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Bilayer graphene with ripples for reverse osmosis desalination

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ABSTRACT

Water desalination is a widely-used strategy to provide fresh water around the world. Herein we report an atomistic simulation study on water desalination in a series of bilayer graphene with different ripples. By carefully analyzing the orientation, density map, and transmembrane velocity of water molecules, it is found that the size of interlayer space formed by ripples affects the water transport. With some appropriate ripples, water molecules pass through bilayer graphene with two or three ordered channels during the transmembrane process. For small and middle ripples, water molecules enter the transport channel with an entrance-angle and need to change their orientation to exit the graphene layers. One of the bilayer graphene (BGR) membranes with ripples, BGR-1.6, exhibits the best performance with water permeance of 1020 kg m h^{-1} bar^{-1} and 98.1% salt rejection, which is three orders higher than commercial seawater reverse osmosis membranes. This theoretical study provides microscopic insights into the role of ripples in governing membrane properties and desalination performance.

1. Introduction

Nowadays, the freshwater shortage is getting globalized with environmental pollution and population increases [1]. Reverse osmosis (RO), a membrane-based water desalination technology, is the most promising solution to problem [2], which offers the highest energy efficiency for producing high-quality water in an environmentally-friendly way. In the RO process, an external pressure is applied on water to overcome the forward osmotic pressure, allowing passage of water through the permeable membrane while partially or completely retaining salt ions [3,4].

In recent years, nanotube-based and graphene-based carbon materials have attracted great attention for their potential application in water desalination due to high flux and excellent ion rejection [5]. Unfortunately, such membranes are difficult to be synthesized and fabricated on an industrial scale [6–11]. Two distinct strategies have been applied to graphene molecular sieves: (i) fabricating nanopores or defects in the basal plane (ii) using nanochannels between stacked graphene layers [12].

Graphene-oxide (GO) is a single sheet of graphene with oxygen functionalities [13]. Recently, GO nanosheets have attracted special interest in the field of water purification membrane, because of their exceptional water permeation and molecular sieving properties [14–18] as well as realistic prospects for industrial-scale production [6,19]. By taking advantage of the extremely fast water transport along the nanochannels between graphene nanosheets, great effort has been made to fabricate highly permeable membranes. For example, in a recent work, reduced GO sheets were deposited by filtration on porous substrates [8], allowing the preferred water permeation with a modest NaCl rejection rate. Kaveh et al. [20] observed the protrusions of graphene sheets on the surface of the modified GO/aramid layer from the scanning electron microscopy images. Their results show that the presence of these protrusions increases the surface porosity of the membrane and leads to a high water flux of 1.8 L/(m^2·h). Some other works [15,21] have also reported the presence of protrusions creates a kind of nanochannel in the form of pores between nanosheets and increases the water flux in the application of desalination.

Interestingly, Guo et al. [22] fabricated a hierarchical graphene material for physisorption hydrogen storage at atmosphere

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pressure. They found the hierarchical graphene material is composed of micrometer-sized wave like sheet in experiments. These wavelike sheets connect with each other to form a well-defined porous structure. As for the simulation of the rippled graphene, there is merely one work [23] about the penetrating by an oxygen atom. From density functional theory calculations, the effect of ripple's curvature on the energy barrier of O permeation was identified. Recently, Dahanayaka et al. carried out pioneering molecular dynamics (MD) simulations to investigate capacitive deionization performance through nanochannels formed by two corrugated graphene layers [24]. Very interestingly, they considered closing, opening and concurrent types of entrance configurations and clarified these effects on water flow rate and ion adsorption.

Inspired by the above theoretical and experimental studies, we attempted to use bilayer graphene with ripples (BGR) as a RO membrane to explore its desalination performance with the help of MD simulations. In this work, we designed well-defined ripples with different curvatures and proposed a few methods to quantify the ripple effect on the water transport properties through BGR membranes. Through detailed analyses on water density map, water orientation and transmembrane velocity of water along the channels by ripples, we theoretically revealed the mechanism of water transmembrane process and suggested the potential of BGRs as next generation RO active layers.

