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Topical Review

Molecular transport across a two-dimensional nanomesh membrane-graphdiyne

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Abstract

The purification and separation technologies are of great importance to industry and agriculture in modern society. Two-dimensional (2D) crystals emerge as superior membrane materials showing desirable molecular permeability and selectivity. Among them, 2D materials with a nanomesh structure show the greatest potential in molecular transport and separation. Here, we highlight the recent theoretical progresses in molecular transport across 2D graphdyne membrane with the nanomesh structure. Firstly, the nonlinear and activated water flow were demonstrated through the graphdyne membranes under external hydrostatic pressure. Then, the superior proton conductivity and perfect selectivity were shown for graphdyne membrane at ambient conditions. Lastly, graphdyne was shown to exhibit perfect small gas molecular transport and selectivity are also discussed.

Keywords: nanomesh membrane, graphdiyne, molecular transport and separation, molecular dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

The purification and separation of water, ions and gas molecules are vital for modern industry and agriculture [1-3]. Among various approaches, membrane technologies exhibit the advantages of facile operation, low energy consumption and easy maintenance [4], and have been extensively explored to realize high-efficiency water desalination and gas separation [5]. At the center of membrane technologies are the membrane materials which transport desirable species and block other species. The conventional membrane materials include polymeric, inorganic and polymer/filler hybrid membranes.

However, these membranes have the obvious disadvantages. The polymeric membranes show an intrinsic trade-off between permeability and selectivity, severe plasticization and fast aging processes [6]. The difficulties of large-scale commercialization, including complicate manufacturing procedures and high cost, restrict the extensive usages of inorganic membranes [7]. The emergence of voids and non-compatibility are the common problems of hybrid membranes [8].

Recently, atomically thin two-dimensional (2D) materials, e.g. graphene, graphene oxides and h-BN, emerge as the superior candidate as molecular sieving materials [9-15]. The ultrathin thickness and nanoscale transport channel endow 2D

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materials superior molecular conductivity and selectivity. The transport and separation mechanisms can be classified into two categories. The first is transmembrane molecular transport through nanopores on the 2D membrane planes. For example, protons can transport through the intrinsic defects on graphene planes forming during the fabrication processes [16]. Within this mechanism, the transport rate can be greatly enhanced by artificially introducing transport channels on 2D materials via oxidation or ion beam etching processes [17, 18]. With the accurate control of etching processes, the nanoporous graphene membranes can exhibit a salt rejection of nearly 100% and the rapid water transport [19]. However, it is extremely hard to control the uniformity of channel size, which may lead to the decrease of selectivity. The second is molecular transport through the nanochannels between adjacent membrane layers. The submicrometer-thick graphene oxides membranes are permeable for water molecules via the interlayer nanochannels and block the transport of gases molecules [20]. Water diffuses in the form of water monolayer through the 2D channels [21]. Besides, the graphene oxides membranes display nice performances in salt rejection. The graphene oxides membranes immersed in water blocks solutes with hydrated radii larger than 4.5 Å [22]. The interlayer spacing between adjacent layers dominates the transport or blockage of solutes, and can be tuned with external pressure [23] and cationic control [24]. However, despite of these efforts, the delicate interlayer spacing is still hard to control in realistic applications.

Graphyne [25] is a novel kind of one-atom-thick carbon allotrope including acetylene groups in the membrane planes. The popular graphyne allotropes, such as α -graphyne, β graphyne and γ -graphyne, exhibit unique nanomesh patterns featuring considerable pore density and perfect pore uniformity. Among them, γ -graphyne is most versatile and can be extended to various types by changing the number of acetylene groups in the linkage, and graphdiyne, graphtriyne, graphtetrayne, graphpentayne and graphhexayne can be thus constructed with 2, 3, 4, 5 and 6 acetylene groups in the linkage, respectively. Graphdiyne (figure 1) is the first experimentally fabricated membrane in the graphyne family via a crosscoupling reaction on the copper surface [26], then graphtetrayne has also been synthesized by a facile synthesis route of cross-coupling reactions [27]. As the first fabricated member, graphdiyne has attracted great attention in both theoretical and experimental studies owing to its excellent mechanical, physical and electrochemical properties [28-32]. Graphdiyne exhibits the uniform distribution of triangle nanopores with a density of $2.5 \times 10^{18} \text{ m}^{-2}$, where the nanopore size is comparable to small molecules, e.g. water molecule, H₂ and CH₄. Both the adequate pore size and large pore density endow graphdiyne a great potential as the molecular sieving material. In this review, we highlight recent theoretical researches of molecular transport across 2D graphdiyne membrane. Three types of molecular transport are reviewed in the following sections: water transport, proton transport and gas molecule transport. The discussion also includes a fundamental understanding of the mechanisms of molecular transport and selectivity.



