



Enhanced hydrophilicity and water-permeating of functionalized graphene-oxide nanopores: Molecular dynamics simulations

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ABSTRACT

In this work, molecular dynamics simulations were employed to study the permeation of ethanol-water mixtures through single-layer graphene oxide (GO) nanopores functionalized with COOH (carboxyl) and COO⁻ (ionized carboxyl) groups. GO-COOH nanopore shows regular behavior with competitive permeation between the two species in the mixture. However, GO-COO⁻ pore exhibits selective permeation of water, suggesting COO⁻ functionalized GO sheets could provide the initial barrier to block ethanol permeation and enhance dehydration separation in GO-based membranes. Our simulation presents the underlying mechanism of the selective water transport is not determined by the pore-size sieving, but has been ascribed as the strong molecular affinity between water and GO-COO⁻ surface. This interfacial interaction can induce the preferential interfacial adsorption and pore occupation for water, simultaneously impede the transport path of ethanol into the nanopore, and consequently give rise to the selective penetration of water in the mixture. The simulation results provide the direct theoretical evidence that ionization of carboxyl groups on GO sheets can be applied to improve the dehydration permeation of alcohol-water mixtures across GO-based separation membranes.

1. Introduction

Graphene-oxide (GO), as an oxidized derivative of graphene, has demonstrated great potential applications in extensive fields [1–5]. In particular, GO-based ultrathin membranes with stack structure provide new and versatile platforms for liquid-phase separations. In this aspect, GO layers could be easily fabricated or assembled into laminate structures with interlayer distance on nanometer scales [1,6,7]. This distinctive stacked infrastructure allows molecules to permeate through the interconnected network formed by GO nanosheets [8–10]. Currently, considerable attentions have been paid to focusing on the dehydration pervaporation process using GO-based membranes for purifying alcohols from aqueous solution [11–16]. Yeh et al. [11] prepared multilayered GO membranes, coated on nanofibrous composite, and high permeating flux could be obtained for ethanol dehydration using the GO barrier layers. Tang et al. [12] synthesized free-standing GO thin films by a pressurized ultrafiltration method and found that the GO films displayed preferential water transport and high selectivity. Recently, Ying et al. [13] also successfully prepared the composite membrane by combining MOF and GO, which exhibited excellent water permeation through pervaporation process for ethanol-water mixtures. In addition, the selective permeation of alcohols and water through GO

membranes has also been evaluated for a series of alcohol-water mixtures [14], and it was observed that water molecules permeate through GO membranes faster than alcohol molecules.

In the GO-based stacked membranes, the percolated network features rich microstructure [17,18] with inclusion of the interlayer capillary gallery, the defect pores in the basal plane of GOs, and the open space between edges of neighboring GO sheets. Molecular permeation through the interconnected network of GO membranes occurs through both the interlayer gallery and the graphene defect pores or interedge voids. Although the capillary nanochannels between GO sheets have been generally accepted as the critical route for molecule permeation [12], defects or pores on GO plane could provide transport shortcuts for molecular permeation across GO-based laminate membranes [19]. Recent experiment [20] investigated the effect of GO oxidation level on methanol permeability across GO laminate membrane. The result implicated that the pore defects on GO sheets could significantly shorten the molecular transport pathway, which is suspected to be responsible for the drastic increase in the methanol permeability across GO laminate membranes. Molecular simulations [21] also shows that fast water transport across GO-based membranes might be largely attributed to the porous microstructures, including wrinkles, holes, and interedge spaces.

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Besides, for GO-based membrane, due to its nonporous laminate microstructure and the transmembrane flow process, molecular transport crossing through single-layer GO sheet is generally the first step, which will provide the initial barrier for molecular permeation. Recent experimental research [22] also proposed that the outer layer of GO stacked flakes might be critical in determining the gas and water vapor permeation properties of the membranes. Furthermore, it should be emphasized that single-layer GO sheets also have great potential to appear as superior membrane materials due to the minimizing transport resistance and greatly increasing water permeability. Therefore, as the basic unit of GO laminate membranes, it is highly essential to investigate the mass transport passing through single-layer nanoporous GO membrane, which has important practical and academic significance for the design and operation of GO membranes.

In the recent work [23], direct computational evidence indicates that hydrophobic nanoporous graphene could act as a promising interfacial-affinity sieving membrane for selective ethanol permeation. Comparatively, GO sheets possess amphiphilic nature with hydrophobic carbon backbones atoms and hydrophilic oxygen-containing functional groups, as a result, the feed transport and surface adsorption for alcohol-water mixtures become complicated. At present, no molecular simulation studies have been reported for the permeation behavior of alcohol-water mixtures through porous GO sheets. Currently, various chemical modifications of GO sheets [24,25] have been fabricated as enhanced separation membranes in aqueous solution desalination [24] and alcohol dehydration pervaporation [25]. In these studies, a tuning strategy of hydrophilicity/hydrophobicity on GO planes has been applied by introducing surface functional groups to improve the separation performance of GO membranes. However, these studies have not explicitly revealed the impact of functional groups along the pores edges or boundary of GO sheets on the interfacial molecular permeation. The corresponding mechanism of the functional groups on permeation separation remains largely unknown.

