analyses are conducted at the membrane interface. As illustrated by number distributions in Fig. 6a and b, the ethanol is entirely rejected by functionalized GY-M membranes due to its large molecular size. For better visualizing the separations, the corresponding final snapshots are presented in Fig. S7. Intuitively, ethanol molecules are abundantly gathering at the membrane interface, where an ethanol jam occurring on the upstream surface in Fig. 6a (i.e., the
sharp peaks at \( z = 7.2 \text{ nm} \) seriously prevents water from approaching the membranes. As a result, the water amount at the membrane interface is relatively low; nevertheless, it is gradually enhanced with the polarity of functional groups according to Fig. 6b. It is found that the greater the polarity of the functional group, the less the accumulation of ethanol at the membrane interface, and the less likely the membrane is to be blocked. Consequently, the collective water flow is largely gathered at the backside of the hydrophilic GY-M-F and GY-M-OH membranes as visualized by snapshots in Figs. S7c–d.

To highlight the distributions of water and ethanol at the membrane interface, the number density contours are analyzed. As evidenced by Fig. 7a and b, nanopores in pristine GY-M and GY-M-H are globally occupied and seriously blocked off by ethanol molecules (\( \sim 16 \text{ N}_{e}/\text{uc} \)) due to their hydrophobic nature. This blocking phenomenon surely augments water transport resistance [46], bringing about the limited water adsorption, as seen in Fig. 7e and f where the contour maps of water are almost flat and its distribution amounts are extremely limited \(( \leq 1.0 \text{ N}_{w}/\text{uc})\) on membrane surfaces. That’s why water fluxes in pristine GY-M and GY-M membranes are relatively low. Despite that, with the help of the polar groups of –F and –OH, the surface blockage is greatly relieved as indicated in Fig. 7c and d, while water distributions \(( \geq 20 \text{ N}_{w}/\text{uc})\) are enormously attracted by these polarized GY-M-F and GY-M-OH membranes as visualized by the colorful contour maps in Fig. 7g and h, thus promoting water flux as high as 225.8 kg \( \cdot \) m\(^{-2} \cdot \) h\(^{-1}\) in the GY-M-OH membrane regardless of the reduced aperture size. Learning from all these contour maps, it is proved that the uptake of water on the functionalized GY-M surface is promoted by polar groups. While for ethanol, its uptakes show an opposite trend and so does its blocking effect.

By using Boltzmann sampling that is frequently adopted in the NEMD system to estimate permeation barriers [37,55], the PMF profiles are calculated as follow: \( G_z = -RT \ln \frac{\rho(z)}{\rho(\text{bulk})} \), where \( R \) denotes the gas constant, \( T \) is the temperature, and \( \rho(z) \) and \( \rho(\text{bulk}) \) symbolize the density profiles of those molecules that are perpendicular to the interface and in the bulk solution, respectively. With increasing the polarity of functional groups, ethanol molecules are facing enormous energy barriers that are too huge to be overwhelmed. In Fig. 6c, the permeation barrier of ethanol even grows up to 33.3 kJ/mol in the hydroxylated GY-M-OH. At the same time, the polar groups can intrinsically promote water transport [34,55], thereby largely reducing water permeation barriers from 17.6 kJ/mol to 5.1 kJ/mol, as seen in Fig. 6d, which instantaneously accelerates water diffusion as stated by Fig. S5b. In a word, the polar groups effectively reduce not only the blocking phenomenon of ethanol but also the water permeation barrier. This is the primary reason why the water flux in Fig. 3f increases with the polar groups regardless of the decrease of aperture sizes.

3.6. Performance comparison

In terms of the trade-off between permeation flux and separation factor (or the concentration in permeate), the PV performance of our computationally designed GYs as scaffolds is compared with the state-of-
the-art membranes for methanol purification and ethanol dehydration in Fig. 8a and b respectively. Please note, there are few experiments reported on graphyne-based membranes in that they are still in the exploratory stage [16, 21]. And the driving force-normalized flux (i.e., permeance) is helpful to grasp the intrinsic membrane properties. For methanol recovery from water, the GY-S membrane with 2.5 Å sized nanopores and +0.005 e/atom charged surface in this simulation shows superior performance with a promising separation factor and methanol flux, over 40 times greater than the available membranes [13, 14, 56, 57].

For ethanol dehydration, the functionalized GY-M-F and GY-M-OH membranes provide an exceptionally high performance, where the water content in permeate always maintains 100 wt%, and meanwhile, its fluxes are almost one order of magnitude higher than these existing membrane materials such as NaA zeolite [9, 58], graphene oxide [59, 60] and polymeric membranes [61, 62]. Simulations of the operando conditions in Figs. S8–S9 also exhibit an unprecedented performance, which further suggests the bright prospect of our computationally designed GY membranes for practical applications of methanol purification and

Fig. 7. Density contours of water-ethanol mixtures adsorbed at functional GY-M membrane interfaces. (a-d) Ethanol adsorption; (e-h) Water adsorption. The unit of density (N_w/uc) is 1/(1.25Å³). Each figure is inserted with the skeletons of functional GY-M membranes, respectively.
ethanol dehydration.

4. Conclusions and outlook

The GY membranes with variable aperture sizes, surface charges and functional groups are computationally designed to examine how GYs can purify ($C_1$–$C_2$) alcohol solutions.

1. For methanol-water separation, the GY-S membrane possesses a superior $S_{m/w}$ of 15.0 with an acceptable methanol flux. The first design strategy of surface charge modification is proposed to improve methanol flux. And it is promoted to 99.1 kg·m$^{-2}$·h$^{-1}$ by the $+0.005$ e/atom charged surface without compromising its separation factor owing to the accelerated diffusion and the strengthened affinity of methanol. Such unprecedented performance of methanol purification is about 40 times greater than the available membranes.

2. The surface charge modification is also effective for methanol-ethanol separation. Accordingly, the highest separation performance is achieved by the $+0.008$ e/atom charged GY-M membrane that not only maintains an infinite $S_{m/e}$, but also exhibits an enhanced methanol flux of about 177.6 kg·m$^{-2}$·h$^{-1}$.

3. For ethanol dehydration, the other strategy is alternatively adopted to facilitate water permeation by functionalizing GY-M with polar groups. With increasing the polarity of functional groups, the blocking effect at the membrane interface is effectively relieved, and the water permeation barrier is remarkably reduced, thus resulting in an increasing trend of water flux with the decrease of aperture sizes. The GY-M-OH membrane shows an exceptionally high ethanol dehydration performance with a 100 wt% water content in permeate and 225.8 kg·m$^{-2}$·h$^{-1}$ water flux, almost one order of magnitude higher than these state-of-the-art membranes.

Overall, this computational study is focused on methanol purification and ethanol dehydration through GY membranes by the engineering of functional groups and surface charges. Despite lots of unsolved challenges in experiments, our molecular understanding shows the great potential of graphynes in membrane separation applications and provides two strategies to develop high separation performance from the bottom-up. Such fundamental insights are useful for the rational design of 2D membranes in practical applications.

Author statement

Quan Liu: Methodology, Data curation, Writing-original draft preparation.
Haipeng Zhu: Investigation.
Gongping Liu: Writing-reviewing and editing.
Wanqin Jin: Conceptualization, Supervision, Writing-reviewing and editing.

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.

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Appendix A. Supplementary data

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