Figure 1. (a) Atomic structure of the graphdiyne membrane. (b) The linkage of acetylene and phenyl groups in graphdiyne membrane.

2. Water transport and desalination

Water scarcity is one of the serious global challenges of our time. The most promising way is to employ the desalination technologies which generate clear freshwater with the aid of efficient desalination membranes. Besides water selectivity over ions and other molecules, high permeability is also needed for desalination membranes to reduce the capital cost [3]. Recently, novel porous nanomaterials, e.g. graphene, graphene oxides, carbon nanotubes, were proposed as the desalination membrane materials [33–40]. The water flow rate across these porous materials are usually very high owing to the slippery and inert transport channels, and is linear with respect to the external pressure. The water flow usually exhibits peculiar behaviors at the nanoscale. For example, the water flow is spatially quantized due to the steric hindrance effect at the entrance of the nanopores [41], and water molecule passes through the nanopore within a single-file transport mode [42]. However, graphene and graphene oxides suffer from the failure in precise control of the size of transport channels, and carbon nanotubes are easily blocked by cations due to the interactions with aromatic rings [43]. The difficulties in the largescale commercialization also hinder the realistic implementations.

The precise control of channel size is easily realized with intrinsic nanomesh materials. For example, the artificial design of g-C₃N₄ nanosheets with self-supporting spacer give rise to better water purification performances than commercial desalination membranes [44]. Given the adjustable nanopore size and uniform and large-density nanopores, graphyne membrane exhibits a great potential in desalination applications. Classical molecular dynamics (CMD) simulations were conventionally used to simulate the desalination processes, and external pressure is applied to driven the transmembrane water transport (figure 2(a)). It is found that α -graphyne, β -graphyne and graphtriyne membranes can transport water molecules and achieve 100% salt rejection of ions, where the selectivity originates from the significantly different free energy barriers for ions and water molecules passing through the nanopores [42, 45, 46]. Graphtetrayne show the better performance of a larger water flow rate of $\sim 13 \, l^{-1} \, \text{cm}^{-2} \, \text{d}^{-1}$ MPa and the same 100% salt rejection owing to its adequate larger pore sizes [41]. Considering the recent successful synthesis [27], graphtetrayne can be a promising membrane material for water desalination. Though graphpentayne and graphhexayne also exhibit the nice





Figure 2. (a) Side view of the system for water transport in CMD simulations. (b) Water flux through graphdiyne versus the pressure and temperature in AIMD and CMD simulations. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nano Research [47] (2019).

water permeability, the large pore size leads to the reduce of salt rejection and relatively bad desalination performance [41].

In general, CMD simulations show that graphdiyne membrane is impermeable for water molecule due to the small pore size (incircle diameter 0.55 nm) [41, 42]. However, firstprinciples electronic structure calculations demonstrate the possibility of water molecule passing through the nanopores on graphdiyne if the transmembrane interaction is considered [48]. The force field method used in CMD simulations is often accused of the bad transferability leading to critical issues in extreme confined systems, while the electronic structure calculations lack the dynamics evidences of water transport. As the first well fabricated membrane in the graphyne family, it remains unclear whether graphdiyne is permeable for water molecules, and this has to resort to the more accurate *ab-initio* molecular dynamics simulations (AIMD) and *ab-initio* parameterized CMD simulations [47].

The observation of water transport through the graphdiyne nanopore is not easy in AIMD simulations. Thus, large pressure and high temperature are required to accelerate the sampling of the transport event. Under the pressure of 2 GPa and the temperature of 400 K, direct penetration of water molecules through graphdiyne membrane was observed, and the corresponding water flow rate is $0.012 \text{ ps}^{-1} \text{ nm}^{-2}$ (figure 2(b)). Ab-initio parameterized CMD simulations, which use the force field parameters obtained by fitting to the ab initio density-functional theory calculations of the water-graphdiyne interaction potential, give rise to the consistent water flow rates in figure 2(b). In the range of small pressures, ab-initio parameterized CMD simulations exhibit the water flow rates of over one order of magnitude larger than those using the conventional Amber99 force field (figure 3(a)). The difference in flow rate derives from the fact that *ab-initio* parameters are constructed based on density function theory calculations of water adsorption and the transmembrane interaction is accurately described. Though the flow rate is indeed too small in the range of small pressure, the obvious flow difference accounts well for the reason why no water permeation was observed in previous studies.

