

Graphene-based Membranes for Fluid Separations

by

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Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and the relevant references are included in this thesis.

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Abstract

Graphene-based materials have attracted great interest to develop ultra-thin and high performance membranes due to their unique 2D structure, one-atomic thickness and high mechanical strength. While many studies have shown excellent performance of graphene-based membranes in fluid separations, scaling up of the membranes is still challenging. In addition, the transport mechanism in the membranes, especially in graphene oxide (GO) membranes is still not well understood.

In this study, graphene-based membranes were fabricated on hollow fibre substrates as a step forward to scaling up. High performance stainless steel-ceramic hollow fibres were developed while exploring suitable membrane substrates. GO and graphene membranes were fabricated on ceramic hollow fibres using two different approaches: solution-processing to produce GO membranes and chemical vapour deposition for graphene membranes. GO membranes were found unstable on hollow fibre substrates due to drying-related shrinkage. The stability problem was overcome by introducing a sacrificial layer during membrane synthesis. A post-treatment modification was carried out to improve the water permeation of GO membranes by creating extra microstructural defects in the membranes. Meanwhile, multi-layer graphene membranes were successfully synthesized on the nickel-plated ceramic hollow fibres. The graphene layer was exceptionally inert and could serve as an excellent protection layer against corrosive chemicals.

The water transport mechanisms in GO membranes in two different modes: pressure-driven filtration and pervaporation, were also studied. During filtration, GO membranes experienced a severe reduction in water permeation which was caused by the compaction of the loosely packed hierarchical microstructure. GO membranes showed a low steady state permeation flux because of the long transport path in the membranes. However, the water permeation was 1-2 orders of magnitude higher in pervaporation. The higher flux was due to the large capillary pressure in the interlayer space, which was induced by evaporation on the permeate side surface. In addition, an interface-related resistance was observed at the pore entrance of GO membranes when tested with water-ethanol mixture in pervaporation, which enabled the measurement of effective interfacial tension of miscible liquids using GO membranes.

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Chapter 1: Introduction

1.1 Background

Water and energy are basic components of life but also critical elements of sustainable economic development. However, nearly 1 billion people in developing countries lack access to basic drinking water service today. By 2025, half of the world's population, including some in the OECD countries, will be living in water-stressed areas [1]. The demands for clean water and energy increase across the globe due to the expanding world population, increasing living standard and climate change. New water and energy solutions with innovative and sustainable technologies are required to meet the growing demands.

Membrane technology can play an important role in producing clean water and to improve energy efficiency in industrial processes. A membrane is a semi-permeable barrier that can selectively separate one or more species or components under a driving force. Membrane processes are generally driven by pressure, concentration or electrical potential difference across the membranes. In principle, the processes involve no chemical additive and small amount of thermal input [2]. Membrane technology has been applied in areas such as water treatments, bioreactors, dialysis, pharmaceutical processes as well as food and beverage productions. It has emerged as a promising separation technology and is an important area of study in chemical and environmental engineering.

Membranes can be classified into two main categories: polymeric and inorganic membranes. Polymeric membranes are widely used in the industries and have a larger market share mainly due to their lower production cost. Commercially available polymeric membranes include cellulose acetate (CA), polyethersulfone (PES), polyamide (PA), poly(vinylidene fluoride) (PVDF), etc. Though polymeric membranes have extensive industrial applications, they generally have low resistance to high temperature and harsh chemical conditions. This has led to studies on inorganic membranes such as ceramic membranes. With good chemical, thermal and mechanical stabilities, inorganic membranes can extend the applications of membranes in more challenging processes, such as high temperature membrane reactors [3].

Membrane material research is one of the key aspects to enable synthetic membranes for large-scale, energy-efficient molecular separations. In the last few decades, microporous

materials such as zeolite, metal-organic frameworks (MOFs) and carbon nanotube have been studied to develop high performance membranes. With well-defined structures, these nanomaterials can be used to fabricate membranes with specific pore sizes and channels to separate molecules of specific sizes. For example, zeolitic imidazolate frameworks (ZIFs) are one of the most studied MOFs and ZIF-8 membranes showed good performance in gas separation, with $\text{H}_2/\text{C}_3\text{H}_8$ and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivities as high as 370 and 12, respectively [4].

Carbon membranes have also been studied for separation application due to their inert properties. Amorphous carbon molecular sieve (CMS) with a bimodal distribution of larger micropores ($\sim 7\text{-}20\text{ \AA}$) connected by smaller ultramicropores ($< 7\text{ \AA}$), can be produced by pyrolysis of polymeric precursors [5]. In a study by Richter et al., CMS membranes showed a very high $\text{H}_2/\text{C}_3\text{H}_8$ selectivity of 10 000 [6]. This type of membrane also showed potential in organic liquid reverse osmosis to separate very similar isomers, such as ortho- and para-xylene [7]. On the other hand, there is also a vast interest in exploring crystalline carbons for membrane applications due to their well-defined structure and high mechanical properties. One-dimensional carbon nanotubes (CNTs) exhibited enhanced mass transport in the hydrophobic nanochannels due to a slip-flow phenomenon [8]. However, fabricating well-aligned CNT membranes with a high pore density is still very challenging.

Graphene, a single layer of sp^2 -bonded carbon atoms packed in a hexagonal lattice, has emerged as an attractive material for membrane applications. This two-dimensional material has exceptional mechanical, thermal, electrical and optical properties [9-12]. Monolayer graphene with one-atomic thickness is considered to be an ideal membrane material since the permeability of a membrane is inversely proportional to its thickness. Currently, there are still some challenges in producing large area graphene for large scale membrane applications. While chemical vapour deposition has been considered as a promising synthesis approach, graphene membranes with minimum defects and well-defined pores are still difficult to fabricate. At the same time, the chemical derivative of graphene, graphene oxide (GO) has also been explored to develop graphene-based membranes as large volume of GO suspension can be synthesized easily using a modified Hummer's method. By assembling GO flakes layer-by-layer, thin film GO membranes with a uniform laminar structure can be produced. The applications of GO membranes have been studied extensively since the report on the fast water transport in GO membranes by Nair et al. [13]

This study focuses on the development of graphene-based membranes for scaling up applications. Both graphene and GO membranes are synthesized on ceramic hollow fibres which have a high surface area per unit volume at the module level. The applications of the graphene-based membranes in fluid separations, such as nanofiltration and pervaporation are investigated. The transport and separation mechanisms in the unique interlayer space in GO membranes are also studied.

1.2 Research objectives

The main objectives of the PhD project are to develop high performance graphene-based membranes on hollow fibre substrates and to understand the water transport phenomenon in the membranes. The work mainly focuses on GO membranes but some study is also carried out to develop pure graphene membranes on hollow fibre substrates. The study is divided to following sections:

(i) To develop hollow fibre substrates for GO membranes

High performance hollow fibre substrates are developed for graphene-based membrane synthesis. Stainless steel (SS) hollow fibres are fabricated using the phase inversion-sintering technique to improve the mechanical properties of inorganic hollow fibres. To further reduce the pore size, dual-layer ceramic-SS/SS composite hollow fibres are synthesized using a co-extrusion spinning technique. The properties of the hollow fibres such as surface morphology, mechanical strength and pore size distribution are studied. The mass transfer resistance of the hollow fibres is evaluated by measuring the water permeation flux. A GO layer is coated on the composite hollow fibre substrates to study the viability of the hollow fibres as the substrates for graphene-based membranes. Gas tightness/permeation tests are carried out to evaluate the integration of GO membranes with the composite hollow fibres.

(ii) To develop highly stable GO hollow fibre membranes

GO membranes are coated on yttria-stabilized zirconia (YSZ) hollow fibre substrates which have a smoother surface. Since the GO coating experiences an excess shrinkage during drying, a sacrificial-layer approach is used to synthesize GO hollow fibre membranes to improve the

membrane stability. The gas permeation/ tightness of the membranes is tested and a long term stability study is carried out. GO hollow fibres are also studied for nanofiltration application to reject organic dyes in liquid solutions. The performance of the membranes in liquid permeation is improved by post-treating them with UV radiation. The effects of UV-treatment on GO membranes are studied using techniques such as SEM, UV-vis spectroscopy, XRD and AFM.

(iii) To study the water transport mechanism in GO membranes in pressure-driven filtration

Since the results of the water permeation flux of GO membranes reported are inconsistent, a systematic study is carried out to understand the real water permeation of GO membranes in pressure-driven filtration. Flat sheet GO membranes are prepared on polyethersulfone (PES) substrates using methods such as vacuum filtration, high pressure filtration, dip-coating and evaporation, and GO hollow fibre membranes are prepared on YSZ hollow fibre substrates using dip-coating. The water permeation of GO membranes is tested for a long time to determine the steady state permeation flux. The membranes are also tested for several cycles to study the change in permeation flux and the dynamic microstructure of GO membranes. The fast transport hypothesis in GO membranes and the Hagen-Poiseuille equation are also discussed.

(iv) To study the water transport mechanism in GO membranes under pervaporation

GO membranes are prepared on flat sheet PES and polyacrylonitrile substrates, and tested for water permeation using two different modes: pressure-driven filtration and pervaporation. The effects of two different driving forces on water permeation flux are studied. To further understand the limiting steps in water permeation in pervaporation, the evaporation rate of free water surface is also measured and compared to the water permeation flux of GO membranes. GO membranes are also tested in pervaporation using a water-ethanol mixture. A pore flow model is proposed to explain the high water permeation flux of GO membranes in pervaporation. A miscible interfacial at the membrane pore entrance is also proposed and the hypothesis is tested with a pressure-driven set-up, which can also be applied to measure the effective interfacial tension of miscible liquids.

(v) To develop graphene hollow fibre membranes

Graphene membranes are developed on ceramic hollow fibres using a CVD approach. A nickel layer is first coated on the surface of hollow fibres using electroless plating, which will serve as catalyst layer for graphene growth. The graphene synthesized is characterized using SEM and Raman spectroscopy. After graphene synthesis, the nickel layer is leached by using nitric acid. Pore creation is also carried out by oxidizing the graphene layer with gold nanoparticles to aid the leaching of nickel. The study is mainly on the membrane synthesis method as challenges are still encountered in the final step when leaching the catalyst layer.

1.3 Thesis structure

The thesis consists of 8 chapters in total to study graphene-based membranes in fluid separations. **Chapter 1** introduces the topic of membrane processes and the use of nanomaterials in membrane applications. **Chapter 2** reviews the literature available on GO and graphene membranes. The review focuses on the syntheses and applications of the membranes, and the transport phenomenon in separation processes.

Chapters 3 to 6 present the experimental work carried out on GO membranes. **Chapter 3** describes the development of stainless steel/ceramic hollow fibre substrates for GO membrane synthesis. **Chapter 4** investigates the stability of GO hollow fibre membranes and describes the sacrificial layer approach used to fabricate defect free GO membranes. The chapter also demonstrates the post-treatment done to improve the membrane performance in nanofiltration. **Chapters 5 and 6** study the transport mechanism of water in GO membranes under two different modes: pressure driven filtration and pervaporation. The chapters describe the experimental work carried out and discuss the effects of membrane microstructure and driving forces on the permeation flux. **Chapter 6** also highlights how the liquid interface observed at the pore entrance of GO membranes can be used to measure the effective interfacial tension of miscible liquids (e.g. water and alcohol).

Chapter 7 describes the development of graphene membranes on hollow fibres, including challenges encountered in the fabrication process. Finally, **Chapter 8** concludes the thesis and provides some recommendations for future work.

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Chapter 2: Literature review

2.1 Graphene oxide membranes

Graphene oxide (GO) is a chemical derivative of graphene, with many oxygen-containing surface functional groups, such as -OH and -COOH . The precise chemical structure of GO has been a subject of considerable debate over the years and one of the most well-known structures is the Lerf-Klinowski model as shown in Figure 2.1 [1, 2]. Compared to graphene, GO is very hydrophilic due to the surface functional groups and can be dispersed in water to form a stable colloidal suspension. It can also be dispersed in a wide range of organic solvents such as NMP, DMSO, THF and ethylene glycol [3].

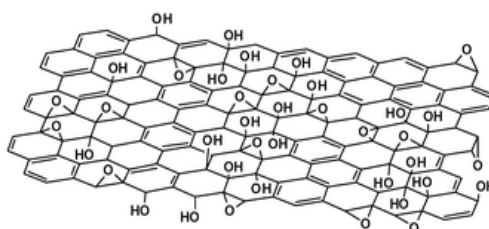


Figure 2.1: Structure of graphene oxide: Lerf-Klinowski model. Reproduced from Ref. [2] with permission from Elsevier.

As the synthesis process of GO is relatively simple and has a high yield, GO has been widely used as precursor for cost-effective large scale production of graphene-based materials [4]. With a high diameter-to-thickness aspect ratio, GO has emerged as an excellent material for thin-film and membrane applications. GO papers or thin film membranes can be synthesized by stacking the GO flakes on top of each other, and they have been studied in various separation applications such as gas separation, nanofiltration and pervaporation.

2.1.1 Preparation of GO suspensions

GO can be synthesized by chemical exfoliation using graphite as the starting material and an overview of the synthesis is shown in Figure 2.2 [5]. During the synthesis, graphite is first oxidized by using strong oxidizing agents to overcome the van der Waals forces between the

graphene or sp^2 carbon sheets. As a result of the oxidation, hydroxyl and epoxy groups are introduced to the carbon atoms in the graphene basal plane, while ketones and carboxylic acid groups decorate the edges of the flakes. The carbon interlayer space will be intercalated and the interlayer distance will increase from 3.35 Å in graphite to more than 6.25 Å in graphite oxide [6]. After that, single layer GO sheets will be exfoliated by sonication or prolonged stirring.

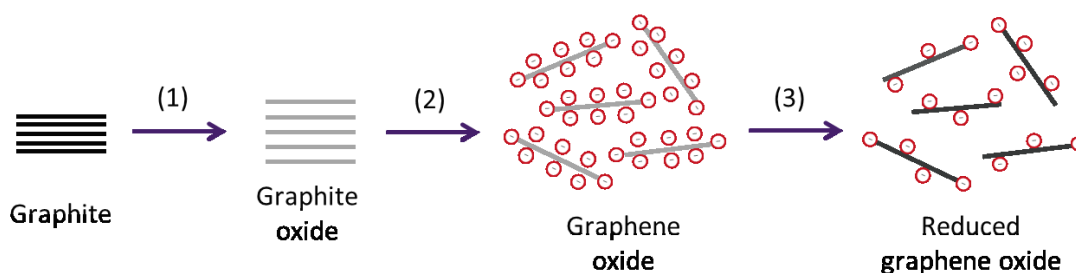


Figure 2.2: Synthesis of GO and rGO dispersions. (1) Oxidation of graphite to graphite oxide (2) Exfoliation of graphite oxide (3) Reduction of graphene oxide

One of the first reports on the oxidation of graphite was by Brodie in 1860 [7]. As graphite is very inert, strong oxidising agents such as potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3) were used to treat the graphite. Staudenmaier later improved the oxidation process by adding in multiple aliquots of $KClO_3$ over the period of reaction, and introducing concentrated sulphuric acid (H_2SO_4) to increase the acidity of the mixture [8]. However, the synthesis process was still very time consuming and was also hazardous due to the high mass ratio of $KClO_3$ to graphite.

In 1958, Hummer reported a synthesis method that has been widely used today. In the method, graphite was mixed with concentrated H_2SO_4 , sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) at 45°C [9]. Less vigorous chemicals were used in the synthesis and the process was claimed to have a higher degree of oxidation of graphite. Several modifications to the Hummer's method have been done, which include increasing the amount of $KMnO_4$, adding phosphoric acid, excluding $NaNO_3$, increasing the reaction time, etc. [10] The aims of these modifications were to increase the degree of oxidation of graphite and to improve the yield of GO, while avoiding the use of very reactive reagents. Though the oxidation step in GO synthesis have been much studied, the purification of GO after the

synthesis is still very time consuming as multiple cleaning steps are required. Nevertheless, the chemical exfoliation process is scalable as large amount of GO can be produced in the low-cost solution-phase process. The starting material graphite is also cheap and abundant.

GO can be converted to reduced graphene oxide (rGO) using methods such as chemical reduction, heat treatment and electrochemical reduction [11]. The number of surface functional groups of rGO are very much reduced, with an increase in the sp^2 area. However, the properties of rGO are still very different from graphene, for example the electrical conductivity is still much lower than graphene, due to the presence of a considerable amount of surface functional groups [12]. rGO can also form large area thin films, and has also be explored for membrane applications [13].

2.1.2 Fabrication of GO membranes

GO thin films or membranes can be synthesized by assembling the GO flakes in parallel [14, 15]. Figure 2.3 shows a free-standing GO membrane and the cross-section of the membrane. Bonded by hydrogen bonds, GO flakes form a uniform laminar structure with interlayer space of 6 to 13 Å, depending on the water content in the membrane [16-18]. The laminar structure of GO membranes can be observed easily from the XRD scan. The interlayer distance between GO flakes can be obtained from the (0 0 1) peak.

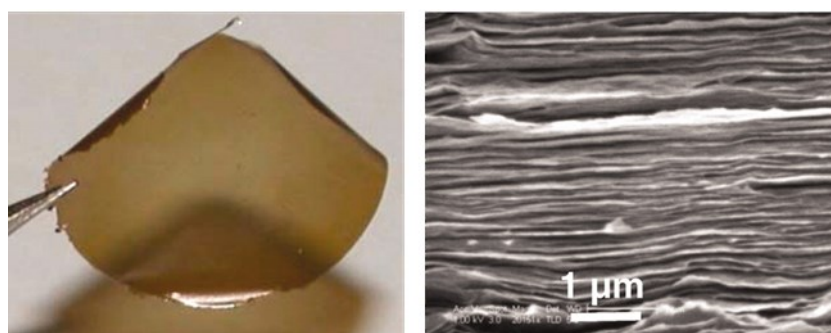


Figure 2.3: (a) Photo of a free-standing GO membrane. (b) SEM image of the cross-section of GO membranes. Reproduced from Ref. [17] with permission from American Association of Advancement of Science.

Graphene oxide (GO) membranes can be prepared using methods such as vacuum filtration, pressurized filtration, dip coating, spray and spin coating, drop casting and direct evaporation [19-22]. All these methods are commonly used in solution-processing of thin films, not only for membrane applications but also for electronics and optoelectronics [23]. The synthesis methods can be categorized into two main approaches: Filtration and evaporation. The self-assembly of GO flakes on the substrates is mainly driven by the hydrodynamic pressure in the filtration approach, but driven by the capillary force in the evaporation approach. The difference in driving forces may affect the fabrication time, the microstructure and the performance of GO membranes.

2.1.2.1 Filtration methods

Filtration is an easy way to prepare GO membranes as GO flakes are well dispersed in water. GO membranes can be obtained by filtering GO suspension through a porous membrane support. Different types of substrates, from polymeric to ceramic, and from flat sheets to hollow fibres, can be used in the filtration method [24-26]. The thickness of the membrane can be controlled by varying the concentration and volume of the GO suspension filtered. Ultrathin GO membranes were prepared on an anodic aluminium oxide (AAO) support by Li et al. using the vacuum filtration [19]. The thickness of the GO layer could reach as thin as 1.8 nm, with an area of about 4 cm². Thicker GO membranes with a thickness larger than 1 µm were also prepared using vacuum filtration [15].

High pressure can also be applied during GO membrane synthesis to reduce the filtration rate. The higher pressure during filtration was also found to affect the microstructure and the performance of GO membranes. In a study conducted by Tang et al., free-standing GO membranes were fabricated by both vacuum and pressurized (20 bar) filtrations [20]. GO membranes fabricated from vacuum filtration were found unstable as observed from the decrease in selectivity during pervaporation tests. The stability problem was claimed to be due to the poor packing of GO sheets in the vacuum filtration method. Tsou et al. studied GO membranes fabricated by three different methods: pressure assisted filtration, vacuum assisted filtration and evaporation (Figure 2.4) [21]. Among them, GO membranes fabricated by pressure-assisted filtration showed the best performance in butanol dehydration, mainly

due to the more ordered laminar structure. The surface roughness and hydrophilicity of GO membranes were also shown affected by the varied membrane microstructures as a result of the different fabrication methods.

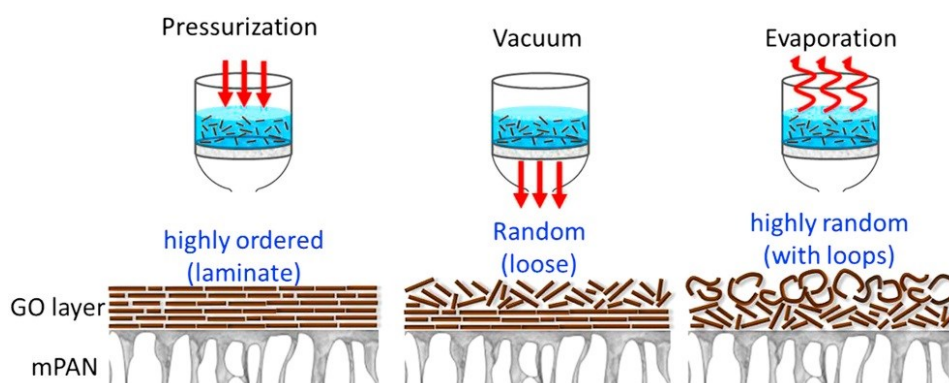


Figure 2.4: Schematic of GO membranes prepared using different methods: pressure-assisted, vacuum-assisted and evaporation-assisted self-assembly. Reproduced from Ref. [21] with permission from Elsevier.

