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Investigation of water-oil separation via graphene oxide membranes: A molecular dynamics study

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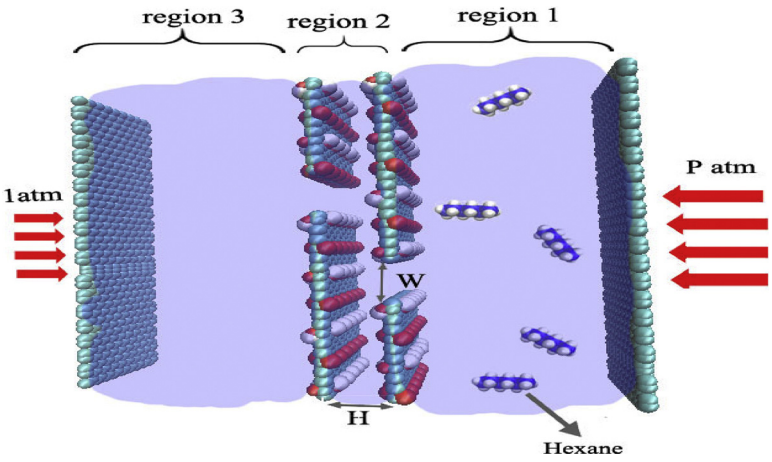
GRAPHICAL ABSTRACT

A schematic illustration of the simulation system box for water-oil separation via graphene oxide membranes.



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ABSTRACT

Recently, graphene oxide has been widely used for the extraction of hydrocarbon compounds. In the present work, the separation of water from a water-oil mixture by two-layer graphene oxide has been studied using molecular dynamics simulation. Several interlayer spacing of graphene oxide layers was considered, and for each gap in each layer of graphene oxide, several sizes were considered and it was determined the efficient interlayer distance as well as gap size which gives highest water-oil separation. The simulation results unveil that as the interlayer spacing and the size of the gap is reduced, the flux and permeability of the water molecules decrease, but the amount of water molecules separating from the oil increases. To study the number of layers' impact for higher separation efficiency, a system containing a graphene oxide layer was also studied and the importance of the number of graphene layers was highlighted. Also, for the analysis of graphene oxide functional groups' effect on separation, a system containing graphene layers was also investigated and the role of functional groups was revealed in hydrogen bond formation between graphene oxide and water molecules. By calculating PMF, the effect of functional groups on the repelling oil molecules from the graphene oxide's gaps was investigated.

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1. Introduction

The process of separating water-oil is one of the most significant operations in the oil industry, and researchers are trying to achieve this by using appropriate tools to increase the separation efficiency [1–6]. There are several methods for water-oil separation such as distillation, electrodialysis, solvent extraction, reverse osmosis [7–9] and carbon nanotubes [10–12]. Each of the methods mentioned has some disadvantages. Recently, membranes have been used extensively in water purification, including graphene [13–16]. Possibility to create precise pores in graphene [17,18] has added the importance of using graphene to water purification. It should be noted that the water flow rate is inversely proportional to the thickness of the membrane, and since the graphene membrane has a thickness in atomic size, it is therefore important to separation process. With the aid of molecular dynamics simulation, it has been shown that graphene membranes have a higher performance than polymer membranes [13–16]. Recent investigations revealed that the pore diameter is a significant factor in the water flux in the membrane, and the membranes with hydrophilic pores show more water flux than the membranes with hydrophobic pores. Hydrophobic pores also increase the probability of hydrogen bonding during passage and cause water molecules to pass through [7,19]. Recently, two parallel graphene with pores were used for water purification [20]. The results show that the crucial factor in water flux is the size of the pores, with larger pores higher amounts of flux would be achievable [20]. It is also revealed that the interlayer spacing affects water flux such that at intervals of about 5 Å, the flux of water is about zero and in larger distances the flux of water increases. Furthermore, the use of graphene oxide in the oil industry has received more attentions and used to extract the different materials and oil components from the water phase and also as a stabilizer for water and oil emulsion [21–28]. Also, Researchers have been able to separate water from a mixture of water and oil with high efficiency using nano sheets of graphene membrane [23]. Graphene oxide is known for its unique properties, including having hydrophilic functional groups such as hydroxyl, and hydrophobic carbon as an amphiphilic material [29], which can be used in water-oil separation. Previously, super-hydrophobic membranes were used to separate water and oil, but trapping of coarse-sized molecules of oil led to membrane contamination, and the membrane soon lost their effectiveness. A group of researchers in an experimental work used a metal mesh membrane coated with graphene oxide nanoparticles to separate water from oil. They found that stainless steel mesh coated with nano-graphene oxide particles was hydrophilic when it is exposed to the air but super-oleophobic when immersed in water environment. So that they have a superior efficiency in separating water from oil. The team proved that complete separation can be achieved for 50% volumetric mixture of water and oil (dichloro-ethane and hexane) [24]. Another research team provided an easy practical method of soaking or spraying paper with graphene oxide to separate water and oil. From their final product, water passes with difficulty, while non-polar oil and its related compounds easily pass through it. Therefore, water and oil separation can be achieved up to 99% efficiency [26]. In the present work, molecular dynamics simulation is used to examine the separation of water and oil using multilayer graphene oxide membrane. The results of the simulation can confirm experimental results and, given its atomic viewpoint, can provide grounds for new ideas in areas such as the separation using graphene oxide membrane [29–32]. The purpose of this study was to investigate the possibility of separating water from a mixture of oil and water using a multilayer graphene oxide membrane and investigating the separation mechanism.