At the same time, the water flux exhibits an obvious nonlinear dependence on the external pressure in the range of large pressures (figure 2(b)), which is dramatically different from the linear water flow in previous studies. The nonlinearity and temperature dependence of water flow indicate an activated process, and the rate can be described by the Arrhenius equation $\Phi = A_0 exp\left(-\frac{E_a}{k_BT}\right)$. The activation energy can be thus estimated by $E_a^{est} = E_{mem} + E_{water} - PV$, where E_{mem} is the contribution from graphdiyne membrane, E_{water} is the contribution from adjacent water via hydrogen bonds, P is the pressure applied, V is the effective volume of transported water molecule, and thus PV is the modulation from external pressure (figure 3(b)). The estimated activation energy E_a^{est} is well consistent with the activation energy E_a obtained from MD simulations. This fact strongly suggests that the activated water flow indeed originates from the ultimate size of the nanopores on graphdiyne membrane and the corresponding interfacial water structure. Graphtriyne and graphtetrayne with slightly larger nanoscale pores exhibit the conventional linear water flow with respect to the external pressure applied [41]. The activated water flow suggests that pressure and temperature can be used as sensitive tools to modulate water flow rate in the range of large pressure, and the linear relationship between water flow and pressure can recover in the range of small pressure.

Further analysis shows that a transmembrane hydrogen bond emerges and constructs a unique two-hydrogen-bond transient configuration. The transmembrane hydrogen bond also offers a superior transport channel for potential transmembrane proton transfer in next section. The water transport is demonstrated to exhibit no configuration selectivity, which is different from the static calculations without considering the realistic interfacial water structures [48]. Despite of the decrease of water flow rate due to the addition of ions [49], graphdiyne membrane can exhibit the superior salt rejection of 100% owing to its ultimate channel size. Thus, graphdiyne can be a superior membrane material for water desalination applications. The activated water flow and working mechanisms found here also offer new insights for the understanding of biological transport [50, 51] and nanofluidic manipulation [52–54].



Figure 3. (a) Water flux through graphdiyne versus the pressure with the *ab-initio* parameters and Amber99 force field in CMD simulations. (b) The estimated activation energy (E_a^{est}) , and the contributions from membrane (E_{mem}) , interfacial water molecules (E_{water}) , and pressure (PV) versus pressure. The activation energy from MD simulations (E_a) is also shown for comparison. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nano Research [47] (2019).



Figure 4. (a) Energy barriers for proton transfer in free and transmembrane H_3O^+ - H_2O complex. (b) Energy barriers for proton transport across various two-dimensional membranes. Reproduced from [65]. CC BY 4.0.

3. Proton transport

Proton exchange membranes (PEM) offer channels for proton transport and block the transport of fuel molecules. The efficiency of PEM dominates the performances of fuel cells, and are the key module of fuel cells. The commercial PEM material Nafion exhibits a fairly good proton conductivity and the nice chemical durability. However, the performances of Nafion are strongly dependent on the working temperature and humidity, which restricts the ranges of applications. Furthermore, the permeability of fuel molecules, e.g. methanol, is large for Nafion, which greatly reduces the performance of direct methanol fuel cells. Thus, seeking novel and highefficiency PEM materials is of fundamental importance to the fuel cell industry.

The 2D materials, e.g. graphene, graphene oxides and h-BN, were demonstrated to show nice proton permeability [14–16]. The transmembrane proton conductivity derives from the natural or fabricated defects on membrane planes [55–57]. Nanopores, such as Stone–Wales defect, are known to reduce the energy barrier of proton transfer through graphene in vacuum [55]. The proton conduction is also enhanced

with the introduction of oxygenated functional groups on ozonated graphene oxide membranes where proton hopping is greatly enhanced via these functional groups [58]. Therefore, the transmembrane proton transport is categorized into three types at the liquid-solid interface: dissociation-penetration, adsorption-penetration and H_3O^+ penetration [59], where the dissociation-penetration and adsorption-penetration are also referred as physisorption and chemisorption processes according to the interactions with membranes [60, 61]. At the same time, in-plane proton conduction is also reported on the reduced graphene oxide films where water molecule is taken as hopping site for in-plane proton transport [62], while hydroxyl functionalized graphene also conduct proton under anhydrous conditions [63]. The nice proton conduction of twodimensional materials is also demonstrated in realistic applications. For example, graphene and h-BN are shown to enhance the performances of direct methanol fuel cell [64]. The proton conduction originates from the nanopores or functional groups on membrane planes, while the intact two-dimensional materials, e.g. graphene, are almost impermeable for proton due to large energy barrier in both chemisorption and physisorption processes [59-61]. Pore drilling technologies, e.g. oxidation,



Figure 5. The trajectories of protons with proton initially located (a) in the bulk water layer below graphdyne membrane and (b) right beneath the nanopore of graphdyne membrane. Reproduced from [65]. CC BY 4.0.

ion beam etching [17, 18], obviously enhance the density of transport channels of nanopores and functional groups, and facilitate proton transport. However, the size and uniformity of nanopores are extremely hard to control. For PEM in fuel cells, the optimal nanopore size is supposed to be between the size of protons and that of soluble fuel molecules to achieve both good proton conductivity and selectivity.