2.1.2.2 Evaporation methods

High temperature evaporation was first reported by Chen et al. to prepare free standing GO membranes where fast vaporization at the GO-air interface drove the self-assembly of GO flakes to form a GO film [14]. Evaporation at room temperature has also been used to fabricate GO membranes. However, the fabrication process is much slower at room temperature due to the low evaporation rate, which can subsequently affect the microstructure of the membrane. Tsou et al. showed in their study that the slow evaporation rate created a highly random arrangement of GO flakes during the membrane formation, which affected the molecular sieve properties of the membrane [21]. Some fabrication processes that involve evaporation are drop casting, dip coating and spaying. All these methods use different approaches to disperse GO solution on the substrates, which could affect the coating thickness of GO membranes and also the self-assembly of GO flakes. Spin-coating was sometimes combined with these methods to obtain a more uniform and thinner coating, and also to increase the evaporation rate. All these methods can be easily applied to flat sheet membranes. However, only dip coating is more feasible for hollow fibre substrates.

Spray and spin coating was used by Nair et al. to fabricate GO membranes on a 25- μm -thick copper foil [17]. The disks were heated to $\sim 50^\circ\text{C}$ during coating to increase the deposition rate. GO membranes with thickness 0.1 to 10 μm were fabricated in the study. The submicrometer-thick membranes were impermeable to all gases. Besides that, both dip coating and drop casting were used by Kim et al. to synthesize GO membranes on a $10\times 10\text{ cm}^2$ polyethersulfone (PES) substrate [22]. As illustrated in Figure 2.5, the PES substrate was immersed in the GO solution, similar to the dip coating, before spin coating in method one. While in method two, the GO solution was dropped on the PES substrate before spin coating. GO membranes with a thickness of 3 to 7 nm were obtained in both methods.

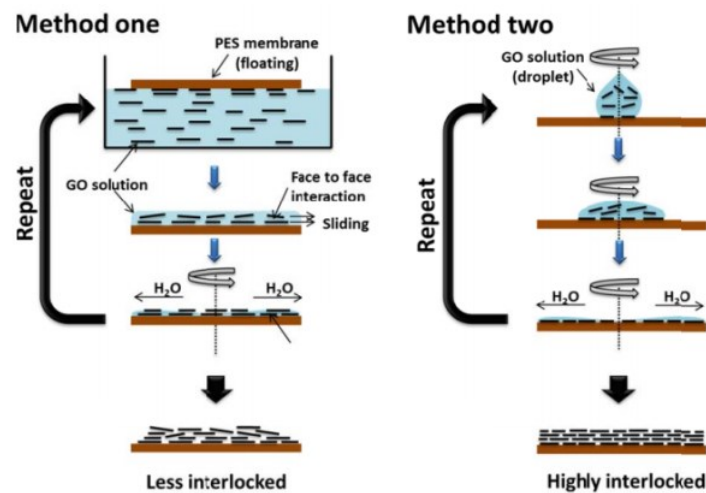


Figure 2.5: GO membranes prepared from Method 1: dip-spin casting and Method 2: drop-spin casting, showing different degrees of order. Reproduced from Ref. [22] with permission from American Association of Advancement of Science.

For method one, the immersion capillary force was higher due to the face to face interaction of GO solution with the substrate surface, causing less interlocked arrangement of GO sheets after the spin coating compared to method two. Knudsen transport of gases was observed in the GO membrane prepared using method one as gas molecules could permeate through the defects between the non-interlocked GO sheets. For method two, the membrane synthesized had a highly interlocked arrangement and the membrane showed a good molecular sieve property with a high CO_2 selectivity.

Akbari et al. recently showed that highly concentrated GO suspension could be dispersed on flat sheets substrate using a shear-aligned method [27]. Highly concentrated GO suspension

was determined by dewatering with hydrogel beads. The concentration could be as high as 60 g/L. With the increase in viscosity as the result of the higher concentration, GO suspension was dispersed on large area of Nylon substrates using a doctor blade. GO membranes prepared using this approach showed well-arranged microstructure, which improved the membranes performance in nanofiltration.

2.1.3 Applications of GO membranes

2.1.3.1 Gas separation

GO membranes have been studied for gas permeation as the well-defined interlayer space could potentially serve as molecular sieves for gas separation. However, Nair et al. showed in an early study that GO membranes with a sub-micrometre thickness were impermeable to all gases including helium [17]. The impermeability of GO membranes was due to the small interlayer distance in the laminar structure especially at low humidity. As shown in their study, helium started to permeate through GO membranes when the interlayer distance of the membranes expanded under a high humidity. However, the permeation was still very slow due to the slow diffusion of He in the interlayer space filled with water molecules.

Although thick GO membranes were found impermeable, thin GO membranes with thicknesses less than 20 nm showed a high gas permselectivity at considerable fluxes. In a study conducted by Li et al., ultrathin GO membranes with a thickness of only 1.8 nm were prepared on an AAO support by vacuum filtration [19]. The membranes showed a fairly high H_2 permeance of about $1.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The selectivities of H_2/CO_2 and H_2/N_2 were 3400 and 900, respectively, which were significantly higher than most of the microporous membranes. The major transport path of gas molecules was speculated to be through the selective structural defects in GO flakes as the permeability of the membranes did not change much after thermal annealing which reduced the interlayer distance.

Chi et al. also successfully prepared ultrathin GO membranes with a thickness of 20 nm using both vacuum filtration and spin coating methods [25]. GO membranes prepared by spin coating showed a lower H_2 permeability but a higher H_2/CO_2 selectivity compared to membranes prepared by vacuum filtration. The higher H_2/CO_2 selectivity of the membranes

prepared by spin coating, 240 compared to 51, was attributed to the more uniformly aligned GO flakes, which minimized the formation of wrinkles and led to a smoother membrane. However, the H₂/CO₂ selectivity was still much lower than what reported by Li et al., though the H₂ permeance was three times higher.

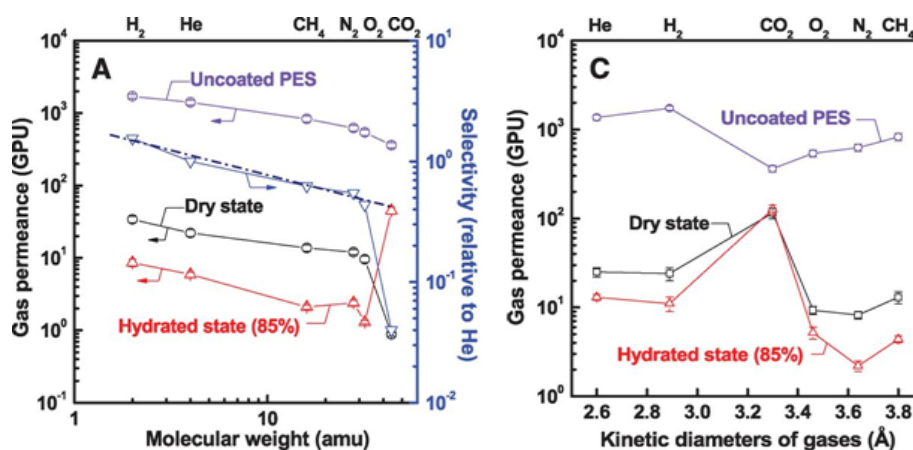


Figure 2.6: Gas permeances of GO membranes under dry and humidified conditions prepared by (a) dip-spin casting and (dashed line represent the ideal Knudsen selectivity) and (b) drop-spin casting. Reproduced from Ref. [22] with permission from American Association of Advancement of Science.

In another study conducted by Kim *et al.*, Knudsen selectivity was observed for GO membranes (thickness <10 nm) prepared by dip-spin casting, as shown in Figure 2.6 (a) [22]. When improving the GO packing, well-interlocked dry GO membranes prepared by drop-spin casting showed a higher CO₂/N₂ selectivity of 20, but with a lower permeation (Figure 2.6 (b)). When the membranes were tested in a hydrated state, the permeation of all gasses decreased except for CO₂ which still retained a similar permeance. This observation showed that GO membranes were promising for gas separation applications where water vapour may be present in the gas mixture, such as post-combustion CO₂ capture, as many membranes would have a deteriorated performance in the presence of water.

GO membranes have also been successfully fabricated on hollow fibre substrates. Huang *et al.* prepared GO membranes on α -Al₂O₃ hollow fibre substrates using the vacuum filtration method [28]. The membrane with a thickness >200 nm showed a high H₂ permeance of 1.0×10^{-7} mol m⁻² s⁻¹ Pa⁻¹, but a H₂/CO₂ selectivity of only 15. The selectivity was much lower than

was reported for the flat sheet membranes discussed earlier. In another study by Zhu et al., GO membranes with a thickness of about 230 nm were prepared on yttria-stabilized zirconia hollow fibres using the same vacuum filtration method [29]. The GO hollow fibres showed a lower H₂ permeance, $4.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ but with a higher H₂/N₂ selectivity, 76.

Gas molecules could transport through GO membranes via several paths such as (1) defect in GO flakes, (2) interlayer space between flakes and (3) microstructural defects in the membranes as a results of imperfect stacking or formation of corrugations, wrinkles and ripples. The microstructure of GO membranes and the synthesis methods affect the performance of GO membranes significantly. Though GO membranes demonstrated remarkable performance in gas separation, the results were inconsistent among the studies. For example, most of the studies showed a low CO₂ permeance which could be due to the strong interaction between CO₂ and the oxygen-containing functional groups in the membranes [30]. However, Kim et al. showed an opposite result in their study with a higher CO₂ permeance compared to other gases. Besides that, due to the thin GO coating (<20 nm), GO membranes were also difficult to be reproduced and a thicker coating was required on hollow fibre substrates in order to form a continuous GO layer [28]. More studies are required to understand the formation of GO membranes and its effects on the microstructure, performance and transport mechanism in GO membranes.

2.1.3.2 Water and solvent filtrations

Nair et al. showed that GO membranes allowed unimpeded permeation of water vapour even though they are impermeable to all other gases [17]. The observations of fast transport of water vapour through GO membranes was attributed to a low-friction flow of a monolayer of water through the two-dimensional capillaries formed by closely spaced GO sheets. Since then, GO membranes have been studied extensively for applications involving water permeation such as pressure-driven filtration, pervaporation and forward osmosis. The interlayer space between GO flakes in GO membranes varies from 6 to 13 Å, increasing with the increase in water content in the membranes [17, 18]. The swelled interlayer space in GO membranes could accommodate 1 to 3 layers of water molecules, allowing water to permeate through.

GO membranes have shown tremendous performance in water filtration application. Table 2.1 lists the performance of GO membranes reported so far. One of the highest water permeation fluxes reported was $71 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMH bar^{-1}) [27, 31], which was much higher than many nanofiltration membranes. With their well-defined interlayer space, GO membranes could also separate molecules by size exclusion. GO membranes have shown good performance in rejecting organic dyes, such as methyl orange and brilliant blue, and the molecular cut-off of the membranes could reach as low as 250 Da.

Table 2.1: GO membranes in pressure driven water filtration

Membranes	Fabrication method	Membrane thickness (nm)	Pure water flux (LMH bar^{-1})	Rejection test	Rejection rate (%)	Refs.
GO/PC	Vacuum filtration	1000	71	Evan blue	85	[31]
GO/Nylon	Shear aligned casting	150	71	Methyl red	90	[27]
GO/PC	Pressure-assisted filtration	70	~5	Na_2SO_4	~72	[32]
rGO/PVDF	Vacuum filtration	22-53	3.3-21.8	Methylene blue	>99	[13]
Corrugated rGO/PC	Vacuum filtration	-	40	Direct yellow	67	[33]
GO/YSZ hollow fibre	Vacuum filtration	1000	1.06	Methyl orange	>99	[34]

Note: PC: polycarbonate, PVDF: polyvinylidene difluoride, YSZ: yttria-stabilized zirconia

GO membranes are stable in various organic solvents such as acetone, methanol, toluene and n-hexane, making them suitable for organic solvent nanofiltration [35]. Similar to when immersing in water, the interlayer space of GO membrane enlarged when immersed in organic solvents. The methanol and acetone permeation fluxes of GO membranes could reach 3.97 and 6.35 LMH bar^{-1} , respectively, while retaining methyl orange with molecular weight of 327.3 Da [8]. The permeation fluxes were higher than most commercial membranes with a molecular weight cut-off lower than 300 Da [27]. rGO membranes fabricated using vacuum filtration by Huang et al. were also tested in organic nanofiltration [35]. Different from the

rGO membranes fabricated by Han et al. [13], the rGO membrane did not undergo a drying process in order to preserve the loose microstructure of the membranes. The loosely packed rGO membranes showed an exceptionally high methanol flux up to 80 LMH bar⁻¹, though the molecular weight cut-off was higher. The membranes did not have any rejections to basic Fuchsin ($M_w = 323.8$ Da) and methylene blue ($M_w = 319.9$ Da), but completely rejected Evan blue ($M_w = 960.8$ Da).

Water transport mechanism

It was proposed that water molecules pass through GO membranes via the narrow interlayer space between the GO flakes, layer by layer during filtration, as shown in Figure 2.7.

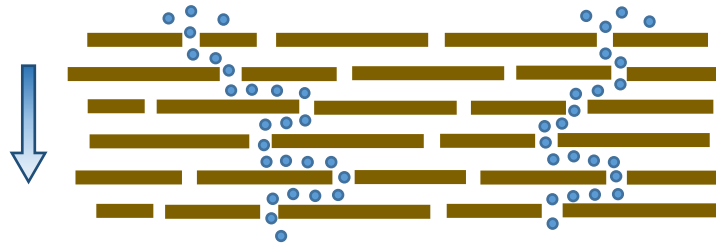


Figure 2.7: Water molecules transport through the interlayer channels in GO membranes

The classic Hagen-Poiseuille (H-P) equation for the water transport in GO membranes can be expressed as [17]:

$$Q_{HP} = \frac{d^4}{12\mu L^2} \frac{\Delta p}{l} \quad (2.1)$$

where Q_{HP} is the permeation flux (m³ s⁻²), d is the pore size or the interlayer distance (m), μ is the viscosity of water (Pa s), L is the average lateral length of GO flakes (m), Δp is the pressure gradient (Pa) and l is the membrane thickness (m). However, the water permeation predicted using the H-P equation was much lower than the water vapour permeation rate observed in the experiment conducted by Nair et al. It was also lower than water permeation flux observed in other studies shown in Table 2.1. As shown in Figure 2.7, the high aspect ratio of GO flakes may create a very high tortuosity for the transport route. The transport path could be longer than 1 mm in a submicron GO membrane, which would result in a very low water permeation rate.

Two possible reasons have been proposed by Nair et al. to explain the high water permeation in GO membranes [17]. Firstly, the driving force Δp in the long interlayer channels in GO membranes was proposed to be much higher, in the order of 10^3 bar, due to the capillary pressure in the laminar structure. However, the explanation was based on their water vapour permeation experiments where water evaporated on the permeate side of the membrane. Secondly, it was proposed that the ultrafast water transport was due to a low friction between the water and the wall in the hydrophobic pristine graphene channels. This explanation was based on the unique structure on GO flakes, where the oxygen-containing groups on the flakes tend to form segregated nano-sized domains (Figure 2.8). 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 unoxidised graphitic domains then form interconnected pathways that are wide enough to allow water molecules to pass through. As the graphitic domains are hydrophobic, water can pass through at a much faster speed than what predicted by the classic H-P model due to the low friction between water and the graphitic wall.

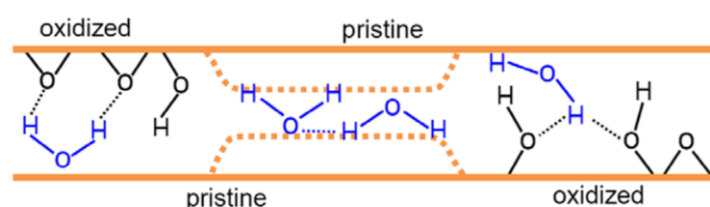


Figure 2.8: Model of graphene capillaries within GO films proposed by Nair et al. Reproduced from Ref. [17] with permission from American Association of Advancement of Science.

Deuterium oxide (D_2O) was used as a tracer to study the ultrafast water diffusion in GO membranes, where the diffusion coefficients of water through the nanocapillaries in GO membranes were found 4-5 orders of magnitude larger than through the sub-micrometre cellulose pores in a microfilter [36]. Besides, confined water between two graphene sheets was observed by high-resolution electron microscopy imaging, which further supported the nanocapillary ultrafast transport of water [37]. However, a study conducted by Wei et al. found that the side-pinning effects from the hydrophilic areas of GO membranes may slow

down the transport of water molecules in the nanochannels due to the strong hydrogen bonded interaction [38]. In addition, Montessori et al. showed in their simulation study that the coexistence of bulk viscous dissipation and spatially extended molecular friction could suppress the fast water transport in the graphitic nanochannels [39].

Porous microstructure attributed to the imperfect stacking or the defects in GO membranes may also contribute to the high water flux of GO membranes. Microstructural defects could serve as shortcuts for water to permeate through the membranes with a shorter transport path. The importance of microstructural defects or shortcuts in GO membranes were demonstrated by Huang et al. [40] In their study, copper nanostrands were added in GO suspension to create extra transport channels in GO membranes, which have subsequently enhanced the water permeability of the membranes.

Separation mechanism of GO membranes

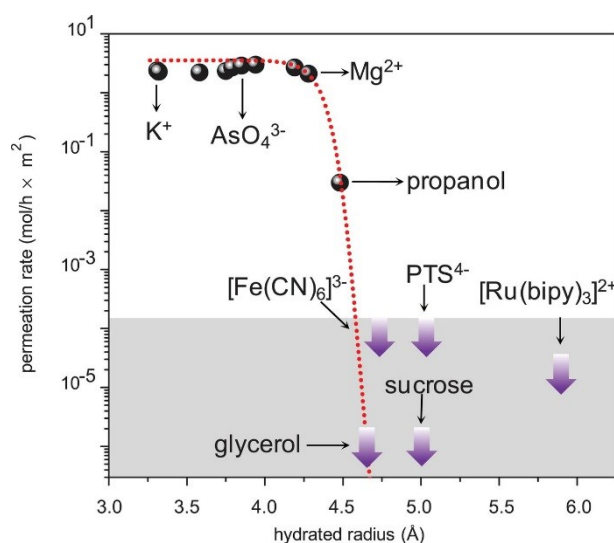


Figure 2.9: Permeation rates of 1 M feed solution through 5-μm-thick GO membranes as a function of hydrated radius. Reproduced from Ref. [16] with permission from American Association of Advancement of Science.

GO membranes showed excellent molecular sieving properties due to the well-defined interlayer space in the laminar structure. The diffusion of molecules in water across GO membranes was studied by Joshi et al. [16] GO membranes showed a clear cut-off at hydrated radius ~ 4.5 Å, as shown in Figure 2.9, where molecules with larger diameter were sieved out.

Even though GO membranes demonstrated promising results in nanofiltration rejecting organic dyes and large molecules, they showed limitation in reverse osmosis for salt rejection as Na^+ , K^+ and Mg^{2+} were found to diffuse through GO membranes [15, 38]. The limitation of GO membranes in desalination is mainly due to the large interlayer space compared to the size of the ions. Mi proposed that the interlayer distance of GO membranes may need to be reduced to 7 Å in order to reject Na^+ [42], which could be done by reducing GO to rGO. However, the more hydrophobic rGO may not be favourable for water filtration. Previous studies also found that water could not fill the capillary channels between GO flakes and permeate through the membrane if the interlayer distance was smaller than 6 Å [43].

The effect of interlayer space on salt rejection was studied recently by Abraham et al. [44] GO membranes with varied interlayer spaces, ranging from 6.4 to 9.8 Å were prepared by placing the membranes in an environment with different humidity. The membranes were then encapsulated using epoxy to retain the interlayer space by mechanically restricting the swelling of the membranes when immersing in water. With an interlayer distance of 6.4 Å, no ion permeation was detected when tested under a concentration driven diffusion process. The small space was also insufficient for water permeation as the available space for permeation was only approximately 3 Å after deducting the carbon layer. In their study, graphene was also added to GO suspension to synthesize GO-graphene membranes. The composite membranes had a smaller interlayer distance in water (10.2 Å) compared to GO membranes (14 Å), due to the increase in hydrophobicity. The membranes showed good salt rejection (about 97 %), with a water permeation of about $0.5 \text{ L m}^{-2} \text{ h}^{-1}$ when tested in a forward osmosis setup.