2. Simulation details

The schematic of the simulation box is shown in Fig. 1. According to the figure, two-layer graphene oxide is used as a membrane located in the center of the simulation box (graphene oxide sheets arranged in red

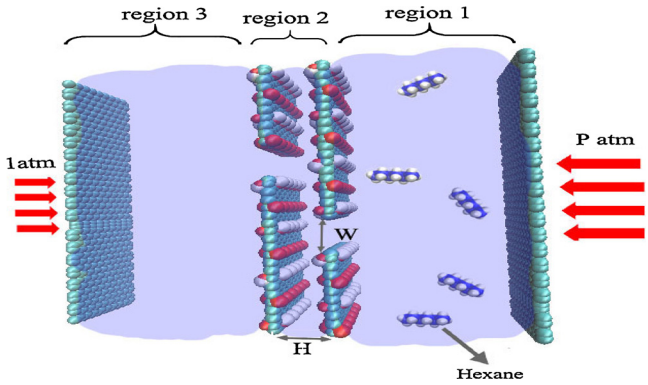

Fig. 1. A schematic illustration of the simulation system box.

in the center of the box) and in each layer of the membrane, spacing between the two sheets created gap. It should be noted that, depending on the size of the gap and the interlayer distance between the two graphene oxide sheets, four systems were investigated based on the schematic Fig. 1. For passing molecules of water through multilayer membrane of graphene oxide, gap space with a width of 9, 10.5, 12 and 13.5 Å (W) have been devised.It is also used for the distance between graphene oxide layers (H) and is referred to as a channel.On the right side of the membrane there is mixture of water and oil containing hexane molecules. Water molecules are transparent and hexane molecules appear as a blue line.Two graphene sheets are used as pistons, one of which is behind the water and oil emulsion. Graphene sheets have been shown in green. The simulation box is only periodic in x and y direction and z direction is considered non-periodic.Small arrows are to show the direction of applied atmospheric pressure and large arrows for the direction of applied pressure in filtration.The simulation of 500 ps without the motion of the pistons took place to equilibrate the system. In each simulated system, the same values are considered for width and channel height.Initially, four graphene oxide systems were investigated, all of which used two-layer graphene oxide as a membrane.These systems include i) a system with W = 9 and H = 9 Angstrom. ii) a system with W = 10.5 Å and H = 10.5 Å. iii) a system with W = 12.0 Å and H = 12.0 Å. iv) a system with W = 13.5 Å and H = 13.5 Å.

From now on, we will name the four systems briefly under the titles of systems 9, 10.5, 12, and 13.5. In addition to the four systems above, two other systems were also simulated. The system contains a single-layer graphene oxide sheet and a system containing a graphene sheet with a gap whose structures are exactly the same as the 12 Å system. The simulation was performed using the LAMMPS package [33] and the simulation input file was prepared using the VMD [34]. The whole simulation was carried out in fixed volume and constant temperature with the NVT statistical ensemble. To stabilize the temperature at 300 K, the Nose-Hoover thermostat was used with a decay ratio of 0.1 ps^{-1} [36,35]. The Verlet algorithm was used to solve newton equation of motion for the particles at each time step of 1 fs. The cutoff radius for the Columbic and Lennard-Jones energy was set to 12.0 and 10.0 Å. Each simulation was performed for 10 ns. In this simulation, the SPC / E model for water molecules and the OPLS force field was used to describe bond, angular, dihedral, van der Waals, and electrostatic interactions between hexane hydrocarbon molecules [38]. To describe the interaction between atoms in graphene oxide and graphene piston, the force field was used in references [39] and [40], respectively. Each layer of graphene oxide consists of 1680 carbon atoms, which have hydroxyl and epoxide groups in both side of the graphene surface, which was similar to that of the previous work of the same group [39]. PPPM method has been used to correct the potential of electrostatic interactions of Columbic and long-range Lenard-Jones. By the SHAKE algorithm [41], O—H bond length and H—O—H angle of water molecules are kept constant at 1.0 Å and 104.59, respectively. The initial configuration of the system comprised of water, oil and membranes