The nanomesh materials exhibit the uniform nanopores and great pore density. Especially, the ultimate size of 0.55 nm of nanopore make graphdiyne membrane a good choice as PEM materials in fuel cells [65]. Density functional theory calculations can be performed to offer a rough estimation of proton conductivity of graphdiyne. As shown in figure 4(a), the energy barrier for proton transfer in $H_3O^+ + H_2O$ complex across graphdiyne membrane exhibits the nearly same profile as that in vacuum (figure 4(a)). The nearly same energy profiles indicate that the graphdiyne membrane imposes no hindrance on the transmembrane proton transfer. This conclusion is reconfirmed with the calculations with hybrid functionals such as B3LYP. What's more, the energy barrier is much smaller than those for proton transfer across other 2D materials



Figure 6. The free energy profile for transmembrane (TM) proton transfer and proton transport in bulk water. The thermal energy k_BT at 300 K is marked as the horizontal dashed line. Reproduced from [65]. CC BY 4.0.



Figure 7. Energy barrier for H_2 , CO, and CH_4 diffusion through graphdiyne membrane. Reproduced from [72] with permission from The Royal Society of Chemistry.

(figure 4(b)), since the transmembrane hydrogen bond can be constructed serving as the bridge for proton transfer across the graphdiyne membrane. The transport mode here resembles the dissociation-penetration above [59], while the stable transmembrane hydrogen bond differentiates them. Even transmembrane $H_5O_2^+$ complex is stable in vacuum, thus dissociation does not occur during proton transfer across graphdiyne membrane. By including realistic interfacial structures of water, *ab-initio* molecular dynamics simulations describe well the dynamic behaviors of protons at the water/graphdiyne interface. Direct transmembrane diffusion of proton is observed in AIMD simulations in Traj_1 of figure 5(a), where proton transport follows the Grotthuss mechanism via forming



Figure 8. Diffusion rate coefficient (a) and selectivity (b) of gas molecules diffusing across graphdyne versus temperature. Reproduced from [72] with permission from The Royal Society of Chemistry.

the transmembrane hydrogen bond. The unbiased simulations imply that the thermal fluctuations are the driving force for the transmembrane proton transport. Figure 5(b) shows the diverse diffusion directions of proton, thus the graphdiyne membrane does not trap the protons.

Further, the free energy barrier for proton transfer across the graphdiyne membrane is nearly the same as that of proton transfer in bulk water (figure 6(a)). The minor difference of energy barrier is due to the slight difference in the equilibrium distance of two oxygen atoms. Both energy barriers are smaller than k_BT at 300 K, which is consistent with the fact that thermal fluctuations serve as the driving force for the observed transmembrane proton transport phenomena. Abinitio molecular dynamics simulations under electric field predict a proton conductivity of 0.6 S cm^{-1} , which is one order of magnitude larger than that of Nafion. Meanwhile, the proton transport rate can be further enhanced with the slight increase of temperature owing to the easily surmountable free energy barriers. Besides the Grotthuss mechanism, H₃O⁺ complex can also directly penetrate the nanopores on graphdiyne with a relative larger energy barrier of 0.55 eV, serving as a secondary transport mode. This is in contrast with another work where two transport modes give the same contributions [66]. The ultimate nanopore of graphdiyne exhibits large energy barriers for fuel molecules, e.g. methanol (1.77 eV) and ethanol (3.56 eV). Therefore, the graphdiyne membrane could exhibit a superior proton conductivity and proton selectivity, and is an ideal candidate as the PEM material. Recently, an experimental study shows that aminated-graphdiyne thin films can be incorporated in direct methanol fuel cells owing to the nice compatibility with Nafion, and the composite membrane enhances the performance and stability of direct methanol fuel cells at a wide range of temperature [67].

