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Dynamic microstructure of graphene oxide membranes and the permeation flux

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ABSTRACT

Graphene oxide (GO) membranes have been reported to be a promising separation barrier that can retain small molecules and multi-valent salts because of the well-defined interlayer space between GO flakes. However, while some studies suggested fast liquid transport through the extremely tortuous transport path, contradictory observations (e.g. low permeation flux) have also been obtained. This paper revealed the dynamic microstructure of GO membranes, which affected the membrane performance significantly. We showed that all GO membranes prepared by varied methods and on different substrates presented a severe reduction in water permeability during filtration, due to the compaction of their original loose microstructure. The water flux could drop continuously from tens of LMH bar^{-1} to < 0.1 LMH bar^{-1} after more than ten hours. This result demonstrated that the structure of GO membranes prepared by current approaches was far from the ideal laminar structure. The high permeability of GO membranes observed could be contributed by the disordered membrane microstructure. Therefore, the transport mechanisms assuming perfect laminar structure in GO membranes, and the fast transport hypothesis may not fully describe the water transport in GO membranes. Interestingly, the loosely packed microstructure of GO membranes was also found reversible depending on the storage conditions.

1. Introduction

Graphene-based materials have been studied extensively for thin film and membrane applications because of their unique two-dimensional structure and one-atomic thickness [1–4]. With excellent chemical and mechanical properties, graphene-based thin films can be applied as separation membranes or protective barriers in environmental and chemical engineering applications [5–9]. Graphene oxide (GO) is a cost effective precursor for large scale production of graphene-based materials [10]. With a high area-to-thickness ratio and a large number of surface functional groups, GO flakes can be stacked on top of each other to form large area GO thin films/ membranes with thickness less than 100 nm, or GO papers with thickness more than 1 μm [11–14]. GO flakes are bonded with hydrogen bonding, forming a laminar structure with interlayer space of 6–13 Å, depending on the water content in the membrane [6,15,16]. With the well-defined interlayer space, GO membranes can separate molecules of different sizes through size exclusion.

GO membranes have been tested for aqueous and solvent nanofiltrations to retain small molecules with molecular weights of few hundreds Dalton [15,17–19]. It has also been reported that they have a very impressive pure water permeation flux, up to 71 LMH bar^{-1} ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), which was remarkably higher than most of the current nanofiltration membranes [20–22]. However, these filtration results were inconsistent among different researchers. For example, GO hollow fibre membranes were prepared by using a sacrificial layer, and they were impermeable to gases and exhibited extremely low permeability to water and acetone under pressure-driven nanofiltration conditions, with only 0.074 LMH bar^{-1} of pure water flux for a 150 nm thick membrane [23].

When looking into the transport passage in GO membranes, it is difficult to justify a high water permeation flux under the pressure-driven conditions. It is believed that the effective transport passage of water in GO membranes is through the tortuous spaces between the stacked GO flakes [6,22]. Considering the high aspect ratio of GO flakes (width-to-thickness ratio up to several thousands), the tortuosity of the transport path is very high in GO membranes; the effective transport path is very long even when the apparent thickness of the membrane is as little as tens of nanometres. Taking a 100 nm thick GO membrane with an average GO flake width of 5 μm as an example, a typical structural characteristics of a GO thin film, the effective transport

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passage can be as long as 200 μm. It can be estimated based on the classic Hagen-Poiseuille (H-P) model that water permeation through such a GO membrane would be extremely slow, $\sim 8 \times 10^{-6}$ LMH bar^{-1}, which is several orders of magnitude lower than the reported fluxes [20,21].

To explain the high permeation flux of water obtained, some hypotheses have been proposed to describe the transport mechanism in GO membranes. One famous hypothesis suggested that water can pass through GO membranes in a low-friction flow [6]. This hypothesis is based on the unique structure of GO flakes, where the oxygen-containing groups on the flakes tend to form segregated nano-sized domains. These oxidised domains would link to the same domains on the neighbouring GO flakes, acting as spacers in the interlayer space in GO membranes. The graphitic domains then form interconnected pathways that are wide enough to allow water molecules to pass through. The low-friction flow hypothesis suggests that the graphitic domains are hydrophobic and water can pass through at a much faster speed than what predicted by the classic H-P model, because of the low friction between the water and the pore wall. However, even with an advancement factor of 1000 times as predicted from some studies under a slip-flow condition, the calculated water flux is still far lower than what has been reported in many experimental studies. Another hypothesis suggesting that the defects on GO flakes could greatly shorten the effective passage for mass transport, thereby significantly enhancing the permeability [7]. However, this is still insufficient to justify the high fluxes observed in GO membranes. Assuming the defective pores in GO flakes can lead to a significant reduction in flake size to an equivalent flake size of 100 nm, even in a GO membrane with a thickness of 10 nm, the classic H-P model only gives a water flux of about 0.6 LMH bar^{-1}, which is still two orders of magnitude lower than fluxes reported by many studies.