Besides considering the interlayer distance, the interactions of the solutes with the surface functional groups and the cation- π interactions are also important for solute separation as charge repulsion could assist in rejecting charged solutes [41, 45]. Due to the surface functional groups, such as $-\text{COOH}$ and $-\text{HO}$, the surface of GO membranes was negatively charged over a wide pH range. The negatively charged surface has enabled GO membranes to reject negatively charged ions via Donnan exclusion. The membrane surface charge could also be altered to positively charged through surface functionalization to reject heavy metals such as Pb^{2+} , Ni^{2+} and Cd^{2+} [32]. Besides the interaction with the functional groups, the

interaction with the sp^2 cluster of GO through cation– π interactions could significantly reduce the permeation of alkali and alkaline earth cations [45].

2.2.3.3 Pervaporation

Pervaporation is a promising alternative to distillation of azeotropic mixtures such as water and ethanol. It can also be applied to separate thermally sensitive compounds and organic-organic mixtures. Compared to many conventional separation technologies, pervaporation has a lower energy consumption and a smaller footprint [46]. During pervaporation, a liquid mixture is fed to the membrane, with either vacuum applied or a sweep gas stream on the permeate side to generate a chemical potential difference for the separation to occur [47]. Polymeric membranes such as polydimethylsiloxane (PDMS) and polyvinyl alcohol (PVA) have been widely studied for pervaporation. Molecular sieves such as zeolite and metal organic frameworks have also been explored for dehydration of organic solvents [48, 49].

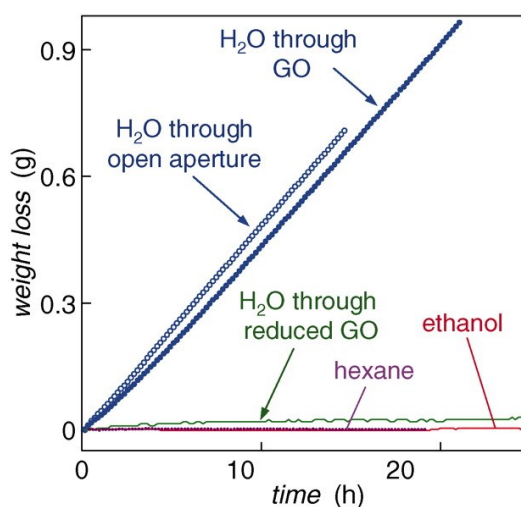


Figure 2.10: Weight loss of a container sealed with a GO membrane. The rate of weight loss reflected the water vapour permeation rate through the membrane. Water evaporated from the container as fast as through an open aperture. Reproduced from Ref. [17] with permission from American Association of Advancement of Science.

In the evaporation experiment conducted by Nair et al., water vapour permeated through GO membranes unimpededly and the permeation rate was almost same as the evaporation rate of water from a free surface, as observed from the weight loss of a container sealed with a

GO membrane (Figure 2.10). However, other organic solvents such as ethanol and hexane were found impermeable through the membrane. The fast water vapour permeation and the high selectivity over other solvents have enabled GO membranes to be applied in pervaporation to separate water from organic solvents.

Table 2.2 lists the performance of GO membranes in pervaporation reported so far. Li et al. conducted the pervaporation tests with pure water and the water flux could reach 1.64 and 5.88 kg m⁻² h⁻¹ at 30 and 70 °C, respectively [50]. The water permeation rate was higher than the glove box experiment conducted by Nair et al. where the water evaporation rate was only approximately 0.48 kg m⁻² h⁻¹ [17]. GO membranes have been tested for dehydration of ethanol, propanol, butanol and dimethyl-carbonate (DMC). The membranes showed a good performance in dehydration of ethanol mixture with a separation factor higher than 100. The performance of the membranes further improved when the molecular weight of the solvents was higher, showing the molecular sieve properties of GO membranes. Similar to what was observed in gas separation, the microstructure of GO membranes could also affect their performance in pervaporation. In the study by Tsou et al., GO membranes prepared by vacuum filtration and evaporation showed a poor butanol dehydration performance, with a separation factor <100 due to their loosely packed microstructure [21].

Though the well-defined interlayer space has granted GO membranes the molecular sieving property, the separation of water in pervaporation was not completely a size exclusion process. As shown earlier in an experiment conducted by Joshi et al., molecules smaller than propanol could permeate through the interlayer distance due to their small diameter [16]. In fact, the water separation mechanism in the pervaporation process predominantly relied on the preferential water sorption. Huang et al. measured the water adsorption ability of GO membranes using a quartz crystal microbalance [26]. GO membranes showed a much higher water adsorption capacity than DMC, explaining the good water separation from DMC in their experiments. The water permeation in GO membranes during the pervaporation process was proposed following a preferential sorption–diffusivity mechanism. However, limited study was carried out to understand the water diffusivity in GO membranes while fast transport hypothesis proposed by Nair et al. has been widely adopted [17].

Table 2.2: GO membranes performance in pervaporation

Membranes	Fabrication method	Thickness	Feed Condition	Total flux (kg m ⁻² h ⁻¹)	Separation factor	Refs.
Free-standing GO	Pressurized ultrafiltration	2 µm	24 °C, 15 wt% H ₂ O/ethanol	~0.3	~170	[20]
GO/Al ₂ O ₃ tube	Pressure-driven filtration	190 nm	30 °C, H ₂ O	1.64	-	[50]
			70 °C, H ₂ O	5.88	-	
		250 nm	28 °C, 10 wt% H ₂ O/ethanol	0.30	410	
			70 °C, 10 wt% H ₂ O/ethanol	1.30	250	
		220 nm	28 °C, 10 wt% H ₂ O/ <i>n</i> -propanol	0.43	1740	
			70 °C, 10 wt% H ₂ O/ <i>n</i> -propanol	1.70	1290	
			28 °C, 10 wt% H ₂ O/isopropanol	0.51	4020	
			70 °C, 10 wt% H ₂ O/isopropanol	2.10	2940	
GO/mPAN	Pressure-driven filtration	231nm	30 °C, 30 wt% H ₂ O/isopropanol	2.05	2331	[51]
			70 °C, 30 wt% H ₂ O/isopropanol	4.14	1164	
GO/mPAN	Pressure-driven filtration	231 nm	30 °C, 10 wt% H ₂ O/ <i>n</i> -butanol	2.54	2241	[21]
			70 °C, 10 wt% H ₂ O/ <i>n</i> -butanol	4.34	1791	
	Vacuum filtration	384 nm	30 °C, 10 wt% H ₂ O/ <i>n</i> -butanol	2.39	74	
	Evaporation	447 nm	30 °C, 10 wt% H ₂ O/ <i>n</i> -butanol	0.93	17	
GO/CHF	Vacuum filtration	1.5 µm	25 °C, 2.6 wt% H ₂ O/DMC	2.05	2331	[26]
			40 °C, 2.6 wt% H ₂ O/DMC	4.1	1164	

Note: mPAN: modified polyacrylonitrile, CHF: ceramic hollow fibres, DMC: dimethyl carbonate. Separation factor = $\frac{y/(1-y)}{x/(1-x)}$, where y and x are the mass fractions of the permeate and the feed components, respectively.

GO membranes showed excellent performance in dewatering of ethanol compared to many polymeric membranes such as poly(vinyl alcohol) [52]. They showed a great balance between

the separation factor and the permeation flux, which is essential for scaling up operation. However, their performance was not as good as some molecular sieve membranes such as zeolite NaA [53, 54]. As demonstrated by Shao et al., zeolite NaA membranes on porous alumina hollow fibres had a separation factor >10000 , with a total flux of $11.1 \text{ kg m}^{-2} \text{ h}^{-1}$ [54]. Though with a relatively moderate performance, GO membranes are still potential for dewatering of organic solvents due to their high chemical stability. The improvement of the membrane performance can also be further studied.

2.1.4 GO membrane modifications

Pure GO membranes showed good performance in gas separation, liquid filtration and pervaporation due to their unique laminar structure and molecular sieve properties. However, some studies also revealed the stability problem of GO membranes, which was mainly caused by the weak hydrogen bonds between GO flakes. Besides that, the high aspect ratio of GO flakes contributes to a long transport path length in GO membranes. The large flake diameter also results in a low effective porosity of the membrane surface as molecules can only enter the membrane through the edge of GO flakes. Both long transport path length and low surface porosity in GO membranes have constrained the permeation through the membranes. Modifications have been carried out to improve the stability of GO membranes and also to improve the membrane performance. GO membrane modifications can be done at different stages: on GO flakes before membrane synthesis, during membrane fabrication process or as a post-treatment step after membrane synthesis.

Pore generation in GO flakes

Fine pores in GO flakes can be created in order to increase the effective porosity of GO membranes and to shorten the transport path of molecules in GO membranes (Figure 2.11). Small pores with diameter about $3 \text{ \AA}$ were successfully created in graphene using ion and electron bombardment [55]. However, this method is difficult to be used on GO flakes in the solution. Other chemical methods using KOH, H_2O_2 and nitric acid have also been used to create pores in GO and rGO flakes in liquid solution [56-58].

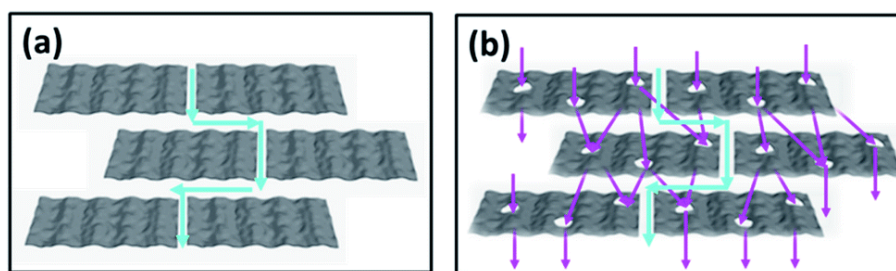


Figure 2.11: Schematic view of mass transport through pristine GO membrane and mesoporous GO membrane after pore creation on GO flakes. Reproduced from Ref. [59] with permission from the Royal Society of Chemistry.

Ying et al. successfully created pores with sizes smaller than 5 nm in GO flakes by re-oxidizing the GO flakes using KMnO_4 , where the strong oxidizing agents reacted with the oxygen-containing functional groups on the carbon skeleton [59]. GO membranes with the extra pores showed an increase in water permeation to 250 LMH bar^{-1} . However, the rejection properties of the membranes were slightly compromised; the membranes showed a higher molecular weight cut-off with a rejection of only 88.5% when tested with Evan Blue ($M_w = 960.8 \text{ Da}$).

Generation of microstructural channels

Besides pore creation in GO flakes, the transport path in GO membranes can also be reduced by introducing more transport channels in between GO flakes in the membrane. Huang et al. synthesized GO membranes with nanochannels by introducing copper hydroxide nanostrands (CHN) in the GO suspension [40]. CHNs with a diameter of 2.5 nm distributed around the GO flakes and created nanochannels in the membrane when being removed. The water permeation of the membrane was 10-fold enhanced compared to GO membranes without nanochannels. However, similar to GO membranes with fine pores created, the rejection performance of the membranes was compromised after the increase in water flux. The membranes could only serve as ultrafiltration membranes and the separation of the membranes was not due to the interlayer space of GO membranes.

Cross-linking of GO flakes

Cross-linking of GO flakes was carried out to improve the stability and the mechanical strength of GO membranes. Polymeric cross-linkers were commonly used and they were added to the GO suspension before membrane synthesis [32, 51, 60]. Zhang et al. showed that the stability

of GO membranes in water was improved significantly after cross-linking with ethylenediamine (Figure 2.12), and the membranes could still retain their structure even in a vigorous sonication process [32]. Besides, a recent study by Yeh et al. found that Al^{3+} ions leached from AAO substrates could act as cross-linkers that hold the negatively charged GO sheets together [61]. Multi-valent ions such as Al^{3+} , Cr^{3+} , Mg^{2+} and Cu^{2+} were incorporated into GO membranes by Li et al. and the membranes showed an extraordinary stability in water [62]. The enhancement in thermal resistance of Al^{3+} cross-linked GO membranes was also demonstrated in Turgut et al.'s study, where the GO film could resist in-air burning on an open flame [63].

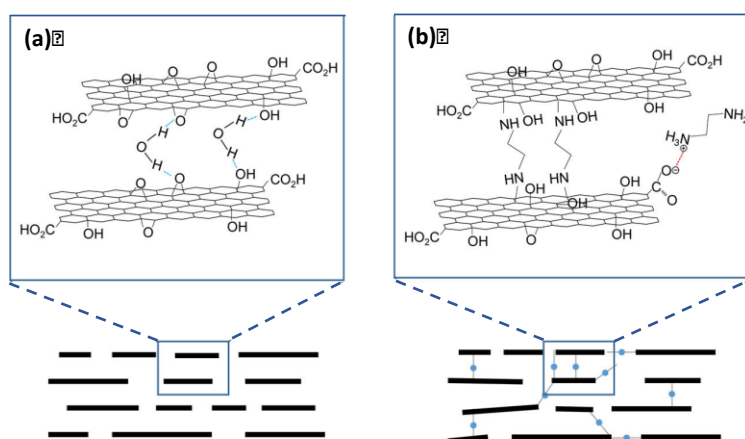


Figure 2.12: Schematic diagrams of (a) pristine GO (b) GO cross-linked with ethylenediamine. Reproduced from Ref. [32] with permission from American Chemical Society.

Besides improving the membrane stability, the interlayer distance of GO membranes could be fine-tuned by introducing cross-linkers in the interlayer space. As demonstrated by Shen et al., the pore size of GO membranes was successfully enlarged from 3.8 to 4.2 Å by using polyethylenimine (PEI) as cross-linker [30]. With the enlarged interlayer space, the membranes showed an excellent H_2 permeation of about 1000 barrer and a H_2/CO_2 selectivity close to 30. Besides that, Hung et al. showed that GO membranes cross-linked with diamine monomers such as ethylenediamine and butylenediamine experienced a smaller expansion in their interlayer space when immersing in water. The smaller expanded interlayer distance, compared to pure GO membranes, led to an improved performance in dehydration of ethanol in pervaporation [51].

Layer-by-layer coating

In the layer-by-layer method, the coatings of GO flakes and the cross-linkers were done layer-by-layer alternately. This is different from the cross-linking method where the cross-linkers are usually added to the GO solution before the synthesis of GO membranes. The coating of each layer could be self-limiting but multi-layer GO flakes may be obtained. Hu et al. added 1,3,5-benzenetricarbonyl trichloride (TMC) in between GO layers using the layer-by-layer method [64]. The TMC added did not only improve the stability of the membranes but also fine-tuned the charges, functionality and spacing of the GO sheets. The thin film composite membranes showed a water flux between 0.9 and 27.6 LMH bar⁻¹, and with a high rejection of Rhodamine-WT ($M_w = 487$ Da), 93-95%. Besides, modifications on the GO flake surface can be done to apply the layer-by-layer approach. In a study by Choi et al., aminated-GO (AGO) was prepared by adding ethylenediamine to GO flakes [65]. Both AGO and GO had opposite charges and therefore could form a strong interaction between each other during the layer-by-layer deposition.

Reduction of GO flakes and GO membranes

Though GO membranes showed excellent performance in nanofiltration rejecting multi-valent ions and molecules with molecular size larger than 200 Da, their application in desalination was constrained by the large interlayer space. One of the strategies to reduce the interlayer space is to reduce GO to rGO, which could be done easily by using reduction agents such as hydrazine and ascorbic acid [11]. rGO membranes could be fabricated using similar methods used for GO membranes. Though the hydrophilicity of rGO membranes was lower due to the decrease in the number of oxygen-functional groups, Hu et al. showed that rGO membranes could still have a high water permeation flux, up to 21.8 LMH bar⁻¹ [13]. However, many rGO membranes reported did not show improved performance in salt-rejections [13, 66]. This could be due to the microstructural defects formed in rGO membranes especially when rGO flakes were used in the membrane synthesis as it involved the stacking of less hydrophilic rGO flakes. In a study by Liu et al., rGO membranes were fabricated by reducing GO membranes with hydriodic acid [67]. The rGO membranes were tested in forward osmosis and showed a high water permeation flux of 57.0 LMH. The salt rejection rate of the membranes was also higher than GO membranes due to the smaller

interlayer space. Besides that, rGO membranes were tested to separate water from oil-water emulsions with the change in hydrophilicity of the membranes [24].

Surface modification of GO membranes

Surface modifications of GO membranes were also carried out to improve their performance. Huang et al. further improved the surface hydrophilicity of GO membranes by coating a thin layer of hydrophilic polymer, N-deacetylated derivative of chitin [68]. The surface modification enhanced the water adsorption on the membrane surface, and subsequently improved the separation factor in dewatering of butanol. Besides that, the surface charge of GO membranes can be modified by the surface modification technique. Due to the deprotonation of carboxylic groups on GO membrane surface, GO membranes are negatively charged over a wide range of pH. Zhang et al. showed that GO membranes with a positively charged surface could be obtained by modifying the surface with hyperbranched polyethylenimine [32]. The surface modified GO membranes showed enhanced rejection (>95%) of heavy metals such as Pb^{2+} .

2.2 Graphene Membranes

Single-layer graphene has a high mechanical strength and is impermeable to all atoms and molecules [66]. However, with tiny pores created, graphene can be applied as membranes to separate molecules by size exclusion, as shown in Figure 2.13.

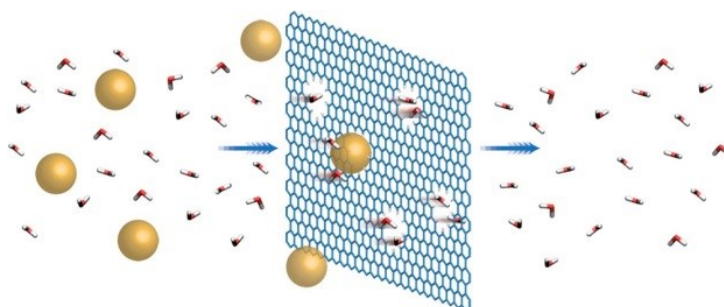


Figure 2.13: Molecular sieving property of monolayer graphene with nanopores. Reproduced from Ref. [70] with permission from Nature Publishing Group.

Graphene has been considered as an attractive material to develop high performance membranes for gas separation and water purification. As the permeability of membranes is inversely proportional to membrane thickness, a monolayer graphene membrane is expected to have an incredibly high permeability.

2.2.1 Theoretical studies of graphene membranes

Molecular dynamic simulations have been applied to study the potential application of graphene in membrane separation. Jiang et al. used first principle density functional theory calculations to study the viability of graphene as a monolayer membrane for H_2/CH_4 separation [71]. In their study, two neighbouring carbon rings were removed to create pores in graphene, as shown in Figure 2.14. The unsaturated carbon atoms were either passivated with hydrogen atoms or substituted with nitrogen atoms. These 2 types of pores had a different diameters (2.5-3 Å) and charge densities, affecting the interaction energy at the pores. H_2 showed a higher flux through the N-functionalized pores, with a high H_2/CH_4 selectivity in the order of 10^8 , due to the relatively low H_2 diffusion barriers [71].

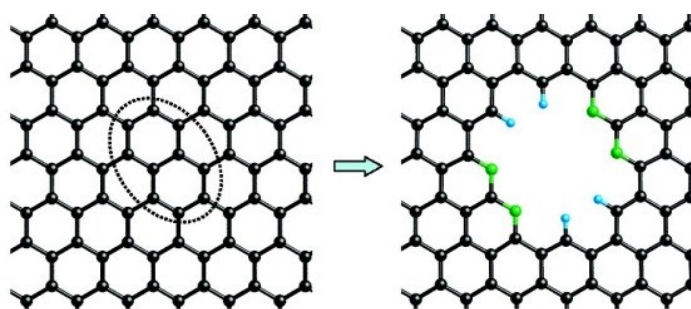


Figure 2.14: Example of nitrogen-functionalized pore within a graphene sheet. Reproduced from Ref. [71] with permission from American Chemical Society.

Du et al. showed that the gas permeability and selectivity of graphene membranes were affected by the size and the shape of the nanopores in graphene membranes, as well as the van der Waals interactions between the gas molecules and the membranes [72]. At small pore size <4.46 Å, the selectivity of H_2/N_2 was high due to the size exclusion effect. However, when the pore size was larger, both H_2 and N_2 could pass through the membrane without any size

restriction and the permeation of N_2 became higher than H_2 . The van der Waals interaction between N_2 and the graphene membrane led to more N_2 accumulation near the membrane surface and therefore increased the permeation [72].

Drahushuk and Strano showed that the gas permeation through a monolayer graphene membrane did not follow the conventional membrane diffusion. The molecule association, translocation and disassociation at the pore sites were shown to be important steps in molecular transport through graphene membranes. At large pores where the pore size was not a restriction, the more strongly adsorbing nitrogen permeated faster than the weakly adsorbing hydrogen. The permeation rate of molecules was also shown to be relatively constant across various larger nanopores in monolayer graphene membranes [73].

In addition to gas separation, graphene membranes were also studied for water filtration. Cohen-Tanugi and Grossman used the classical molecular dynamic simulation to study the separation of NaCl in water through the nanopores in graphene [74]. The simulation data suggested that pores with a diameter smaller than 5.5 Å could prevent salts from passing through graphene membranes. The presence of functional groups at the edge of the pores, especially the -OH groups, could increase the hydrophilicity and the water permeation of the membranes. Graphene membranes were predicted to have water permeation flux higher than 1000 LMH bar⁻¹, which would be 2–3 orders of magnitude higher than the commercial reverse osmosis membranes. In another study conducted by Konatham et al., ion exclusion was found to be only effective for non-functionalized graphene at small pore size ~7.5 Å [75]. Carboxylic functional groups at functionalized graphene enhanced ion exclusion but the effect became smaller when the pore size became larger. These functional groups increased the pore free-energy barriers due to the electrostatic and steric effects, and rejected the permeation of ions.