2. Computational details

Fig. 1a–d shows four kinds of bilayer graphene membranes with different curvature ($\boldsymbol{\rho}$) of the ripple. The $\boldsymbol{\rho}$ values vary from 0.7 to 1.6 nm^{-1}, which were calculated from $\boldsymbol{\rho} = 1/\boldsymbol{r}$, where $\boldsymbol{r}$ is the radius of curvature measured by fitting the coordinate of BGR. The longest distance ($\boldsymbol{l}$) between graphene layers were in a range of 0.66–1.01 nm. According to the previous report about bilayer graphene [24,25], we set the closest distance of two graphene layers at 0.34 nm. Our choice of rippled graphene bilayer was based on previous study [26] and our test. Fig. 2a shows that water cannot permeate through the rippled channels during the simulation period when $\boldsymbol{\rho} = 0.5\ nm^{-1}$. While if we set $\boldsymbol{\rho} = 1.8\ nm^{-1}$, the salt rejection (95.9%) was found lower than the commercial high-flux RO membrane (97.5%) (see Fig. 3). For simplicity, the studied membranes were named according to $\boldsymbol{\rho}$ value of each BGR: BGR-1.6 ($\boldsymbol{l} = 1.01$ nm), BGR-1.1 ($\boldsymbol{l} = 0.85$ nm), BGR-0.9 ($\boldsymbol{l} = 0.71$ nm) and BGR-0.7 ($\boldsymbol{l} = 0.66$ nm). The unit cell of single-layer graphene with ripples was first optimized via $Dmol^3$ software, then bilayer graphene was constructed by two mirror symmetrical graphene monolayers. To simulate the desalination process, two flat graphene layers perpendicular to BGR with a dimension of 5 nm × 5 nm were placed on both ends of BGR, and the atoms of these two graphene layers overlapping the interlayer region of BGR were removed to offer water channels (Fig. 1e). The double-ended graphene layers were used to guide the water to pass through the BGR.

The whole simulation system was shown in Fig. 1f, the left chamber (feed) was filled with 0.6 mol/L NaCl solution (41 Na^+, 41 Cl^- ions and 3729 water molecules), whereas the right chamber (permeate) contained 3811 water molecules. The salt concentration of the feed chamber is similar to the seawater (35 g/dm^3). The dimension of the two chambers was about 5 × 5 × 5.5 nm^3. The BGR membrane was fixed in the middle of the simulation box ($\boldsymbol{z}$ from 7.0 to 17.0 nm) with a thickness of 10 nm. The MD simulations were performed in the NVT ensemble, at 300 K for 100 ns The pressures on the left and right pistons (using two graphene plates) were 601 bar and 1 bar, respectively, corresponding to a pressure gradient of 600 bar. The strategy extended by Zhu et al. [27] was employed in our systems to create a corresponding pressure gradient between two sides of the BGR membrane. The applied force on each C atom of the piston is given by $\Delta P = nf/A$, where f is a constant force along the $\boldsymbol{z}$ direction of the system, ΔP is the chosen pressure (feed: 601 bar, permeate: 1 bar), A is the area of the $\boldsymbol{x}$–$\boldsymbol{y}$ plane (5 × 5 nm^2), and n is the number of C atoms in each piston (880 C). The force exerted on each atoms of the left and right pistons are 1.701 × 10^{-12} N and 2.841 × 10^{-15} N, respectively. The two graphene plates were originally placed at $\boldsymbol{z} = 1.5$ nm and $\boldsymbol{z} = 22.5$ nm. Here a 1.5-nm distance on both sides was reserved to

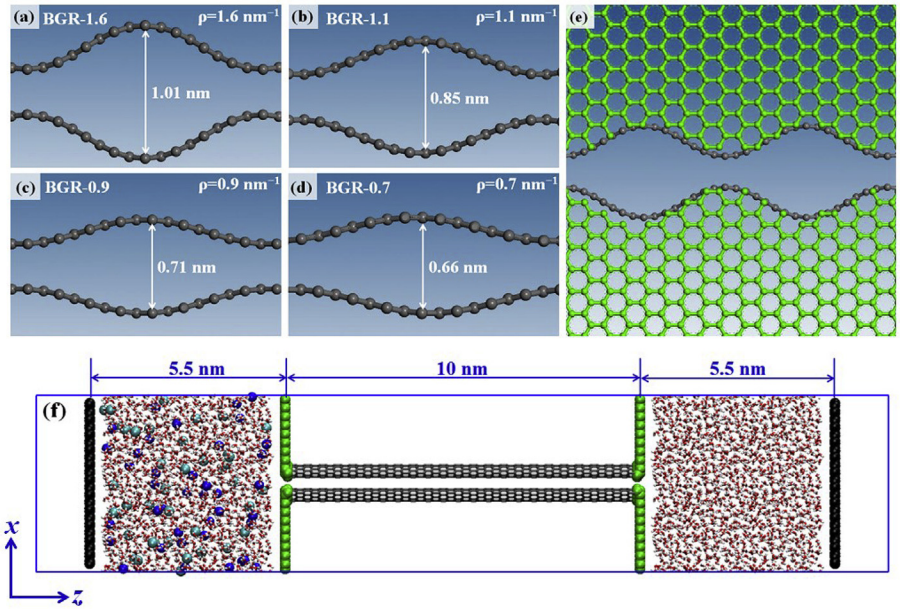

Fig. 1. Bilayer graphene models with different ripples: (a) BGR-1.6, (b) BGR-1.1, (c) BGR-0.9, (d) BGR-0.7. (e) Side view of BGR with double-ended layers (in green). (f) Simulation system of desalination via RO. The feed and permeate pistons (in black) were exerted by a pressure of 601 bar and 1 bar, respectively. C: grey, green and black, O: red, H: white, Na^+: blue, Cl^-: cyan. (A colour version of this figure can be viewed online.)