In this work, non-equilibrium molecular dynamics (MD) simulations were conducted to investigate the molecular permeation of ethanol-water mixtures through functionalized GO nanopores. According to the well-known Lerf-Klinowski model [26], there exist considerable carboxyl groups on GO sheets during oxidization process, especially on the periphery of the basal plane, and meanwhile the content of carboxyl groups on GO nanosheets can be effectively enhanced through some feasible methods of carboxylation [24,27]. Moreover, the ionization degree of carboxyl groups is often affected by pH [28,29], and at high pH conditions COOH groups on GO sheets can be deprotonated to COO⁻ group. Due to the significantly different hydrophilic natures between COOH and COO⁻ groups, it is reasonably speculated that the two modified GO membranes could reveal different water permeation behavior. Based on these actual situations, carboxyl (COOH) and ionized carboxyl (COO⁻) functionalized GO nanopores were considered in our GO membrane models. The selective transport behavior and different surface affinity mechanisms were identified. We computationally demonstrate that porous GO sheet with specific pore chemistry has important function in enhancing dehydration permeation for the separation of ethanol-water mixtures.

2. Simulation method

The schematic representation of the simulation box used in our study was illustrated in Fig. 1 (top panel). The single-layer GO sheet (46.9 Å × 46.8 Å), with a pore in its center, was placed parallel to the xy plane in the center of simulation box (46.9 Å × 46.8 Å × 110 Å) surrounded by water-ethanol mixture. In this simulation, we considered two types of nanoporous GO structures functionalized with carboxyl and ionized carboxyl groups, which are denoted as GO-COOH and GO-COO⁻, respectively (bottom panel in Fig. 1). In those GO structures, hydroxyl and epoxy groups randomly distributed on the two both planes based on the Lerf-Klinowski model [26,30,31]. The pore on GO

sheet was constructed by drilling out 37 benzene ring units on GO sheet, and the COOH and COO⁻ groups were grafted uniformly to the pore rim. The introduction of functional groups yields the pore with effective diameter ~ 10 Å, which was calculated as the distance between the ends of two opposite functional groups (see Fig. 1). For both GO-COOH and GO-COO⁻ sheets, the oxidization concentration 20% was considered in our simulation, which was defined as the ratio between the number of oxygen-containing groups and that of carbon atoms on GO sheet. This choice of oxidization concentration was based on the actual oxidation degrees of GOs in different experimental measurements by XPS, which is in the range of 0.20–0.44 [32,33].

All the sp² carbon atoms in GO were frozen and treated as neutral Lennard-Jones (L-J) spheres using the parameters proposed by Cheng and Steele [34], while the functional groups were flexible and modeled using the all-atom optimized potential for liquid simulations (OPLS-AA) force field. This force field has been successfully applied in the system of GO in aqueous solutions and compared consistently to experimental results [21,29]. Ethanol and water molecules were represented by the OPLS-AA model [35] and the SPC/E model [36], respectively. For all pairwise L-J terms, the Lorentz-Berthelot mixing rules were applied. The cutoff distance for the L-J interactions was set to be 10 Å. The long-range electrostatic interactions were calculated using the particle-particle mesh (PPPM) method.

All molecular dynamics simulations were performed at 300 K with a time step of 1 fs using the LAMMPS package [37] and the canonical ensemble (NVT) was employed during the whole simulation. During the non-equilibrium MD simulation, periodic boundary condition was applied in the x and y direction, and a rigid graphene plate was placed at the right side of the simulation box as a piston, which was used to push the solution molecules toward the membrane at a prescribed external pressure. To generate the desired pressure difference (ΔP), the applied force (f) was exerted on each carbon atom of the piston based on the equation $f = \Delta P \cdot A / n$, where A is the area of the rigid graphene plate and n refers to the total number of carbon atoms of the plate. The hydrostatic pressure difference of 300 MPa was generated to simulate the non-equilibrium permeation of ethanol-water mixture for 12 ns. Note that it was quite common to apply a high pressure in non-equilibrium MD simulation to reduce thermal noise and enhance signal/noise ratio [38,39], so that reasonable simulation statistics can be obtained within nanosecond time scale.

3. Results and discussion

We first simulated the permeation of an equimolar ethanol-water mixture passing through GO-COOH and GO-COO⁻ nanopores. As shown in Fig. 2, the molecular penetrating numbers are given for each species as a function of simulation time. The rough linear relation displays relatively stable pressure-driven permeation transport. For the GO-COOH sheet, it can be observed that both water and ethanol molecules can competitively pass through the GO pore. The higher flux of water might be due to its smaller molecular size with higher mobility. However, it is interesting to notice that GO-COO⁻ pore only allows water penetration, whereas ethanol is completely rejected. This implies that the nanoporous GO sheets with COO⁻ groups have the selective water permeation for ethanol-water mixture by blocking ethanol permeation. The two GO nanopores exhibit almost identical pore sizes (see Fig. 1), which are obviously larger than the kinetics diameters of both ethanol (4.5 Å) and water (2.6 Å) molecules. This means the selective permeation of ethanol-water mixture through the GO-COO⁻ nanopore is not caused by the mechanism of pore-size sieving.

To reveal the separation mechanism, we simulated the interfacial adsorption behavior of ethanol-water mixture near the GO nanopores. Fig. 3a shows the density profiles along the z-direction for ethanol and water in the mixture near GO-COOH and GO-COO⁻ pores, which were obtained within an imaginary cylinder, with the axis perpendicular to the GO sheet and the cylinder diameter equal to the pore size.

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