In summary, the molecular simulation studies show that graphene is a promising material for gas separation and water filtration given their ultrathin thickness and exclusive molecular sieve properties. However, in order to achieve a high selectivity and permeation flux, the characteristics of pores in graphene such as the pore size, the termination of unsaturated sites and the functional groups at the pore sites have to be well controlled.

2.2.2 Synthesis of graphene membranes

Graphene can be synthesized using two main approaches: top-down and bottom-up. In the top-down approach, stacked layers of graphite were separated to yield single-layer graphene sheets. Examples of methods involving the top-down approach are mechanical exfoliation, liquid-phase exfoliation and graphite oxide exfoliation. High quality graphene with a single crystal can be obtained using mechanical exfoliation as demonstrated in the scotch-tape experiment [76]. The success in isolating high quality single layer graphene has enabled fundamental studies on the properties of graphene. However, the area of the graphene obtained using this method was still in the micron range [77], constraining their practical applications especially for membrane fabrication. In liquid-phase exfoliation, graphene can be obtained by sonicating graphite flakes in solvent [78]. While in graphite oxide exfoliation, graphene oxide was first obtained before being reduced to rGO or graphene [5]. The yield of graphene in these two methods can be higher than mechanical exfoliation, but getting large area of graphene flakes is also challenging. Graphene thin films can be obtained by stacking the graphene flakes similar to GO films, but the continuity will be limited especially at a small thickness. Besides that, a complete reduction of graphene oxide to graphene is difficult to achieve.

The bottom-up methods such as chemical vapour deposition (CVD) and epitaxial growth involve synthesising graphene from alternative carbon containing sources. In the CVD method, metal substrates such as nickel and copper are used as a catalyst surface for graphene synthesis at high temperature, with carbon source such as methane [79]. The area of graphene synthesized will be determined by the area of the catalyst surface. While in the epitaxial growth, graphene can be prepared by heating up a SiC substrate to very high temperature, 1400-1900 °C [80]. The preferential sublimation of silicon from the SiC surface will leave behind excess carbon atoms which subsequently undergo graphitisation to form a graphene layer. The synthesis temperature can be lowered to 700-800 °C with a thin layer of nickel deposited on the surface of the SiC [81, 82]. Though both of these methods require high temperature and specific substrates for graphene synthesis, the graphene obtained can have a large area and with a good quality.

2.2.2.1 Chemical vapour deposition

In the last decade, CVD has been much explored to synthesize large area graphene for various applications including membrane separation [83-87]. During CVD, the catalyst substrates were first heated with a small amount of hydrogen, either under high vacuum or atmospheric pressure. The temperature was then maintained at elevated temperatures for substrate annealing where the surface was reduced and cleaned. After that, carbon source will be introduced to the reaction chamber for graphene growth. Light hydrocarbons such as methane and solid polymers can be used as the carbon precursors for graphene synthesis [87, 88]. At the end of the synthesis, the substrate will normally be cooled rapidly to room temperature.

Transition metals such as Ni, Cu, Pd, Ru and Ir have been studied for graphene synthesis in the CVD method [79]. The differences in catalytic activity and carbon solubility could lead to different graphene growth rates and mechanisms. The catalytic activity affects the decomposition of carbon precursors on the metal surface and a higher temperature is required for graphene growth if the activity of the metal catalyst is lower. For example, graphene can grow on Pt at a relatively low temperature (750 °C) [89] compared to Cu (1000 °C) due to the strong catalytic ability of Pt in dissociation of CH₄ and H₂. Besides that, the solubility of carbon is also an important parameter in controlling the growth of graphene, which affects the growth mechanism and kinetics. Cu has a low carbon solubility of 0.001-0.008 wt% at 1084 °C compared to Ni, 0.6 wt% at 1326 °C, leading to a different growing mechanism on the metal surface [79]. Metal alloys such as Cu-Ni and Ni-Au have been studied to optimize the graphene growth using the CVD methods [90]. As Ni is much reactive and has higher carbon solubility, a small amount of Ni in Cu could lower the graphene growth temperature.

Ni and Cu are two most commonly used substrates for CVD and the graphene growing mechanism on these two types of surface have been much studied. Figure 2.15 summarized the growing mechanism of graphene with CH₄ as the carbon precursor [91]. During the CVD reaction, chemisorption of H₂ and physisorption of CH₄ first take place on the surface sites of the metal substrates. CH₄ decomposes on the metal surface into active carbon atoms. For Cu substrates, the carbon atoms nucleate on the substrate surface to form graphene layer.

However, as the carbon solubility of Ni is much higher, the carbon atoms diffuse into the substrate instead of nucleating on the surface. Graphene will only form on the nickel surface through precipitation at the end of the reaction when the substrate is cooled down rapidly as the dissolved carbon atoms diffuse back to the substrate surface. The cooling rate was found important in determining the quality of the graphene synthesized on Ni substrates. As shown by Yu et al., medium fast cooling rate at $\sim 10^{\circ}\text{C s}^{-1}$ yielded a good quality graphene with less than 4 layers, while a higher cooling rate at $\sim 20^{\circ}\text{C s}^{-1}$ resulted in the formation of multi-layer graphene due to insufficient time in attaining a good crystallinity [92].

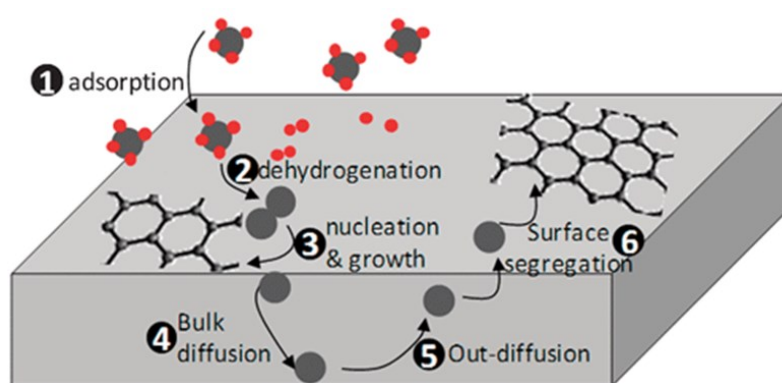


Figure 2.15: Graphene growth mechanism during CVD on Ni and Cu catalyst surface. Reproduced from Ref. [91] with permission from the Royal Society of Chemistry.

Carbon-isotope-labelling technique has been used in conjunction with Raman spectroscopic mapping to study the growth mechanism of graphene on Cu and Ni substrates [93]. Graphene composed of ^{12}C and ^{13}C gave a slightly different Raman shift, enabling the study of the growth mechanism. In the study, methane with ^{13}C was first fed to the furnace during the CVD process. The carbon source was then switched to methane with ^{12}C in the middle of the synthesis. Figure 2.16 showed the Raman maps of graphene on the Cu and Ni substrates. Graphene showed separated isotopes on the Cu substrate as surface nucleation happened during the CVD deposition. However, graphene with randomly mixed isotopes was observed on Ni substrates. Carbon atoms of both isotopes diffused into the substrate during the reaction and the graphene layer only formed on the surface through precipitation during the rapid cooling step.

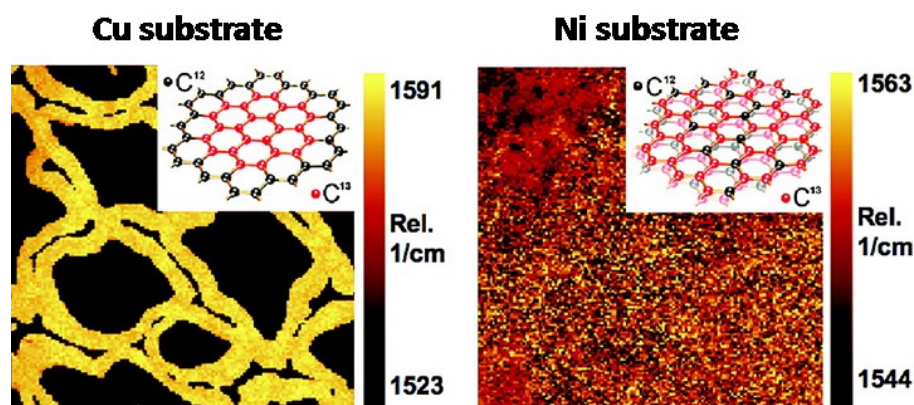


Figure 2.16: Raman maps of graphene on the Cu and Ni substrates. The bright area corresponds to the G peak from ^{12}C . Reproduced from Ref. [93] with permission from American Chemical Society.

Graphene synthesized by CVD can be transferred to different types of substrates for various thin film applications [83, 85, 87, 94]. In most cases, a thin layer of PMMA was first spin-coated on the graphene surface so that the graphene layer could be handled more easily after detaching from the metal substrates. The metal substrates can be etched using etching agents such as nitric acid and FeCl_3 . The PMMA layer could be washed off easily using acetone after graphene is transferred to other substrates. Graphene has been successfully transferred to flat porous substrates and tested for gas separation and water filtration [22, 55, 95].

2.2.3 Applications of graphene membranes

2.2.3.1 Gas separation

Micrometre-sized pristine graphene membranes were fabricated using mechanical exfoliation by Koenig et al. [96]. The exfoliated graphene flake was clamped to a 5- μm -diameter silicon oxide substrate and ultraviolet-induced oxidative etching was used to introduce pores in the graphene membrane. The membrane setup is illustrated in Figure 2.17. The microcavity was filled with a test gas species and the gas molecules leaked out from the microcavity rapidly when the etched pores were bigger than the molecule size. The experimental H_2 leak rate matched the calculations of Blankenburg et al. [97] but was several orders of magnitude lower than the value calculated by Jiang et al. due to a higher H_2 energy

barrier in the experiment. Chemical termination in the pore was found to be important as it affected the energy barrier at the pore sites [96].

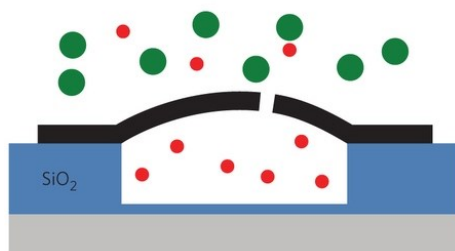


Figure 2.17: Schematic of a microscopic graphene membrane on a silicon oxide substrate with etching pore. Reproduced from Ref. [96] with permission from Nature Publishing Group.

Celebi et al. successfully prepared graphene membranes with a larger area using the CVD method [98]. The graphene synthesized was transferred onto a SiNx frame having 49 pores, each with a diameter of 4 μm . A focused ion beam (FIB) was used to create pores with a narrow size distribution ranging from <10 nm to 1 μm . The ultrathin graphene membranes showed an extremely high gas permeability, in good agreement with the predictions of two-dimensional transport theories. The H_2 permeance of the membrane could be as high as $\sim 1.0 \times 10^{-2} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, more than three orders of magnitude higher than the existing gas separation membranes with similar selectivity. However, the H_2/CO_2 selectivity of the membranes was only 4.6 due to the large pores ($\sim 7.6 \text{ nm}$) generated by using the FIB drilling method.

Multilayer graphene membranes were fabricated by Kim et al. using the CVD method [22]. Monolayer graphene films were first synthesized on a Cu foil with an area of $15 \times 20 \text{ cm}^2$. The monolayers were then transferred and stacked to form multilayer graphene membranes. The multilayer graphene was then transferred to a poly(1-methylsilyl-1-propyne) (PTMSP) substrate. Defects may have been generated in the graphene layer during the synthesis and the transfer as observed from the electrical resistance and the gas permeation. However, these defects could be mitigated by increasing the number of graphene layers. The O_2/N_2 selectivity increased from 1.5 to 6 when the number of graphene layers was increased from

1 to 5. Though the selectivity was not as high as the carbon molecular sieve membranes, the O_2 permeance was still considerably high ($\sim 10^2$ Barrer).

A similar method was used by Boutilier et al. to synthesize multilayer graphene membrane [99]. Defects formed during the synthesis process and gas leakage through the defects reduced exponentially by stacking the graphene layers. The leakage rate dropped to almost zero when 5 layers of graphene were stacked and interlayer transport was observed to be negligible in graphene membranes. Even though with tears and intrinsic defects, the study showed that a selective graphene membrane could still be achieved by controlling the pore size and the resistance of the membrane supports [99].

2.2.3.2 Water permeation

Graphene membranes have also been studied for water permeation application. In a study by Surwade et al., single layer graphene membranes were synthesized using the CVD method and transferred to a silicon chip with a 5- μm hole [100]. Pores with sizes ranging from 0.5-1 nm and a density of 1012 cm^{-2} were successfully created by using an oxygen plasma etching process. The membranes showed a high water permeation flux $\sim 250\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$ (with osmotic pressure as the driving force) and a salt rejection rate of nearly 100%.

Producing large area of defect-free graphene membrane remains a challenge. As shown in gas separation application in the previous section, the defects created during synthesis and transferring of graphene membranes may degrade the molecular properties of graphene membranes. In a study by O'Hern et al., graphene membranes with an area of 25 mm^2 were fabricated by transferring a single layer of CVD synthesized graphene onto a porous polycarbonate substrate. Consistent defects/intrinsic pores of diameter 1-15 nm formed in the graphene during the CVD synthesis, allowing salt ions such as KCl to permeate through the membrane [95]. The same research group later developed a multi-scale leakage-sealing process, enabling the fabrication of centimetre-scale graphene membranes. To seal nanoscale defects, a layer of hafnia with a thickness of $\sim 3.5\text{ nm}$ was first deposited onto the graphene surface using atomic layer deposition. Next, nylon-6,6 was formed in substrate pores underlying larger defects via interfacial polymerization. The sealed membrane

exhibited ~70% rejection of MgSO_4 under forward osmosis but NaCl could still transport across the membranes [101].

Though graphene membranes prepared using the current methods still could not be applied for desalination like predicted in the simulation studies, they still showed high water permeation flux, rejecting multivalent ions or larger molecules. Large area graphene membranes (63 cm^2) were synthesized by Qin et al. using the CVD method. The membranes were transferred to PES substrates followed by pore creation with ion bombardment and acid etching. Polystyrene nanoparticles were also filtered on the membrane surface to eliminate large pin holes and defects. The membranes showed a high water permeation of 50 LMH bar^{-1} and a molecular weight cut off $<329 \text{ Da}$, showing good potential for nanofiltration application [102].

With pore size larger than 10 nm , graphene membranes could also be applied for ultrafiltration. Graphene membranes with a pore size of 50 nm were prepared by Celebi et al., as discussed in the gas separation section. The membranes were also tested for water permeation and the water flux could reach about $10,000 \text{ LMH bar}^{-1}$, about 3 times higher than most of the ultrafiltration membranes [98]. Wei et al. also prepared graphene membranes using the CVD method. Copper oxide nanoparticles were used to generate more pores in graphene at high temperature. With similar pore size of about 50 nm , the membrane showed a water permeation flux up to $4600 \text{ L m}^{-2} \text{ h}^{-1}$ when tested at 0.2 bar . The water permeation flux was higher than the membranes prepared by Celebi due to the higher pore density in the membranes (15 compared to 4.7%) [103].

2.3 Challenges and gap of knowledge

2.3.1 Graphene oxide membranes

Due to the relatively simple and cost-effective synthesis process, GO has been widely used to produce graphene-based materials. GO membranes can be synthesized easily using solution-processing methods such as filtration and spin coating, and they have been tested for applications such as gas separation and nanofiltration. Though GO membranes have shown

promising performance in membrane separation applications, there are still some shortcomings in the membranes produced, constraining their applications in industrial scale.

Stability

The stability problem of GO membranes has been reported where the molecular sieve properties of GO membranes degraded over time [34]. The re-dispersion of GO flakes was also observed in water-based applications, which led to a disintegration of GO membranes. Yeh et al. showed that the stability problem of GO membranes in water was due to the weak hydrogen bonds between GO flakes [61]. More studies on understanding and solving the stability problem of GO membranes are required to improve their long-term stability.

Repeatability

As discussed in the gas separation section, the performance of GO membranes was not consistent among studies and ultrathin GO membranes with a thickness <20 nm were difficult to be reproduced. The inconsistency in GO performance could be due to the lack of understanding in the membrane formation mechanism and the physiochemical properties of GO membranes. A recent study showed that the oxidation state of GO, as reflected by the different C/O ratio, could affect the interlayer distance of GO membranes [104]. More study can be carried out to understand the effects of physiochemical properties of GO flakes and the membrane microstructure on the membrane performance.

Scaling up and geometry

Though GO membranes have shown exceptional performance in water filtration and gas separation, they were mostly produced on flat sheet substrates and many were on expensive substrates such as AAO [19, 25]. Scaling up flat sheet GO membranes can be very challenging. In contrary, hollow fibre membranes can be scaled up more easily even with a thin coating layer on the surface. Studies on fabricating GO membranes on hollow fibres can be carried out to improve the membrane scalability.

Interlayer space and salt rejection

GO membranes showed good performance in nanofiltration, rejecting multi-valent ions and large molecules >200 Da. However, in order to apply GO membranes in desalination, the interlayer space of the membranes has to be further reduced. Some studies demonstrated that the interlayer space could be reduced by incorporating rGO or graphene flakes in GO

membranes [44]. Though the salt rejection has been much improved, more study has to be done to enhance the water permeation flux.

Transport mechanism

Despite the high tortuosity in GO membranes, the high water permeation flux of GO membranes was explained by some studies using the frictionless flow in the carbon-nanochannels in the membranes [17, 27]. However, some studies found that the side-pinning effect from the hydrophilic groups in GO membranes could slow down the water transport [38, 105]. The slow water permeation in the interlayer distance could also be caused by bulk viscous dissipation and spatially extended friction [36]. More study can be done to understand the transport mechanism in GO membranes, which could also be applicable to membranes synthesized by using other 2D materials.

2.3.2 Graphene membranes

To realize a single-layer graphene membrane, it is crucial to have a robust method to synthesize monolayer graphene with minimum defects or a controlled defect size. CVD has shown to be a promising method to synthesize large area graphene membranes [86]. However, there are still some challenges in the fabrication process, which have to be overcome.

Minimizing defects

Small defects in graphene created during the CVD synthesis and the transfer process could serve as pores for permeation. However, large defects will degrade the performance of graphene membranes especially for gas separation and desalination where pore sizes smaller than 1 nm are desirable [74, 98]. The CVD synthesis process can be further studied to determine single or few-layer graphene membranes with minimum defects. Besides that, the methods of transferring graphene to a porous substrate need to be further improved and graphene membrane synthesis without a transferring step could be explored.

Pore creation methods

A defect-free graphene membrane is impermeable to all gases and liquids. In order to obtain a high membrane performance, fine uniform pores have to be created in graphene membranes. Some pore creation methods such as ion bombardment and plasma oxidation

have been demonstrated [55, 100]. However, the efficiency of these methods in creating membranes with a high pore density has not been fully achieved. Some other methods such as nanoparticles have been tested but the pores created had a pore size larger than 50 nm [103]. Pores with smaller sizes are desirable as graphene membranes have potential for applications such as desalination.

Scale up and geometry of graphene membranes

Graphene membranes in a hollow fibre geometry are desirable for scale up purposes. GO membranes can be synthesized on hollow fibre substrates using methods like filtration and dip-coating. However, fabricating graphene membranes on hollow fibre substrates can be more difficult. CVD is a promising method to synthesize large area graphene membranes but the current technique requires a transfer step and is not feasible for hollow fibre substrates. Direct growth of graphene on the hollow fibre substrate is desirable in order to create a continuous layer of graphene membrane.

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Chapter 3: Development of hollow fibre substrates for graphene-based membranes

Abstract:

Stainless steel (SS) hollow fibres were developed to improve the mechanical properties of inorganic hollow fibre substrates for graphene-based membrane synthesis. Strong, porous stainless steel hollow fibres were fabricated through the phase-inversion and sintering techniques. The pore size of the hollow fibres were reduced by incorporating ceramic nanoparticles around the stainless steel particles. A co-extrusion spinning technique was used to fabricate dual-layer SS/SS-ceramic hollow fibres in one step. The outer layer is a mixture of stainless steel and yttria-stabilized zirconia (YSZ), creating a separating layer with small pore sizes. The inner layer consists of stainless steel, which provides high mechanical strength to the hollow fibres. The mean pore size of the composite hollow fibre membranes was reduced to approximately 300 nm. The composite hollow fibre were used as substrates to prepare GO membranes by coating. The membranes were evaluated using a gas tightness test. Though the substrates were found unsuitable for thin film coatings due to the rough surface, they showed a high water permeation flux, $\sim 3000 \text{ LMH bar}^{-1}$, making them attractive in microfiltration for value-added products.