4. Gas separation

The separation of gases plays a fundamental role in diverse industrial applications, e.g. purification of H_2 and isotope separations. The rise of 2D materials paves new ways for gas separation. For example, graphene [68] and graphene oxides [69, 70] were demonstrated to exhibit excellent gas

permeability and selectivity owing to the natural and fabricated nanochannels. The two-step adsorption-translocation mechanism was found for gas molecules passing through the ultrasmall nanopores of 2D materials, and the translocation rate can be well fitted with the Arrhenius equation [71]. The selectivity of gas molecules is dependent on the energy barriers for gas molecules passing through the nanopores, which is related to gas molecule size, nanopore shape and modification.

Graphdiyne membranes exhibit a pore size comparable to most gas molecules, e.g. H₂, CO, CO₂, CH₄, O₂, N₂, therefore, graphdiyne can be an ideal membrane for gas purification and separation [72, 73]. Figure 7 exhibits the energy barriers of 0.1 eV, 0.33 eV and 0.72 eV for H₂, CO and CH₄ molecule passing through the graphdiyne membrane, respectively. The barrier of H_2 molecule is easily surmountable (figure 8(a)), and the estimated H_2 permeation rate is 10^4 times faster than that of porous graphene [74]. The larger energy barriers of CO and CH₄ give rise to a good selectivity of H₂ in figure 8(b). Classical molecular dynamics simulations also demonstrated the permeation barrier of ~ 0.11 eV for H₂ molecule passing through graphdiyne [32]. Graphdiyne can also be used in the separation of O_2 from noxious gas molecules, exhibiting the great potential in medical industry [75]. Besides, the ultimate nanopore on graphdiyne can be exploited to separate helium isotopes owing to the differences of zero point energy and tunneling effects at low temperatures [76, 77]. The increase of working temperature can greatly enhance the transport rate owing to the activated transport behavior, but it also decreases the gas molecule selectivity. Thus, the balance between conductivity and selectivity requires a proper working temperature for gas separation in realistic applications. The best working temperatures are strongly related to the industrial setups and realistic demands, e.g. the stability of equipment, the energy cost and the separation efficiencies.

At the same time, the energy barriers for gas molecule permeation through graphdiyne can be modulated with pore modifications and external conditions. For example, it is demonstrated that the injected positive charges into graphdiyne membrane substantially improves the H_2 purification performance by decreasing H_2 penetration barrier and increasing CO and CH₄ penetration barriers [78]. The nitrogen-modified graphdiyne also exhibits a reduced H₂ diffusion barrier and the enhanced H₂ purification performances [79]. The graphdiyne modified with fluorine and oxygen can well separate N₂ and CO₂ from CH₄ in a wide temperature range [80]. Further, the energy barriers can be tuned with the addition of extra driving force acting on gas molecules to enhance the transport rate [32], while external electric field leads to increase of energy barrier for polar gas molecules, e.g. CO, CO₂ [81]. The stacked two-layer structures can also be exploited to enhance the transport rates of gas molecules by increasing the concentrations of gas molecules at the interface [82].

5. Conclusion and outlook

The uniform and large-density nanopores with an adequate pore size endow graphdiyne the great potential in molecular sieving applications. In aqueous solutions, graphdiyne exhibits the activated water flow across the membrane with a 100% salt rejection. Furthermore, graphdiyne shows a proton conductivity over the commercial PEM Nafion and superior proton selectivity. In the atmosphere, graphdiyne also exhibits good H₂ permeability and selectivity over CO, CH₄, and other molecules. Another great advantage of graphdiyne membrane is that it can sustain an extreme uniaxial stress as high as 40 GPa and exhibits superior mechanical strength [41]. The rational design of supporting substrates can further enhance the mechanical strength of 2D materials [83]. The inertness of carbon atoms also endows graphdivne the nice chemical stability. In a word, graphdiyne, as the representative nanomech membrane, can be a versatile molecular sieving material.

Since the first large-area synthesis of graphdiyne [26], the fabrication technologies of graphdiyne have been significantly explored [28, 84, 85]. Graphdiyne membrane can be fabricated at the gas/liquid and liquid/liquid interface with the bottom-up synthesis scheme [86] and even can be fabricated at arbitrary substrates [87]. Ultrathin single-crystalline graphdiyne films have been synthesized on graphene through a solution-phase van der Waals epitaxial strategy [88]. The versatile applications of graphdiyne in catalysis, energy storage and electronics have been well studied in the past [89–92]. However, the application of graphdiyne in molecular transport is still in its infancy [67]. Therefore, both the experimental and theoretical efforts should be devoted to the researches of graphdivne membrane in molecular transport, e.g. the synthesis of large crystalline graphdiyne and the incorporation into realistic devices.

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