When trying to understand the transport mechanism, the microstructure of GO membranes such as the stacking of GO flakes in the membranes is often overlooked. Though the characteristic interlayer space of GO membranes is important in determining the separation properties of the membranes [15], the microstructures of GO membranes such as the stacking or self-assembly of GO flakes and laminae, and the alignment of defects within membranes, have a significant influence on the performance of the membranes [13]. The microstructure of GO membranes was shown to be affected by the membrane preparation methods used [13,24]. However, it is still unclear to what extent the microstructure will affect the permeation flux, and this has prevented us from understanding the transport in GO laminar structures. Chong et al. showed that a pristine, well-laminated GO membrane could be turned into a more disordered structure by UV irradiation, and the water permeation was improved from 0.074 to 2.75 LMH bar^{-1} [23]. The finding demonstrates a critical role of the microstructure when understanding the transport mechanism in GO membranes.

In this paper, we systematically studied the change in permeation performance and microstructure of GO membranes during the pressure-driven filtration process. We demonstrate here that of all membrane preparation methods used, GO membranes underwent serious compaction and the microstructure turned from a loose structure into a tighter structure, and consequently reduced the water permeability significantly. The loose microstructure was restored when the membrane was dried and therefore the decline in permeability could be reproduced in repeated measurements. This result suggested that the reported high fluxes through GO membranes are not an intrinsic property of GO laminae, and the disorder induced short pathway in the membranes could have contributed to most of the measured high fluxes. Therefore, the explanation of high water permeation flux using the slip-flow fast transport hypothesis may need further verification.

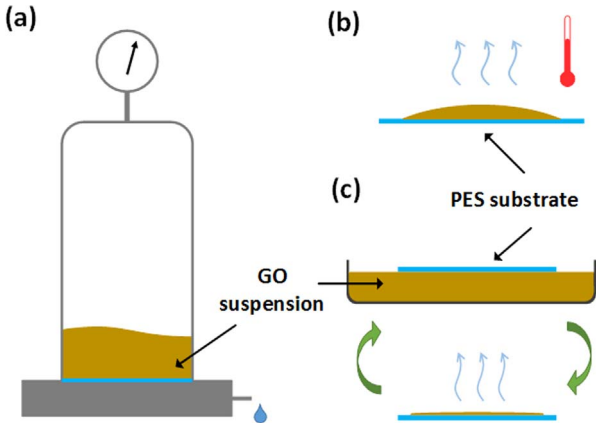

Fig. 1. Schematics of GO membrane syntheses on PES flat sheet substrates: (a) high and low pressure filtration; (b) high temperature evaporation; (c) dip coating.

2. Experiments

2.1. Preparation of GO membranes

GO suspension was synthesized using a modified Hummer's method, as described in our previous study [17,23]. The GO suspension was centrifuged to control the size of GO flakes, which was determined to be 5 – 10 μm from SEM. GO flat sheet membranes were prepared using 4 different methods: low pressure/ vacuum filtration, high pressure filtration, drop-casting/evaporation and dip-coating (Fig. 1a-c). Supor® polyethersulfone (PES) microfiltration membranes with a pore size of 0.2 μm were used as the substrates of the GO flat sheet membranes. A dead-end filtration cell (Sterlitech HP4750 Stirred Cell) was used in both low and high pressure filtration methods. GO membranes were prepared by filtering 20 ml of 0.1 g/L GO suspension at 1 bar (low pressure/vacuum filtration) and 10 bar (high pressure filtration). For drop casting/evaporation method, 1 ml of 4 g/L GO suspension was dropped on the surface of a PES substrate and the suspension was evaporated rapidly at 80 °C in an oven for 1 h (Fig. 1b). For dip-coating, one side of the PES substrate was wetted with 2 g/L GO suspension and was allowed to dry in air for 1 h (Fig. 1c). The wetting-drying process was repeated for 8 times.

GO hollow fibre membranes were prepared using dip-coating as it was a simple method to prepare GO membranes in a hollow fibre geometry. Yttrium stabilised zirconia (YSZ) hollow fibres with a diameter of 2 mm were used as the substrates. The YSZ hollow fibres were fabricated through a combined phase-inversion/sintering process [25]. The substrates had a smooth surface, in which the average surface pore size was about 80 nm. During GO coating, the hollow fibre, with one end sealed, was dipped into a GO solution with a concentration of 0.1 g/L. The hollow fibre was then dried in the air for 1 h before the next dip was taken place. The dip-coating process was repeated 6 times to get a sufficient coating thickness and surface coverage.

2.2. Water permeation and rejection tests

Pure water permeation and nanofiltration dye-rejection of GO membranes were evaluated in a dead-end mode. The GO flat sheet membranes were tested using the same dead end filtration cell used for membrane fabrication, while the hollow fibre membranes were tested by mounting into a sample cylinder filled with water as shown in ref. [17]. The filtration tests were conducted at 6 bar, unless otherwise stated. For pure water flux measurement, the amount of water permeated through the membrane was monitored by measuring the mass of water collected and the real time measurement data was recorded by a computer. Methyl red (M_w = 269.3 g/mol) dye solution was used to test the rejection rate of GO membranes. Methyl red is a non-charge