3.1 Introduction

Ultrathin graphene and graphene oxide (GO) membranes have to be supported on a substrate for membrane separation, especially for large scale applications. Membrane substrates such as anodic aluminium oxide (AAO) have been widely used to develop thin GO membranes [1-3]. With uniform pore size and high porosity, AAO substrates have a low mass transfer resistance and are excellent substrates for thin film membranes. However, they are very costly and difficult to handle due to their weak mechanical property. Polymeric substrates such as polycarbonate [4], poly(1-methylsilyl-1-propyne) [5], nylon [6] and polyacrylonitrile [7] have also been used to fabricate GO membranes. However, most of these supports are planar/flat sheet membranes and their potential for scaling up is limited by the low membrane area to volume ratio at module level.

Instead, hollow fibre substrates are ideal for membrane module assembly. With a small diameter ranging from hundreds of micrometres to a few millimetres, hollow fibre membrane module could have a high surface area per unit volume [8]. Inorganic hollow fibres membranes are explored in this study as they have excellent chemical and thermal stability compared to polymeric membranes. This enables the potential use of graphene-based hollow fibre membranes in more challenging applications involving harsh environments such as organic solvent nanofiltration and pervaporation.

Of all types of inorganic hollow fibre substrates, ceramic hollow fibres made of alumina, titania and yttria-stabilized zirconia (YSZ) have been studied extensively in recent decades and they can be produced using a combined phase-inversion and sintering process [9-11]. Hollow fibres produced using this method could have a highly asymmetric and porous structure, contributing to fast mass transfer in the membranes. However, the mechanical strength of ceramic hollow fibres can be a constraint for industrialization, which is mainly caused by the small diameter and their porous microstructures. Studies on improving the mechanical strength of ceramic hollow fibres have been carried out. By fabricating the hollow fibres into a multichannel geometry, the increase in the cross-sectional area have shown to increase the fracture load [12]. However, ceramic hollow fibres are still very brittle in general. They are prone to cracks especially in industrial filtration processes where high flow rate and vigorous vibration may be involved.

Ductile metal hollow fibres have attracted much attention because of their potential to address the issue of mechanical strength of inorganic hollow fibres. Stainless steel (SS) is particularly an attractive material as it also has excellent chemical and thermal resistance. Stainless steel hollow fibres can be fabricated using the same method used in fabricating ceramic hollow fibres: the combined phase-inversion and sintering method [13, 14]. This approach allows a continuous production of large amounts of hollow fibres in one step, and the microstructure of the membranes can be tuned to adapt different applications. The ductility and flexibility of stainless steel hollow fibres have been demonstrated by Li et al., where spiral stainless steel hollow fibres were fabricated [15]. The spiral hollow fibres could act like a spring, with good extensions and contractions. Some studies have been done to investigate the sintering conditions of stainless steel hollow fibres to improve the mechanical properties. Rui et al. found that the H_2 sintering atmosphere will aid the removal of polymer

binder and avoid oxidation on the metal surface [16]. The bending strength of the stainless steel hollow fibres could reach 384 MPa after sintering at 1100 °C in H₂, which was much higher than most of the ceramic hollow fibres. Wang et al. further improved the mechanical properties of stainless steel hollow fibres by fabricating the hollow fibres in a three-channel structure [17].

Though the mechanical properties of the hollow fibres were much improved, the mean pore size was still very large, in the micron range. This has constrained their practical applications for example in microfiltration and as a substrate for thin film membranes. There are very limited studies focussing on the reduction of the pore size of stainless steel hollow fibres. The sol-gel technique has been tested to reduce the pore size of porous stainless steel supports. Though the pore size could be reduced to about 300 nm, a 2-step coating was required and the porosity of the coating was not tested [18]. In this chapter, a phase-inversion assisted co-extrusion technique was used to fabricate dual-layer SS/SS-YSZ hollow fibres in one step. The outer layer was a mixture of stainless steel and YSZ, where YSZ nanoparticles with diameters between 30-60 nm were used to fill up the large pores between the stainless steel particles and to reduce the effective pore size of the hollow fibres. The stainless steel inner layer provided high mechanical strength to the hollow fibres and a strong integration between the two layers was archived with the presence of stainless steel in both layers. With the success in reducing the surface pore size, SS/SS-YSZ hollow fibres were also tested as a substrate to prepare GO hollow fibre membranes in this chapter.

3.2 Experimental

3.2.1 Preparation of stainless steel and dual-layer SS/SS-YSZ hollow fibres

Stainless steel 430-L (average particle size = 15 µm, Alfa Aesar), stainless steel 316-L (mean particle size = 3 µm, Sigma Aldrich) and 3-YSZ (Inframat®, primary particle size 30-60 nm, Inframat Corporation) were used as supplied. Poly(methyl methacrylate) (PMMA) (average M_w ~120,000 by GPC, Sigma Aldrich) was used as the polymeric binder. N-methyl-2-pyrrolidone (NMP, HPLC grade, VWR) was used as the solvent. Arlacel P135 (polyethylene

glycol 30-dipolyhydroxystearate, Uniqema) was used as an additive. De-ionized water was used as the external and internal coagulants.

Two types of single-layer stainless steel hollow fibres, SS430-L and SS316-L were prepared, while only SS316-L was used to fabricate the dual-layer SS/SS-YSZ hollow fibres. The fabrication processes of both single-layer stainless steel and dual-layer SS/SS-YSZ hollow fibres were based on the combined phase-inversion and sintering technique [8, 9]. Firstly, uniform suspensions of stainless steel and SS-YSZ mixture were prepared by ball milling. The compositions of the suspensions are listed in Table 3.1. The suspensions were milled for at least 48 h. Then, the suspensions were degassed with stirring to remove bubbles entrapped, prior to transferring into stainless steel syringes that were controlled by syringe pumps (Harvard PHD22/2000 and Chemyx Nexus 6000).

Table 3.1: Fabricating parameters of stainless steel and SS/SS-YSZ hollow fibres

		Suspension 1	Suspension 2
Suspension composition (wt%)	Solvent	21.51	22.73
	Stainless Steel	71.68	49.20
	Polymer	6.45	6.82
	Additive	0.36	0.28
	Ceramic	-	20.97
Fabrication	Extrusion rate (ml min ⁻¹)	Suspension 1	8
		Suspension 2	2
	Bore liquid rate (ml min ⁻¹)		30
	Air gap (cm)		5

The suspensions were extruded through a triple orifice spinneret into the external coagulation bath (Figure 3.1 and 3.2(a)). For bare stainless steel hollow fibres, only Suspension 1 was extruded. While for SS/SS-YSZ hollow fibres, both Suspensions 1 and 2 were extruded to form dual-layer hollow fibres, as illustrate in Figure 3.2(b). Meanwhile, DI water was introduced through the central bore of the spinneret via another syringe pump, serving as the internal coagulant. Details of the spinning parameters are listed in Table 3.1. After the phase-inversion was completed, the precursor hollow fibres were removed from the external

coagulant bath. They were dried and straightened, and then cut into a required length for the subsequent high temperature sintering.

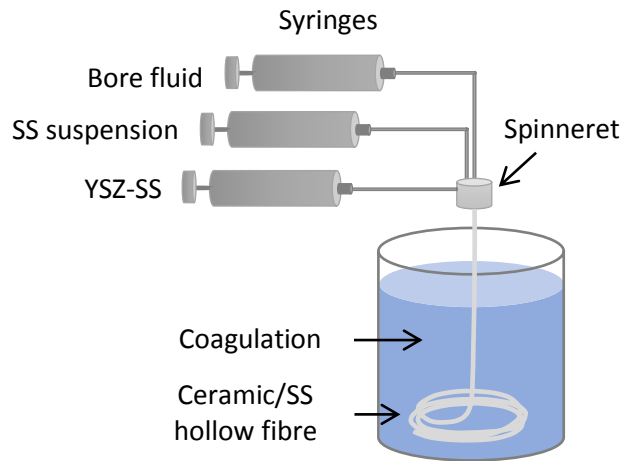


Figure 3.1: Schematic of the set-up for the preparation of hollow fibres using the phase inversion method

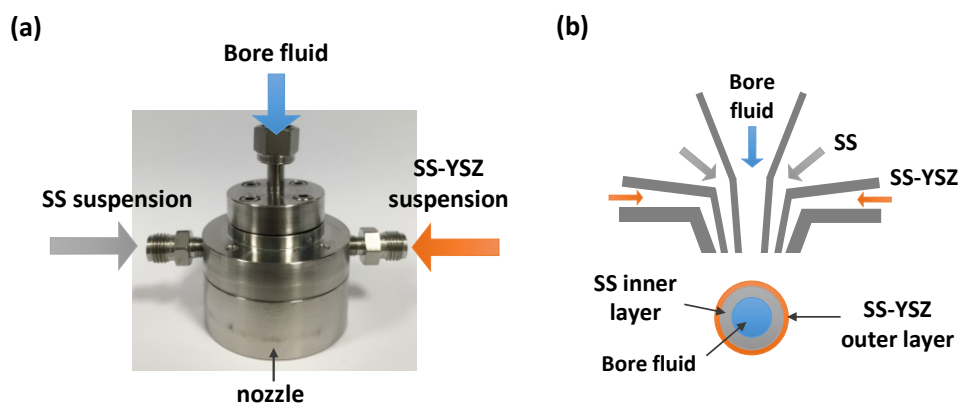


Figure 3.2: (a) Photograph of the triple-orifice spinneret used in fabricating dual-layer SS/SS-YSZ hollow fibres. (b) Schematic diagram of the nozzle of the spinneret.

Both of the stainless steel and SS/SS-YSZ hollow fibres were sintered in a controlled atmosphere. At the beginning of the sintering process, the temperature of the furnace was increased from room temperature to 600 °C at a rate of 5 °C min⁻¹. Vacuum was applied to the system while H₂ and He were supplied to the furnace at a 1:1 ratio. During this period, the polymer binder, PMMA was degraded and carried away from the furnace by the sweep gas. After the removal of polymer binder, the furnace temperature was increased to the desired

sintering temperature, 1000-1150 °C, at a rate of 10 °C min⁻¹. Only H₂ was supplied to the furnace tube to provide a reducing environment during the sintering process. The hollow fibres were sintered for 30-120 minutes to avoid over-sintering and densification, so that the porous structures of stainless and YSZ could still be retained. Longer sintering time was used for low sintering temperature as the sintering rate was lower at low temperature (e.g. 1000 °C). At the end of the sintering, the furnace tube was withdrawn from the furnace to cool the hollow fibres down rapidly under a H₂ atmosphere.

3.2.2 Preparation of graphene oxide hollow fibre membranes

Graphite powder (particle size <150 µm, Sigma Aldrich) was used as the starting material in the GO suspension synthesis. Sodium nitrate (NaNO₃, >99%), potassium permanganate (KMnO₄, >99%) and 30 % hydrogen peroxide from Sigma Aldrich, and sulphuric acid (H₂SO₄, 95%) from VWR were used in the synthesis. GO dispersion was prepared through a modified Hummer's method [19, 20]. Briefly, graphite powder was mixed with NaNO₃ and H₂SO₄ in an ice water bath, with KMnO₄ gradually added to the mixture after that. The ice water bath was removed after 5 h and the mixture was stirred continuously for 5 days. Water was added at the end of the reaction and exfoliation, and H₂O₂ was added to remove the remaining manganese ions. The resultant GO dispersion was washed with deionized water for several cycles, and then centrifuged to control the size of GO flakes, which was determined to be 5-10 µm from the SEM. The GO dispersion was diluted to a concentration of 0.1 g L⁻¹ and was used for coating of GO membranes.

SS/SS-YSZ dual layer hollow fibres were used as the substrates for the GO membranes. To deposit GO membranes onto the surface of hollow fibres, the hollow fibre was immersed in a GO dispersion with one end sealed and the other end connected to a vacuum pump. When vacuum was applied from the lumen of the fibre, water was sucked into the fibre and the water flow directed the GO flakes to the outer surface of the hollow fibre substrate. GO membrane was formed by stacking the flakes layer by layer, with the aid of pressure difference and water permeation. The thickness of the GO membrane was controlled by changing the initial concentration of the GO dispersion and the duration of filtration.

3.2.3 Membrane characterization

Sintering behaviour of the SS316-L and YSZ powders were studied using a dilatometer (NETZSCH, model DIL 402C). The powders were pressed into 5 mm-diameter cylindrical pellets under a maximum pressure of 240 MPa. The pellets were heated to the target temperature at 5 °C min⁻¹, in flowing argon (50 ml min⁻¹) for the stainless steel samples and in static air for the YSZ samples. The changes in the length of the samples were recorded using a displacement transducer.

The morphologies and microstructures of the hollow fibres and GO/SS-YSZ/SS membranes were characterized by using a scanning electron microscope (LEO Gemini 1525 FEGSEM and Zeiss Auriga Crossbeam). The pore size and the pore size distribution of the hollow fibre substrates were determined by using gas-liquid displacement measurements with PoroLux 1000 Porometer. The mechanical strength of the hollow fibres was evaluated by using an Instron material testing system (Model 5544) with a 10 kN load cell. A three-point bending method was used, where the samples were positioned onto a sample holder with a span of 25 mm. The fracture force was obtained and the bending strength was then calculated using the following equation:

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (3.1)$$

where F denotes the measured fracture force (N), L , D_o and D_i represent the length, the outer and the inner diameters of the fibre (m), respectively. In the case where the hollow fibre did not fracture, yield strength was calculated using the force applied at the yield point.

3.2.4 Membrane performance tests

The pure water permeation of the hollow fibres was evaluated using a dead-end filtration method at 1 bar, in an out-to-in mode, as shown in Figure 3.3. Epoxy resin was used to seal one end of the hollow fibre, and the other end on a stainless steel holder. The hollow fibre membrane was then mounted into a sample cylinder filled with deionized water. The permeate through the membrane was collected and the permeation flux, J (L m⁻² h⁻¹ bar⁻¹) was calculated based on the equation:

$$J = \frac{V}{A \times t \times \Delta p} \quad (3.2)$$

where V is the permeate volume (L), A is the effective membrane area (m²), t is the time of permeate collection (h), and Δp is the transmembrane pressure gradient (bar).

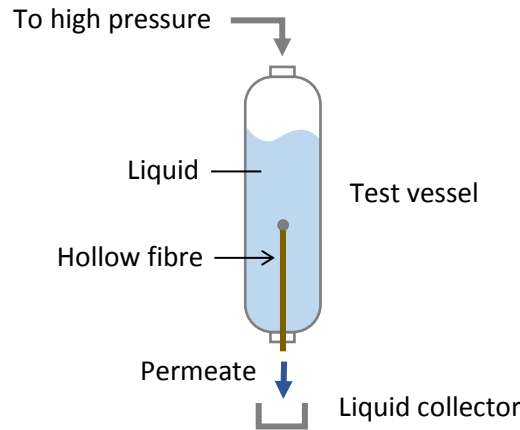


Figure 3.3: Experimental setup for nanofiltration and permeation tests

The fouling test was conducted using a cross-flow mode and bovine serum albumin (BSA) was used as a model protein to investigate the fouling resistance of the composite hollow fibres. The test was carried out for 3 cycles and in each cycle, pure water was first used as the feed for 30 min, and then followed by 1.0 g L⁻¹ of BSA solution for another 30 min. A constant 1 bar transmembrane pressure was applied and the weight of permeate was recorded by a computer in real time. After each cycle, the hollow fibre was cleaned by backwashing the membrane with pure water at 3 bar. The backwashing was carried out for 5 min and was repeated 3 times, with clean circulation water change in between.

The gas-tightness/gas permeation tests were conducted with a setup made of Swagelok VCR[®] fittings. The setup is equipped with a high-precision pressure transducer (Mensor CPT6180) with reading uncertainty of 0.01%. A scheme of the setup is shown in Figure 3.4. All the connection joints of the setup were carefully tested to be leak-free. The GO hollow fibre was sealed on a stainless-steel sample holder with epoxy resin, and mounted into the gas chamber of the setup. The chamber was swept by the testing gas for 3 min to remove impurity gases, and then pressurized by the gas to a target pressure. The inlet and outlet of the chamber were

closed, leaving the GO hollow fibre membrane the only path for gas to leak/permeate. The pressure inside the gas chamber was monitored by the pressure transducer and was recorded by a computer.

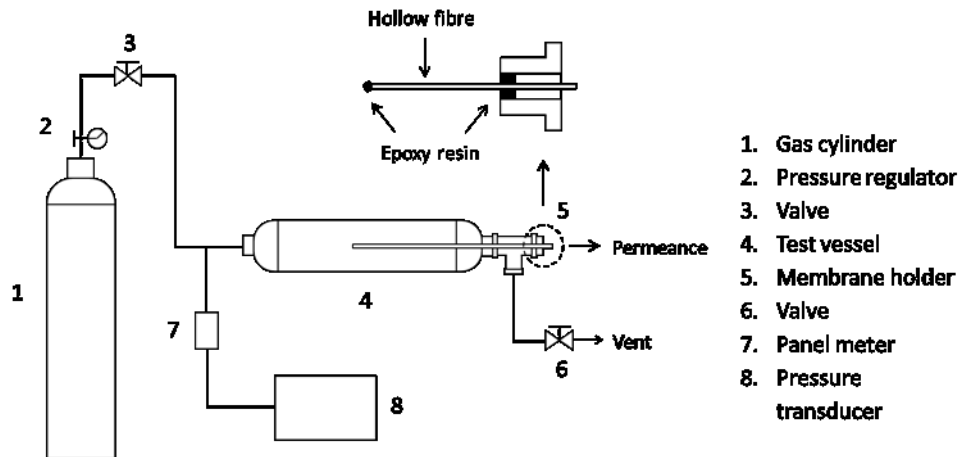


Figure 3.4: Scheme of the gas-tightness/gas-permeation setup used in this study.

The permeance of the gas through the membrane can be calculated using the pressure-drop rate recorded:

$$P = \frac{V}{\Delta p R T A} \times \frac{dp}{dt} \quad (3.3)$$

where P denotes the permeance ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$); V is the volume of the gas chamber (m^3); Δp is the pressure difference across the membrane (Pa), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$); T is the measured temperature (K); A is the membrane surface area (m^2); and dp/dt is the pressure drop rate.

3.3 Results and Discussion

3.3.1 Single layer stainless steel hollow fibres

Two types of stainless steel powders, SS430-L and SS316-L were used to fabricate the single-layer stainless steel hollow fibres. One of the major differences between these two types of stainless steel is the chemical composition; a significant amount of nickel is present in SS316-

L. In addition, the SS430-L and SS316-L powders used have different particle sizes, 15 and 3 μm , respectively. This enables us to study the effects of particle size on the membrane properties.

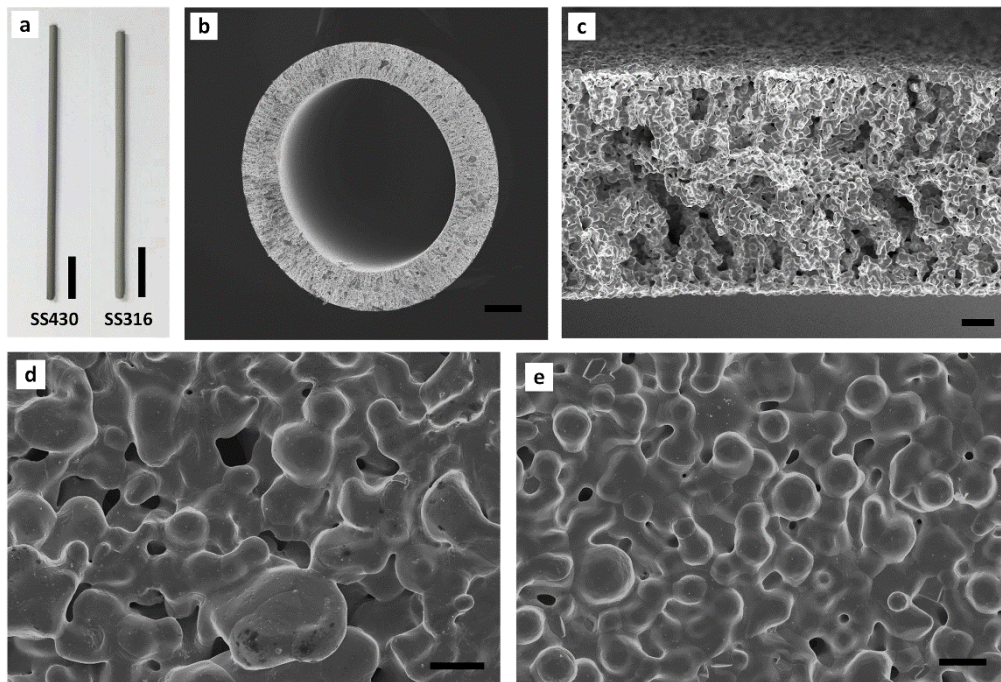


Figure 3.5: (a) Images of stainless steel hollow fibres. Left: SS430-L; Right: SS316-L; (b, c) SEM images of the cross-sections of SS316-L hollow fibres; SEM images of the surface morphology of stainless steel hollow fibres: (d) SS430-L; (e) SS316-L. (Scale bars: (a) 10 mm (b) 200 μm (c) 20 μm (d) 10 μm (e) 5 μm)

Figure 3.5(a) shows the pictures of the bare SS430-L and SS316-L hollow fibres after sintering and they looked similar in light grey. As the hollow fibres were highly porous, they are not as shiny as dense stainless steel. Minimum oxidation occurred during the sintering as it was often observed in previous literature that chromium oxide formed from oxidation would lead to a greenish surface [16]. The SEM images of the cross-section of the SS316-L hollow fibres are shown in Figure 3.5(b) and (c). The hollow fibre had a symmetrical round shape and with some finger-like micro-channels, similar to the micro-channels commonly observed in ceramic hollow fibres fabricated using a similar technique [21]. Overall, the hollow fibre still looked very porous and the thickness of the hollow fibre was as thin as 250 μm . Figures 3.5(d) and (e) show the surface morphologies of the SS430-L and SS316-L hollow fibres, respectively.

The stainless steel particles were very well sintered and formed a good network with each other. The stainless steel grain surface was also very clean and free of secondary oxide phases, which was very different compared to what has been reported in previous studies [15-17], implying minimum oxidation during the sintering. The low level of oxidation could also be confirmed from the electrical conductivity measurement. The SS316-L hollow fibre showed a high electrical conductivity, $1.16 \times 10^6 \text{ S m}^{-1}$, close to the standard literature value of $1.35 \times 10^6 \text{ S m}^{-1}$ for SS316-L [22].

A rapid cooling procedure was carried out in our study to avoid possible oxidation of stainless steel hollow fibres during the cooling process as stainless steel is prone to oxidation at temperature ranging from 650-1000 °C. At this temperature range, a very small amount of moisture (~100 ppm) could lead to serious oxidation [23]. Porous stainless steel components are even more sensitive to oxidation than dense components during the cooling process due to the porous microstructure and the large reactive surface area. In industrial practice, rapid cooling of sintered metal components is done by rolling the samples from the sintering zone to a quenching zone in an industrial furnace, which is similar to the process used in this study. As the stainless steel hollow fibres were sintered in an oxygen-free environment, carbonization of the polymer binder and thus the residual carbon could be a problem that hinders the particle sintering. Previously, commonly used polymer binder in the phase inversion process, polyethersulfone has been found difficult to be removed in an inert or reducing atmosphere [24], though it was suggested that H_2 atmosphere could remove carbon effectively at high temperature [16]. Carbonization on stainless steel particle surface could affect the mechanical strength of stainless steel hollow fibres as the carbon residue prevents necking between stainless steel particles and therefore leads to unsuccessful sintering. It was reported by Schmeda-Lopez et al. that the bending strength of stainless steel hollow fibres was much lower than what was expected as carbonization took place during the sintering process [25]. In this study, a different polymer binder, PMMA was used in the phase inversion process. PMMA was found to undergo thermal degradation easily at high temperature in both H_2 and inert gases, making them an excellent polymer binder for metal hollow fibres. The successful removal of polymer could be confirmed by the clean stainless steel surface and the good sintering between the stainless steel particles, as shown in the SEM images in Figure 3.5.

The mechanical properties of the stainless steel hollow fibres were studied using a three-point bending method. As illustrated in Figure 3.6, both the SS430-L and SS316-L hollow fibres showed impressive extensions and were very ductile, which is a typical behaviour of metallic materials and indicates oxidation-free sintering. Due to the limitation of the equipment used, the measurement could only be done accurately until an extension of about 5 mm and the samples did not fracture until the end of the test, therefore the true bending strengths were not obtained.

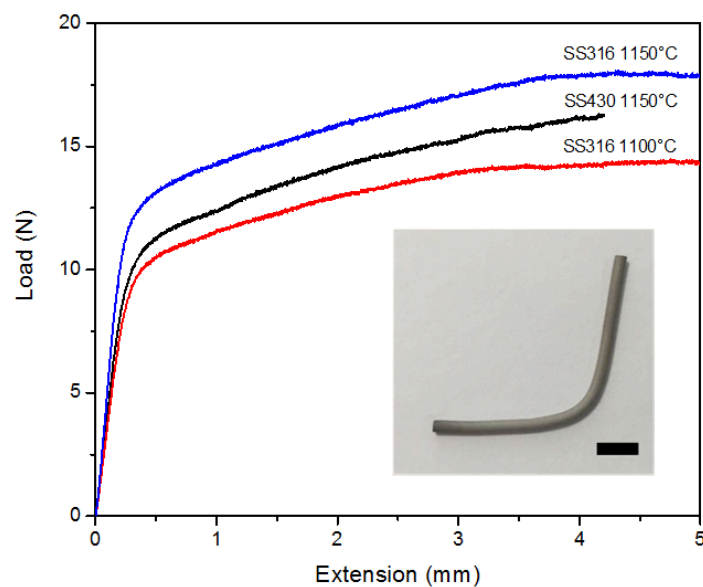


Figure 3.6: Extension-force bending curves of the stainless steel hollow fibres with different sintering temperatures. Insert: SS316-L hollow fibre sintered at 1100 °C after the bending stress test. (Scale bar: 5 mm)

Figure 3.6 (insert) also shows the picture of an SS316-L hollow fibre after the bending stress test. It did not fracture even after bending for more than 60 degrees. Although we could not obtain the actual bending strength of the stainless steel hollow fibres, it could be estimated by using the maximum loading shown in Figure 3.6 that the bending strength of SS316-L hollow fibres sintered at 1150 °C was higher than 431 MPa. SS316-L hollow fibres sintered at 1050 and 1100 °C also did not break at the end of the mechanical strength tests and showed a high bending strength >400 MPa. The bending strength was higher than what reported previously especially at a similar sintering temperature [16, 26]. This could be contributed by

sintering in a reducing H_2 environment in combination with rapid cooling. As the hollow fibres experienced a long extension, their yield strength was also calculated using the load at the yield point where non-linear deformation began. The yield strengths were 303.2, 290.4 and 262.0 MPa for stainless steel hollow fibres sintered at 1150, 1100 and 1050 °C, respectively. The yield strength of inorganic hollow fibres was seldom reported in the literature. However, the yield strength of the stainless steel hollow fibres in this study was higher than the bending strength of most ceramic hollow fibres reported.

The SS430-L hollow fibres sintered at 1150 °C showed a bending strength of 394 MPa and a yield strength of 267.9 MPa. They also had a good extension like the SS316-L hollow fibres. However, at lower sintering temperatures, 1050 and 1100 °C, the SS430-L hollow fibres broke during the bending tests after experiencing an extension of 1.5-2.0 mm. The larger SS430-L particles may require a higher temperature to achieve a good sintering. Furthermore, the ferritic SS430-L is also generally more brittle and has a lower tensile strength compared to the austenitic SS316-L [22].

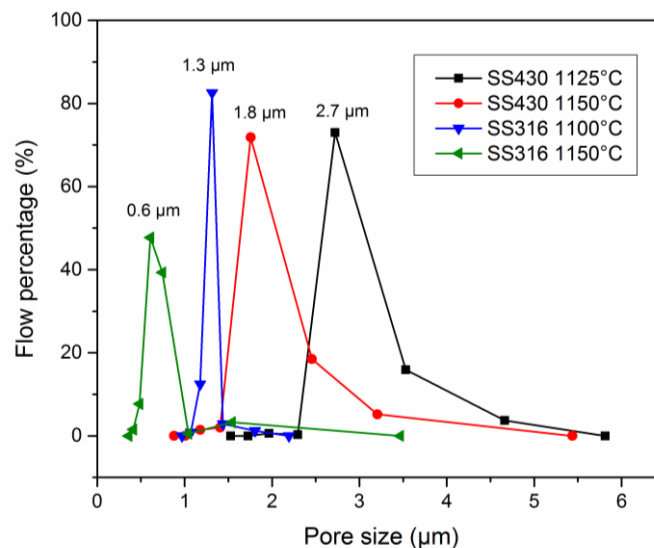


Figure 3.7: Pore size distributions of both types of stainless steel hollow fibre membranes sintered at different temperatures.

The pore size of stainless steel hollow fibres was measured using gas-liquid displacement and the pore distributions are shown in Figure 3.7. The pore size was affected significantly by the sintering temperature. For example, the SS430-L hollow fibres sintered at 1125 °C had a peak

pore size of 2.7 μm and the pore size reduced to 1.8 μm when the sintering temperature was increased to 1150°C. The SS430-L hollow fibres also showed a broad pore distribution, with a large bubble point pore size > 5 μm . By changing the stainless steel powder to SS316-L which has a smaller particle size (4 μm compared to 15), the pore size of the hollow fibre was reduced to 1.3 μm . The pores also showed a narrower distribution, with a flow percentage higher than 80% at the peak pore size. Though the pore size of stainless steel hollow fibres was much reduced, it was still bigger than 1 μm , similar to all the previous studies [16, 17, 26]. In order to be suitable for thin film coating and most microfiltration applications, the reduction of mean pore size down to the sub-micron level, and a bubble point pore size smaller than 1 μm are desired. By further increasing the sintering temperature to 1150°C, the mean pore size of SS316-L hollow fibres could be further reduced to about 600 nm, but the bubble point pore size was still bigger than 1 μm . Additionally, the porosity of the hollow fibre was also reduced significantly at such high sintering temperature, and the pure water flux was very much decreased, as shown later.

3.3.2 Dual layer ceramic stainless steel hollow fibres

The large pore size of SS hollow fibres is mainly due to the large stainless steel particles used in fabricating the hollow fibres. Higher sintering temperature and longer sintering time may reduce the mean pore size. However, these conditions will also densify the membrane and decrease the porosity of the hollow fibres drastically. The pore size of stainless steel hollow fibres may be reduced by using stainless steel particles in sub-micron size. However, stainless steel powder in submicron size is not readily available and costly. Besides, the sintering process can be difficult to control if the particles size used is too small as sintering of fine metal particles is generally very fast at high temperature and densification may occur in a short time, leading to very tight windows of sintering temperature and time.

In order to reduce the pore size of stainless steel hollow fibres, nano-sized YSZ particles are introduced in this study to fill up the large voids between stainless steel particles, as illustrated in Figure 3.8. YSZ powder with a particle size ranging between 30-60 nm was used in our study. The nanoparticles are significantly smaller than the stainless steel particles and the large voids formed in stainless steel hollow fibres. The YSZ particles in the voids will reduce the effective

pore size of stainless steel hollow fibres while still retaining the porous microstructure in the hollow fibres. Nano-size ceramic powders are commercially available at an affordable price and have been commonly used to produce ceramic hollow fibres with pore size in the submicron range [10]. In this study, dual-layer SS/SS-YSZ composite hollow fibres were fabricated using a one-step co-extrusion method. The inner layer was purely SS316-L, which provided the hollow fibre with good mechanical strength. The outer layer was a mixture of YSZ and SS316-L, creating a separating layer for the hollow fibres with a reduced pore size.

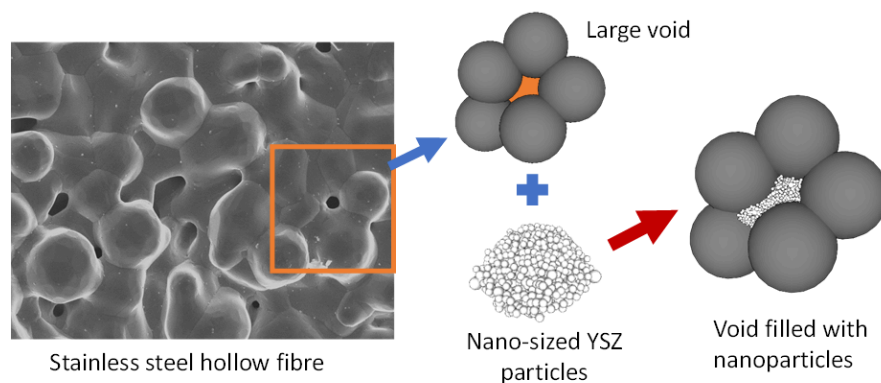


Figure 3.8: Working principle of the introduction of YSZ nanoparticles into the stainless steel hollow fibres.

To choose the proper sintering temperature for the dual-layer SS/SS-YSZ hollow fibres, the sintering behaviours of the SS316-L and YSZ powders were first investigated using the dilatometer (Figure 3.9). The YSZ sample started to sinter at about 900 °C and the shrinking rate reached the maximum at 1150 °C, while the SS316-L sample started to sinter at about 1000 °C and the shrinking rate reached the maximum at 1160 °C. It should be noted that though the shrinking rate of the stainless steel sample shown in Figure 3.9 was much lower than the YSZ sample, it does not necessary indicate a much smaller shrinkage of stainless steel in the hollow fibre samples during sintering. This is because the ductile stainless steel particles could be deformed during the sample preparation for the dilatometry as a very high pressure (240 MPa) was used. The voids between stainless steel particles could have been reduced, leading to a much lower initial porosity than the YSZ sample and thus a lower shrinking rate during the test. From the dilatometry results, it was decided that sintering temperatures

ranging from 1000 to 1150 °C should be investigated to obtain hollow fibres with a strong mechanical strength whilst keeping the porosity.

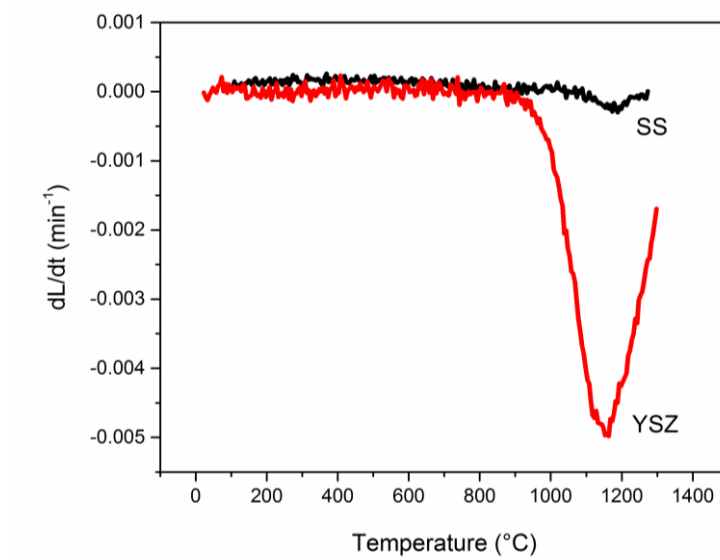


Figure 3.9: Sintering behaviours of the SS316-L and YSZ powders.

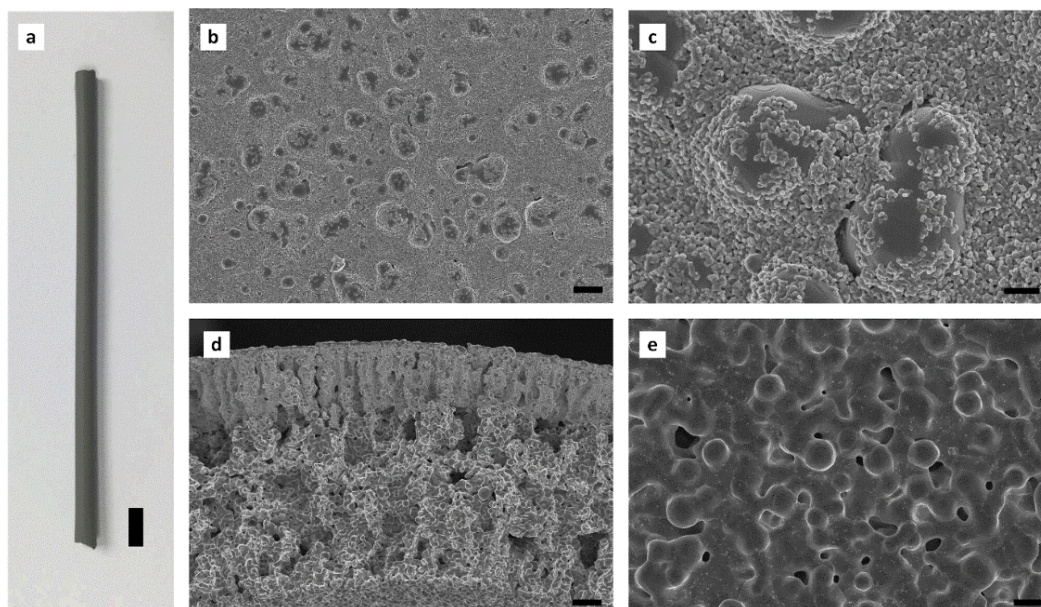


Figure 3.10: (a) Image of a dual-layer SS/SS-YSZ hollow fibre. SEM images of the morphology of the SS/SS-YSZ hollow fibres: (b, c) Outer surface (d) cross-section and (e) inner surface. (Scale bars: (a) 5 mm (b) 4 µm (c) 1 µm (d) 20 µm (e) 4 µm)

Figure 3.10(a) shows the image of a dual-layer SS/SS-YSZ hollow fibre after sintering. The hollow fibre looked slightly greyish compared to the single-layer SS316-L hollow fibres due to the presence of YSZ particles. The SEM images of the outer surface of the composite hollow fibres are shown in Figure 3.10(b) and (c). It can be seen that the stainless steel particles were distributed evenly on the surface, showing a homogenous mixing between the stainless steel and YSZ phases. The large stainless steel particles were surrounded by well packed YSZ particles. As the sintering between these two materials are minimal, small gaps might be observed near the surface of stainless steel particles, which may have contributed to the bubble point pores. However, since the thickness of the outer layer is approximately 40 μm , the continuous phase of YSZ could still provide a good pore distribution to the hollow fibres. Figure 3.10(d) shows the cross-section of the dual-layer hollow fibres and it can be noticed that the two layers are very well attached. Ceramic materials such as YSZ generally have a weak adhesion with metal surfaces even after sintering. A dual-phase outer layer containing the stainless steel phase was designed to enforce the integration between the two layers. The stainless steel phase was used to bridge the two layers, meanwhile the YSZ and stainless steel phases were entangled in the outer layer, imposing a mechanical interaction to bind the ceramic phase with the metallic phase. The volume percentage ratio of stainless steel to YSZ in the outer layer was 65:35, assuring a strong continuous framework of stainless steel, with YSZ particles filled in the void of the framework. The electrical conductivity of the dual-layer SS/SS-YSZ hollow fibres reduced to $5.58 \times 10^5 \text{ S m}^{-1}$, which was about 50% lower than the single-layer stainless steel hollow fibres. The lower conductivity could be caused by the resistance from the YSZ phase. But the dual-layer hollow fibres were still very conductive, demonstrating a good connectivity between the stainless steel particles in the hollow fibres. They may also be useful for electroplating application. Some finger-like microstructures were also observed as the result of the phase inversion process. The SEM image of the inner surface of the hollow fibres is shown in Figure 3.10(e). The stainless steel particles were well sintered and they look similar to what observed in the single-layer stainless steel hollow fibres.

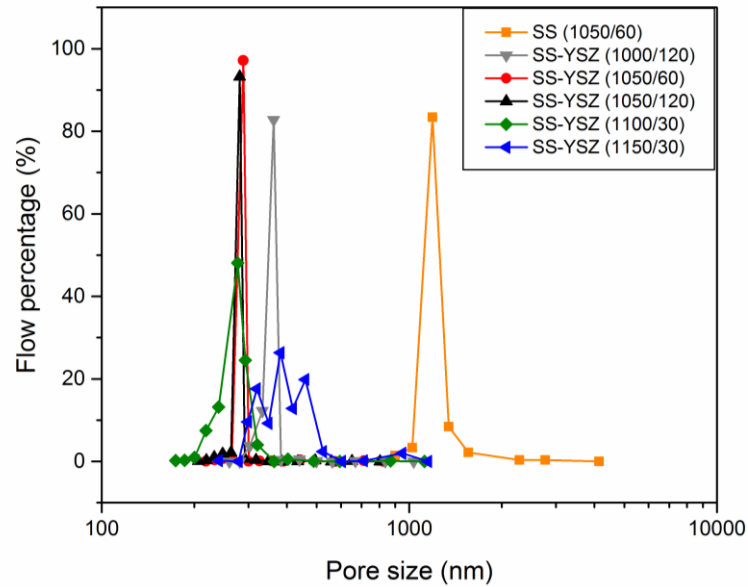


Figure 3.11: Pore size distribution of SS/SS-YSZ hollow fibres with different sintering conditions (temperature (°C)/ time (min)). The mean pore sizes were reduced significantly by introducing a second layer with the incorporation of YSZ particles.

The pore size distributions of the dual-layer SS/SS-YSZ hollow fibres were measured and the results are shown in Figure 3.11. At sintering temperature 1000 °C, the mean pore size of the hollow fibres was reduced to 370 nm. The YSZ phase did not only reduce the mean pore size, but also gave a narrower pore size distribution and a smaller bubble point pore size. The mean pore size of the hollow fibres continued to reduce to 289 nm when the sintering temperature was increased to 1050 °C. However, the pore size did not change much with a longer sintering time as it only reduced to 281 nm when the sintering time was increased from 1 to 2 h at sintering temperature 1050 °C. Sintering of YSZ may be more sensitive to sintering temperature than sintering time. The hollow fibres had a very narrow pore size distribution at sintering temperature 1050 °C with more than 90% flow at the peak pore size. Similar mean pore size, 288 nm was determined at sintering temperature 1100 °C, but with a broader pore size distribution. However, when the sintering temperature was further increased to 1150 °C, the mean pore size did not further decrease but increased to 418 nm, and the pore size distribution became broader. It is worth mentioning that the small gaps observed between the stainless steel phase and the YSZ phase (Figure 3.10(c)) might have contributed to the broader pore size distributions. The effect may not be significant when the flow through the gaps is much smaller compared to the flow through the porous YSZ phase. However, for the

hollow fibres sintered at 1150 °C, the porosity of the YSZ phase was considerably reduced, as indicated by the dilatometry result in Figure 3.9, and the flow contribution from the gaps became more significant, leading to an increase in the mean pore size. The gaps could be potentially narrowed by changing the volume ratio between the stainless steel and YSZ phases, though other properties such as the permeation flux may also be affected. Overall, the introduction of YSZ phase has reduced the pore size of stainless steel hollow fibres significantly, making them very promising for microfiltration applications.

The pure water permeation of SS/SS-YSZ hollow fibres was tested and the results are shown in Figure 3.12. At low sintering temperatures of 1000 and 1050 °C, the hollow fibres showed high water fluxes of about 3500 and above 2500 LMH bar⁻¹, respectively. The SS/SS-YSZ hollow fibres showed a relatively high permeation flux compared to most of the inorganic hollow fibres of similar pore sizes, as shown in Table 3.3. This could be due to the porous structure of the SS/SS-YSZ hollow fibres especially in the inner stainless steel layer. The water permeation of single-layer stainless steel hollow fibres could be as high as 17500 LMH bar⁻¹, indicating a low permeation resistance in the inner layer of SS/SS-YSZ hollow fibres. The introduction of the YSZ particles reduced the pore size but retained a high water flux as the YSZ phase was still highly porous. Besides, there are also some finger-like microstructures in the outer layer of the SS/SS-YSZ hollow fibres which could have enhanced the mass transfer in the membranes. The water flux of SS/SS-YSZ hollow fibre was affected significantly by the sintering temperature and decreased to 1420 LMH bar⁻¹ at the sintering temperature of 1100 °C. The water flux was only 213 LMH bar⁻¹ at the sintering temperature of 1150 °C. The low flux could be caused by the high sintering rates of both stainless steel and YSZ particles at high temperatures. As observed in the single-layer SS316-L hollow fibres, the water flux decreased to about 7200 LMH bar⁻¹ at sintering temperature of 1100°C, and to only about 3100 LMH bar⁻¹ at 1150°C. Higher sintering temperature did not change the pore sizes of the stainless steel layer considerably but reduced the porosity significantly as reflected from the water permeation flux. Rui et al. showed in their study that the porosity of stainless steel hollow fibres decreased from 35 to 15% when the sintering temperature was increased from 1100 to 1150 °C [16]. And a further increase in the temperature will lead to a formation of dense stainless steel hollow fibres as reported by Luiten-Olieman et al. [14]

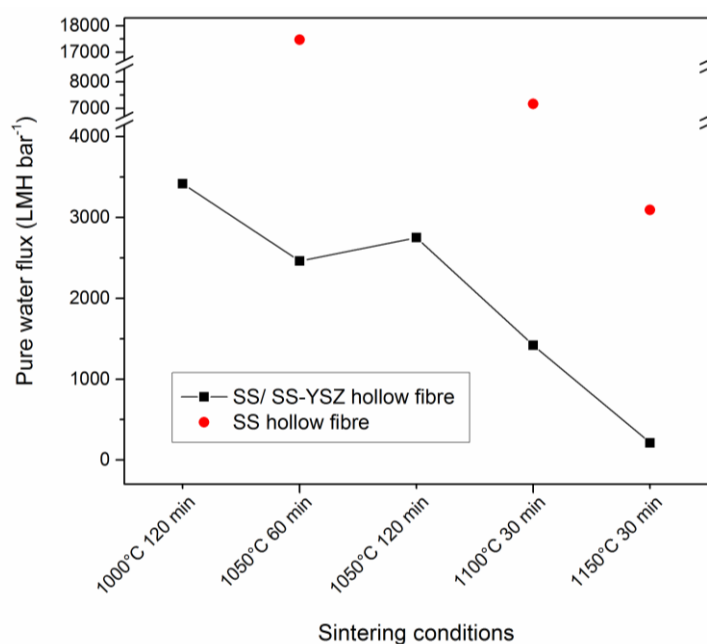


Figure 3.12: Pure water permeation fluxes of SS316-L and SS/SS-YSZ hollow fibres.

The sintering temperature also imposed significant changes in the outer layer of the SS/SS-YSZ hollow fibres. The SEM images of the YSZ phase on the outer layer are shown in Figure 3.13. It can be noticed that small YSZ nanoparticles became larger with diameter slightly larger than 100 nm after sintering. At sintering temperature 1000 and 1050 °C, the surface was still very porous and this could have contributed to the high water flux of SS/SS-YSZ hollow fibres sintered at this temperature range. Note that the YSZ particles formed very limited necks with each other at sintering temperature 1000 °C. The loosely packed particles could also explain the larger mean pore size of the SS/SS-YSZ hollow fibres sintered at this temperature as shown previously. When the sintering temperature was higher (1100 and 1150 °C), the YSZ particles formed a denser surface, leading to a low water permeation flux. At 1150 °C, the surface was so dense that only small amount of pores can be observed, which explains the low water permeation flux. Besides, longer sintering time did not affect the water permeation of the SS/SS-YSZ hollow fibres significantly as shown in the case at sintering temperature 1050 °C (Figure 3.12). This makes the sintering easy to control as they are relatively insensitive to sintering time.

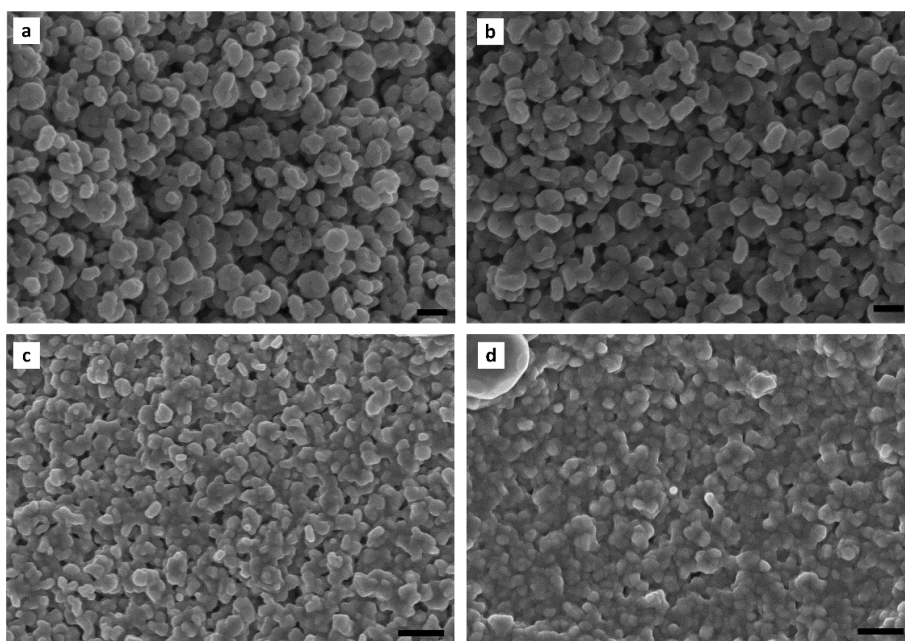


Figure 3.13: Surface morphology of YSZ phase on the SS/YSZ-SS hollow fibres with different sintering conditions: (a) 1000 °C 120 min; (b) 1050 °C 120 min (c) 1100 °C 30 min (d) 1150 °C 30 min. (Scale bars: (a, b) 200 nm (c, d) 500 nm)

3.3.3 Graphene oxide membranes on SS/SS-YSZ hollow fibre substrates

From the high water permeation flux, both stainless steel and SS/SS-YSZ hollow fibres demonstrated a low mass transfer resistance, an important requirement for membrane substrates. However, due to the large surface pore size $>1\ \mu\text{m}$, single layer stainless steel hollow fibres were not suitable serving as a substrate of thin GO membranes. Therefore, only the dual-layer SS/SS-YSZ hollow fibres were used in synthesizing GO hollow fibre membranes.

Figure 3.14 showed an SEM image of the GO flakes synthesized by the modified Hummer's method and the size of the GO flakes ranged from 5-10 μm . Vacuum filtration was used to fabricate the GO hollow fibre membranes and the surface of the SS/SS-YSZ hollow fibre turned brown after GO coating as shown in Figure 3.15(a). Figure 3.15(b) shows an SEM image with both the surface of the substrate and the GO coating layer. The specimen was obtained from fracturing the GO hollow fibre when preparing the SEM sample, where part of the GO layer peeled off. The image indicates a weak adhesion between the GO membrane and the substrate. The thickness of the GO layer was approximately 250 nm, as shown in Figure 3.15(c).

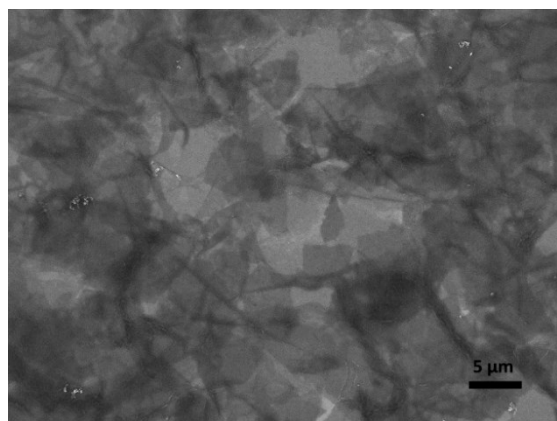


Figure 3.14: SEM image of GO flakes synthesized using the modified Hummer's method

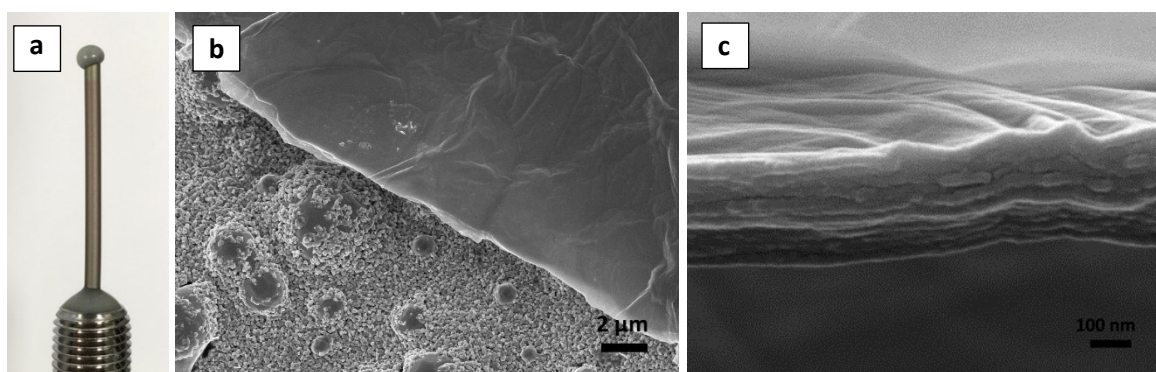


Figure 3.15: (a) Image of GO/SS-YSZ/SS hollow fibre membrane. (b) SEM image of the surface of GO hollow fibre membrane. Upper part: GO layer; Lower part: hollow fibre substrate. (c) Cross-section of GO layer of the hollow fibre membrane

The GO hollow fibre was tested for gas permeation. Ultrathin GO membranes with thickness less than 20 nm were found having a high hydrogen permeation by Li et al. [1] However, thick GO membranes with thickness of about 1 micron were impermeable to all gases including He, as demonstrated by Nair et al. [27] Though these studies showed two extreme cases of GO membranes, the gas permeation would still be a good indication of the quality of the GO membrane layer coated on the hollow fibres. The permeation test was conducted with nitrogen on Day 1, followed by helium on Day 2 and nitrogen again on Day 5. The results of the gas permeation are shown in Figure 3.16.

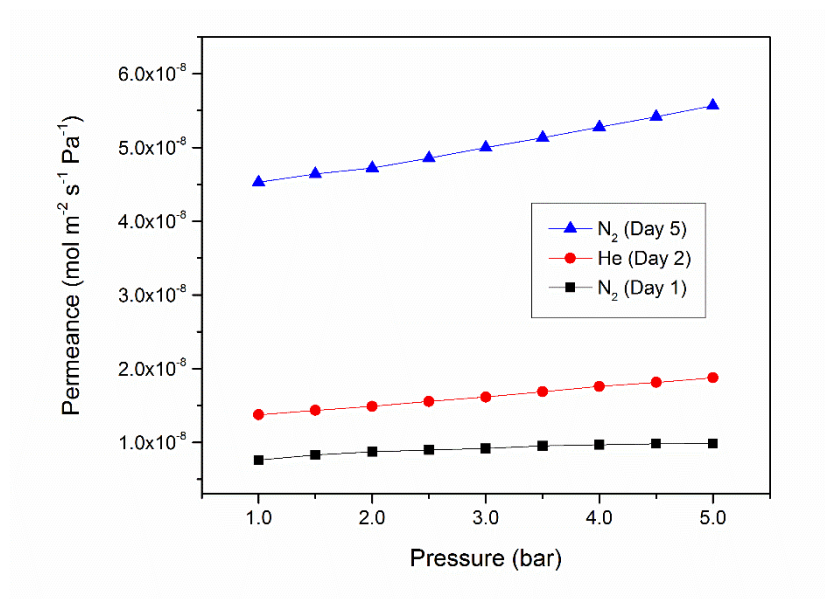


Figure 3.16: The results of gas permeation of a GO/SS-YSZ/SS hollow fibre. The tests started with nitrogen and then followed by helium. The permeation of nitrogen was repeated after 5 days to test the stability of the coating layer.

The GO hollow fibre membrane showed a nitrogen permeance lower than $1 \times 10^{-8} \text{ mol m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ on Day 1, with a slight increase with the pressure difference. When tested with helium on Day 2, the permeance was higher than the nitrogen permeation flux. However, the average He/N₂ selectivity was only about 1.8, which was lower than the calculated Knudsen selectivity, 2.6. Though with a considerable gas permeance, the GO hollow fibre membrane did not show a molecular sieve property. As reported by Li et al. and Chi et al., GO membranes could have an incredibly high selectivity between He and N₂ of more than 1000 [1, 2]. The low selectivity of GO membranes observed in our study could be due to the presence of defects in the membranes, as a result of imperfect coating of the GO layer on the hollow fibre substrates. AAO substrates with a smooth surface were used in those two studies where the high selectivity of He was obtained. The surface roughness of the hollow fibre used in this study may have affected the coating of the thin GO membrane.

The N₂ permeation test was repeated after 5 days to study the stability of the GO layer and the permeance was found increased more than 5 times compared to the permeance on the first day. The permeance also increased noticeably with the increase in pressure, which indicated a viscous flow pattern as a result of the presence of large pores or defects in the

membranes [8]. The results showed a strong evidence of the change in microstructure of GO membranes over time. The stability of GO membranes on hollow fibres will be further studied and discussed in the next chapter.

In summary, the dual-layer hollow fibres may not be suitable serving as a substrate for thin graphene-based membranes mainly due to the surface morphology. Though the YSZ phase of the hollow fibre surface had a high homogeneity (Figure 3.10), the overall dual-phase surface looked slightly rough (Figure 3.7) due to the presence of large stainless steel particles. The hollow fibres also showed bubble point pore sizes larger than 800 nm, which might affect the coating of thin GO layer. Nevertheless, the SS/SS-YSZ hollow fibres still showed great potential for other applications such as microfiltration as they exhibited a high water permeation flux.

3.3.4 Dual layer ceramic stainless steel hollow fibres in microfiltration

To further investigate the potential of the dual-layer SS/SS-YSZ hollow fibres in microfiltration application, a fouling test was carried out with BSA solution using a sample sintered at 1050 °C for 120 min. In the beginning of the test, the hollow fibre membrane showed a very high water flux of about 3000 LMH bar⁻¹, as shown in Figure 3.17. However, when the circulation liquid was changed to BSA solution, the flux reduced drastically to about 450 LMH bar⁻¹. The flux continued to drop to only 280 LMH bar⁻¹ after 30 min. The reduction of flux to only about 10% of the initial flux was commonly observed in microfiltration membranes [28]. The drop in flux is also normally more serious for membranes with a high permeation flux as shown in previous studies [29]. After backwashing using clean water at 3 bar, the water flux of the hollow fibre was recovered to about 1000 LMH bar⁻¹ in the second cycle, and about 800 LMH bar⁻¹ in the third cycle. The recovered water flux was only about a third of the initial flux in the first cycle, which could be due to some irreversible fouling. However, it was noticed that the water flux increased gradually over time during the pure water permeation test in cycles 2 and 3. Some of the foulant on the surface and in the pores may have been further washed off during the permeation test. Considering flux recovery is closely related to the cleaning protocol, more effective cleaning protocols that take advantage of the inert membrane property can be derived. For example, the use of high temperature steam or more aggressive cleaning agents can be considered.

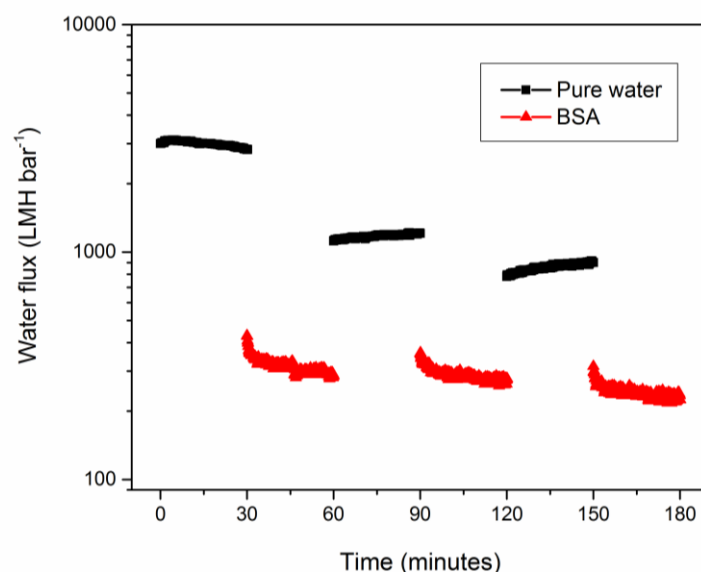


Figure 3.17: BSA fouling test result of a SS/SS-YSZ hollow fibre (1050 °C 120 min). Permeation flux during three cycles of pure water/BSA solution permeation tests. The operating pressure difference was 1 bar, and the membrane was backwashed with clean water after each BSA solution test.

Table 3.2: Mechanical strength of SS316-L and SS/SS-YSZ hollow fibres with different sintering temperatures

Sintering temperature (°C)	Sintering time (min)	SS hollow fibres		SS/SS-YSZ hollow fibres	
		*Bending strength (MPa)	Yield strength (MPa)	Bending strength (MPa)	Yield strength (MPa)
1050	60	414.0 ±13.6	262.0 ±8.4	212.7 ±10.8	194.1 ±16.9
1100	30	420.4 ±17.1	290.4 ±13.5	237.3 ±18.7	217.8 ±19.3
1150	30	431.2 ±13.3	303.2 ±9.3	279.8 ±12.1	235.7 ±9.8

* As SS hollow fibres were not fractured at the end of the bending test, the bending strength shown in the table was calculated based on the maximum load during the test. The real bending strength is believed to be higher than the value shown in the table.

The mechanical strength of the dual-layer SS/SS-YSZ hollow fibres was studied. As shown in Table 3.2, the bending strength of the hollow fibres ranges between 213-280 MPa. The bending strength were calculated based on the maximum load when the fibres fractured. The yield strength of the fibres was also calculated based on the load at the yield point where the

deformation began. The dual-layer hollow fibres are not as strong as the single-layer SS316-L hollow fibres, which could be due to the lower stainless steel loading on the outer layer. Both the mechanical strength and the permeation flux can be further improved by reducing the thickness of the outer layer, as the strong mechanical properties are mainly contributed by the inner stainless steel layer, while the permeation resistance is mainly from the outer separating layer.

However, the mechanical properties of SS/SS-YSZ hollow fibres are still considerably higher compared to other inorganic hollow fibres with similar pore sizes (Table 3.3). Alumina hollow fibres generally showed a bending strength lower than 100 MPa in order to achieve a water permeation flux higher than 1000 LMH bar⁻¹. Multichannel ceramic hollow fibres showed an improved fracture load with a larger cross-sectional area, but it is difficult to compare their mechanical strength without the bending strength information. Other than the bending strength and fracture load, the dual-layer SS-YSZ hollow fibres experienced an extension of 0.5-1.5 mm before fracture, a ductile property that is seldom observed in ceramic hollow fibres and would significantly reduce the chance of failure in practice.

Commercial stainless steel tubular membranes, for example, the FerroCep® tubular membranes produced by Hyflux Ltd. [30] have an outer diameter of 21.5 mm, which is about 10 times larger than the SS/SS-YSZ hollow fibres produced in our study. The SS/SS-YSZ hollow fibre membranes will therefore provide a significantly larger membrane area at the module level. The inner surface of the FerroCep® tubular membranes are coated with a titanium oxide layer, serving as a separating layer. From the water flux per module information and the module dimension available online, the water flux was estimated to be about 1200 LMH bar⁻¹. In general, the SS/SS-YSZ hollow fibres can serve the same purpose as the commercial stainless steel tubular membranes, but with a higher permeation flux and a larger membrane area to volume ratio.

Table 3.3: Comparison of performance of inorganic hollow fibres with pore size smaller than 1µm

Membranes	Mean pore size (nm)	Water flux (LMH bar ⁻¹)	Bending strength (MPa)	Fracture Loading (N)	Span (mm)	Ref.
SS/SS-YSZ hollow fibres (This work)	324	213	279.8 (235.7*)	32.8 (27.9**)	25	
	288	1420	237.3 (217.8*)	27.8 (25.6**)	25	
	294	2460	212.7 (194.1*)	23.0 (21.0**)	25	
Alumina hollow fibre	280-500	550	100			[24]
	180	<100	150			
Alumina hollow fibre	100	1069	58.3			[21]
	100	1874	41.8			
	100	997	39.7			
Alumina hollow fibre	288	2486				[31]
	384	4043				
	422	5183				
4-Channel Al ₂ O ₃ capillary tube	520	790		19.5	40	[32]
	600	840		24.0	40	
7-Channel Al ₂ O ₃ capillary tube	183	1550		9.8	60	[12]
	183	1070		14.3	60	
7-Channel YSZ/Al ₂ O ₃ capillary tube	235	1642		22.9	60	[33]
SiC hollow fibre	500	1200	~43			[34]

Note: *Yield strength and **loading at yield point

3.4 Conclusions

Stainless steel hollow fibre membranes with impressive mechanical strength were prepared by applying vacuum and rapid cooling in the sintering process. The SS316-L hollow fibres showed an extension longer than 5 mm and had a bending strength higher than 400 MPa. The high pure water flux demonstrated the highly porous microstructure in the single-layer stainless steel hollow fibres. Dual-layer SS/SS-YSZ hollow fibres have been successfully

fabricated using a one-step co-extrusion phase-inversion process. By introducing YSZ nanoparticles in the outer layer, the mean pore size of stainless steel hollow fibres has been successfully reduced to about 300 nm. The SS/SS-YSZ hollow fibres showed a high water permeation flux compared to many inorganic hollow fibres with similar pore sizes. The dual-layer hollow fibres also demonstrated excellent mechanical properties compared to ceramic hollow fibres, showing great potential for scale-up applications. Though the hollow fibres is attractive for application such as microfiltration, their usage as substrates for thin film graphene-based membranes may be challenging due to the inhomogeneous surface as the surface roughness is of paramount for thin film coating.

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Chapter 4: Sacrificial-layer stabilised graphene oxide hollow fibre membranes for nanofiltration

Abstract:

Graphene oxide (GO) membranes have demonstrated great potential in gas separation and liquid filtration. For large scale applications, GO membranes in a hollow fibre geometry are of particular interest due to the high-efficiency and easy-assembly features at module level. In this chapter, GO membranes were fabricated on ceramic hollow fibre substrates. However, GO membranes were found unstable on hollow fibre substrates in dry state, due to a shrinkage process during drying. The stability problem was overcome by introducing a polymer sacrificial layer between the GO membrane and the substrate, which created a space to allow stress-free shrinkage. Defect-free GO hollow fibre membranes were very stable in air, however they showed a low water permeation flux when tested in nanofiltration. To improve the membrane performance, GO hollow fibre membranes were post-treated with UV radiation, which was found to create microstructural defects in the membranes. The microstructural defects served as shortcuts for liquid permeation and the UV-treated GO membrane showed enhanced pure water and acetone permeation fluxes of 2.8 and 7.5 L m⁻² h⁻¹ bar⁻¹, respectively.

4.1 Introduction

Graphene oxide (GO) membranes have demonstrated great potential as effective separation barriers in environmental and chemical engineering applications [1-5]. With the large number of oxygenated surface functional groups and the high area-to-thickness ratio, GO flakes can be assembled to form multilayer thin films or membranes by stacking on top of each other in parallel [6, 7]. Although GO membranes thicker than 1 µm were found to be impermeable to gases including helium [5], GO membranes as thin as a few tens of nanometres were shown to have high gas permselectivity at considerable fluxes [3, 4]. GO membranes have also shown potential in aqueous solution nanofiltration to retain molecules with molecular weights of several hundred Dalton [8-10], and have been tested for pervaporation to separate water from organic solvents [11, 12]. Water molecules were found to be able to travel fast within

the interlayer space between GO flakes, and the separation of molecules in GO membranes was proposed to be due to the interlayer distance between the GO laminates [5, 13].

Although GO membranes have shown great potential in separation processes, it is still far from real industrial applications due to unsolved engineering problems. In practice, ultrathin GO membranes need to be supported on a substrate for large scale applications to withstand high pressure difference across the membrane. So far, planar polymeric or ceramic supports have been used for GO membranes in most laboratory studies [3, 4, 9], but they are difficult for mass production and their membrane area to volume ratio is limited. Towards engineering perspectives, much effort has been put on preparing GO membranes on hollow fibre supports, often with a diameter of 1 mm or smaller, in order to achieve the highest membrane area to module volume ratio (up to 9000 m²/m³).

Inorganic hollow fibres are excellent candidates due to their robust mechanical properties and inert chemical nature, which enable them to work under extreme conditions. Stainless steel (SS) and SS/ceramic composite hollow fibres have been developed in Chapter 3 to further improve the mechanical strength of inorganic hollow fibres. Though the SS/ceramic hollow fibres showed enhanced mechanical strength, the inhomogeneous surface morphology may be not be suitable for thin film coatings. Therefore, ceramic hollow fibres with a smooth surface morphology were used in this chapter. Recent research also revealed that ceramic substrates released multi-valent cations, which could help to crosslink GO flakes and stabilized GO membranes in water; GO membranes prepared with polymeric substrates, in contrast, were unstable in water [14]. The use of GO/ceramic hollow fibre composite membranes was recently reported for dehydration of dimethyl carbonate and for nanofiltration [12]. However, our recent research revealed that supported GO membranes are unstable in dry state, at least on ceramic hollow fibre substrates [15]. This is due to the shrinkage generated during drying, which produces enormous tensile stress in the GO membrane and leads to defects. To tackle the instability problem, GO hollow fibre membranes can be reserved in water after initial drying to avoid further shrinkage, so that fatal defects can be prevented. Such a strategy was shown to work well, but the resultant membranes could only be used for limited wet separation processes such as nanofiltration and pervaporation. Besides, tailoring GO membranes via post-treatments for different purposes would be difficult since many post-treatments are only possible in a dry

environment. Thus, effective approaches to stabilise GO hollow fibre membranes in dry state are needed to expand the applications of GO membranes.

This chapter presents an effective approach to solve the stability problem by using a sacrificial layer during the membrane fabrication. The sacrificial layer is used to create extra space between the ceramic hollow fibre substrate and the GO membrane. When the sacrificial layer is washed off, the resultant gap in between allows the GO membrane to shrink freely without introducing stress.

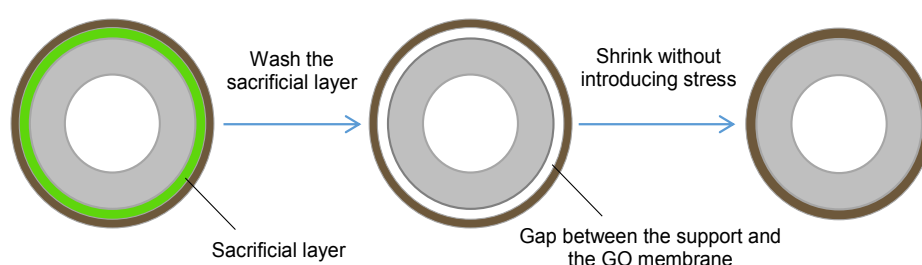


Figure 4.1 the working principle of the use of sacrificial layer to stabilise GO membrane on a hollow fibre substrate.

The idea is schematically shown in Figure 4.1. With the improved stability of the GO membrane, potential post-treatments can then be carried out to alter the properties of the membranes. This chapter also presents UV treatment as an example of post-treatment on the stabilized GO hollow fibre membranes. The UV post-treatment was found to create microstructure defects in GO membranes which subsequently improved the water and solvent permeation of the membranes.

4.2 Experimental

4.2.1 Preparation of graphene oxide hollow fibre membranes

GO suspension was synthesized using a modified Hummer's method, as described in Chapter 3. The GO suspension was centrifuged to control the size of GO flakes, which was determined to be 5 – 10 μm from SEM. The GO dispersion was diluted to a concentration of 0.1 g L⁻¹ and

was used for coating of GO membranes. Yttrium stabilised zirconia (YSZ) hollow fibres were used as substrates for the deposition of GO membranes. The YSZ hollow fibre were fabricated through a combined phase-inversion/sintering process, and the green fibres were sintered at 1150 °C to gain mechanical strength [16]. GO membranes were deposited on the surface of hollow fibres via vacuum filtration and the details were described in Chapter 3. The thickness of the GO membrane was controlled by changing the initial concentration of the GO dispersion and the duration of filtration.

4.2.2 Preparation of sacrificial stabilized GO hollow fibre membranes

Poly(methyl methacrylate) (PMMA) was used as the sacrificial layer. To prepare GO hollow fibre membranes with a sacrificial layer, the YSZ hollow fibre substrate was first coated with a PMMA solution (15 wt% PMMA in N-Methyl-2-pyrrolidone) by dip-coating at controlled dipping and withdrawing rates. The coated polymer solution layer was then immersed into water to form a porous polymer layer via a phase-inversion process. A GO membrane layer was then deposited onto the PMMA layer through the same method as described in Section 4.2.1. After initial drying in ambient air for 15 min, the GO/PMMA/YSZ hollow fibre was immersed into ethanol to extract water and form connections between the GO flakes. Then, the hollow fibre was immersed into acetone for at least 2 h to leach the PMMA layer. After drying in ambient air, the GO hollow fibre membrane was assembled on a stainless steel holder for tests.

4.2.3 Material characterization

The morphology of the membranes was observed by a scanning electronic microscope (LEO Gemini 1525 FEGSEM). The surface morphology was also characterized by a Bruker Innova Atomic Force Microscope in a tapping mode. XRD (XRD, X'pert Pro PANalytical) was used to determine the average interspace between GO flakes in GO membranes. The water contact angle of GO membranes was measured using a drop shape analyzer (DSA 10 MK2, Krüss GmbH, Hamburg, Germany).

Flat GO membranes on polyethersulfone (PES) substrate were used, instead of hollow fibres, in XRD, water contact angle measurement and AFM to ensure accurate diffraction angle and water contact angle measurements, and a more uniform surface for AFM scanning. The flat sheet membranes were synthesized using the same vacuum-facilitated filtration method on a Supor® PES microfiltration membrane, with a pore size of 0.2 µm.

4.2.4 Membrane performance tests

The gas-tightness/gas permeation of GO membranes were tested using a pressure-drop setup as shown in chapter 3. Briefly, the GO hollow fibre membrane was inserted into a pressurized gas chamber and the gas permeation was determined by monitoring the pressure change in the chamber while gas permeating through the membrane.

The nanofiltration dye-rejection tests were conducted using a dead-end mode as shown in Chapter 3. The GO hollow fibre membrane was mounted into a sample cylinder, in which a dye water solution was filled and pressurized to 5 bar. The permeate through the membrane was collected and analysed after the initial 24 hours to avoid possible interference from the adsorption on GO flakes. The dye concentration of the feed and the permeate were determined by a UV-spectrometer (UV-2101PC, Shimadzu), and the rejection is calculated through the definition below:

$$R_{Dye} = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (3.1)$$

where R_{Dye} is the rejection of the GO membrane to the dye, c_p and c_f are the concentrations of the permeate and the feed, respectively.

4.2.5 UV-post treatment of GO hollow fibre membranes

Sacrificial layer stabilised GO hollow fibre membranes were exposed to UV light generated by two Pen-Ray® Mercury lamps in a black box. The UV light source had a wavelength of 230 nm at an intensity of 5.4 W cm⁻². During the post treatment, a GO hollow fibre was placed parallel to the UV light, as shown in Figure 4.2, with a distance of 4 cm between the fibre and the UV

light. GO hollow fibre membranes were divided to four surface sides and each side was exposed to the UV light at a certain exposure time.

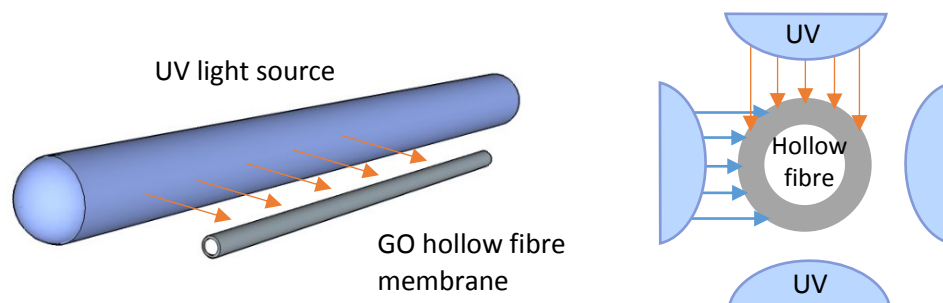


Figure 4.2: GO hollow fibre membrane was placed in parallel to the UV light beam

4.3 Results and Discussion

4.3.1 Stability problem in GO hollow fibre membranes

GO suspension was first coated on YSZ hollow fibres by using vacuum filtration without applying a sacrificial layer. The YSZ hollow fibre support has an outer diameter of 1 mm, and a high pure water flux of $1200 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which ensures a negligible permeation resistance in the substrate compared to the GO membrane layer. The GO coating can be observed from the SEM scanning as shown in Figure 4.3. The coating was well adhered on the surface of ceramic hollow fibre, with thickness of about 500 nm.

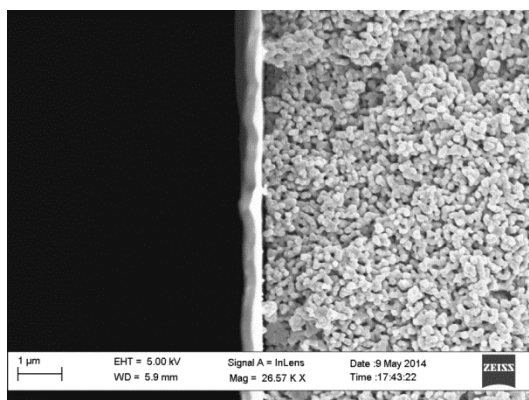


Figure 4.3: SEM image of the cross section of GO/YSZ hollow fibre membrane

To evaluate the GO coating on the substrates, the GO hollow fibre membrane was first tested for N₂ permeation. Some studies showed that ultrathin GO membranes had a high gas permeation and can be used to separate H₂. However, in a study by Nair et al., GO membranes were found impermeable to all gases when the thickness is larger than 100 nm. Therefore, a GO coating at the thickness of 500 nm is unlikely to show a high gas permeation.

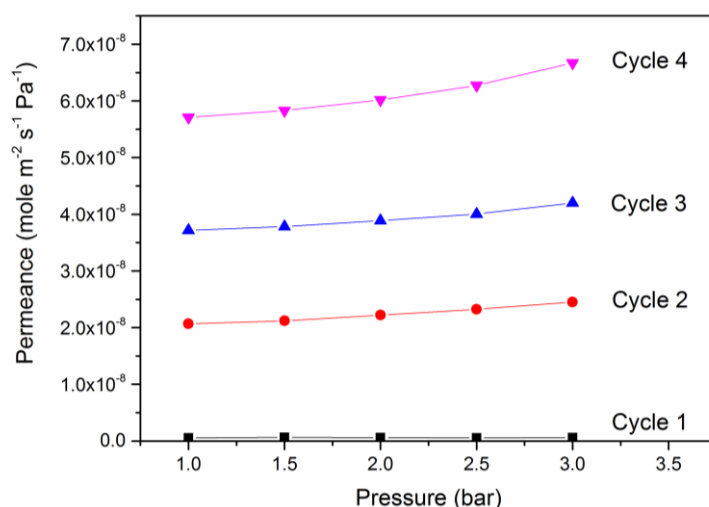


Figure 4.4: The result of repeated N₂ gas permeation tests of a dry GO/YSZ hollow fibre membrane without using a sacrificial layer. The timeline of each test cycle was 1 day, 2 days, 4 days and 7 days after the GO membrane was dried for cycle 1, cycle 2, cycle 3 and cycle 4, respectively.

The gas permeation results are shown in Figure 4.4. In the first cycle, GO hollow fibre membrane showed a permeance of $\sim 6.0 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The permeance was very low though the membrane was not impermeable as expected from the literature [5]. The permeation test was repeated on Day 2 (Cycle 2), Day 4 (Cycle 3) and Day 7 (Cycle 4). The gas permeation of the same membrane increased over time when the test was repeated, implying continuous development of defects in the membrane. In addition, from the second cycle onwards, the permeance of the membrane increased with the increase of pressure, indicating a viscous flow of gas molecules through the membrane. Viscous flow happens when the free mean path of the molecule is much smaller than the pore size, and the molar flux of the gas can be described by Hagen-Poiseuille law [16]:

$$J = -\frac{\varepsilon r_p^2 p}{\tau 8\mu RT} \left(\frac{dp}{dz} \right) \quad (3.2)$$

where J is the total permeation flux ($\text{mol m}^{-2} \text{s}^{-1}$); ε is the membrane surface porosity; τ is the tortuosity; r_p is the pore radius (m); μ is the viscosity (Pa s); p is the pressure; R is the ideal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$); and dp/dz is the pressure gradient across the pores or membranes (Pa m^{-1}). The viscous flow behaviour indicated the presence of large pores or defects in the GO membrane and the nitrogen permeation was not due to the molecular sieve properties of GO membranes.

Surface smoothness of membrane substrates is a common cause of poor coating of thin film membranes. Different types of ceramic hollow fibres, alumina and YSZ were used to coat GO membranes by Aba et al. [15] However, a similar problem was observed where defects developed over time in GO membranes on both substrates, and the gas permeation of the membranes increased over time. In addition, the YSZ hollow fibre substrates used in this study have an average surface pore size of 75 nm, which is comparable to the anodic aluminum oxide (AAO) substrates used in the literatures [4, 9].

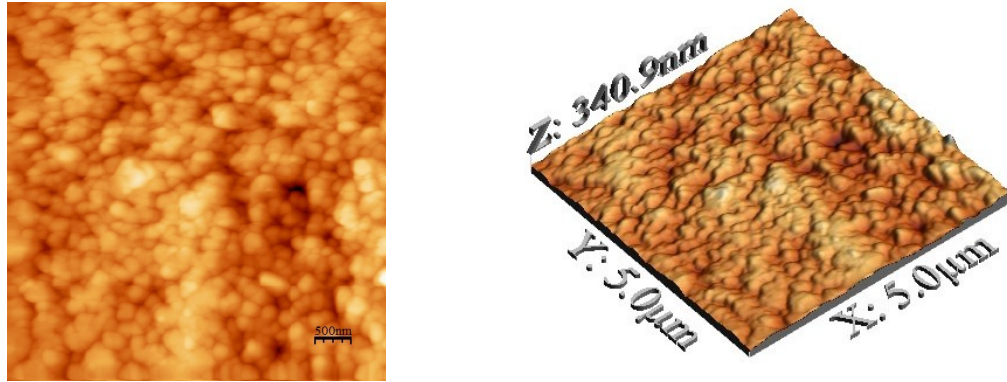


Figure 4.5: AFM images of the outer surface of YSZ hollow fibres (2D and 3D views)

Figure 4.5 shows the AFM images of the outer surface of the YSZ hollow fibres. The root mean square (rms) roughness of the substrate was about 38 nm. The surface roughness (rms) of the hollow fibre substrates were much lower than many hollow fibres reported previously, mainly due to the small YSZ particles used in the fabrication [17]. The smooth surface of the YSZ

hollow fibres should enable a good coating of GO membrane especially the diameter of a single GO flake was about 5 μm , which was considerably larger than the surface pore size of the substrate. Therefore, the change in gas permeation of GO membranes could be due to the change in microstructure of the GO layer. Since the GO membranes were coated using a solution-based method, it was very likely that the microstructure of the membrane changed during the drying process. Evaporation of water could cause shrinkage of GO layer and it was well-known that stress is often introduced in multi-layer composite materials because of the asynchronous change of different layers [18].

The shrinkage of GO membranes were studied by Aba et al. with free-standing GO stripes prepared by vacuum filtering [15]. After an initial drying, the GO strips were placed in a sealed bottle that was filled with silicone gels. The GO strips experienced a linear shrinkage of 1% after one day and remained at the same length after that. For the shrinking ratio observed, GO membranes could be exposed to a maximum tensile stress of 320 MPa, as calculated from the elastic modulus reported, 32 GPa [7]. This far exceeded the maximum fracture stress of GO membranes, 120 MPa. In addition, the maximum strain at the fracturing point of GO membranes was reported to be smaller than 0.6 %, much smaller than the 1 % shrinkage during the drying of GO membranes. Therefore, it was very likely that the stress induced by the shrinkage could create micro- or even macro-cracks in GO hollow fibre membranes. As the micro-cracks formed could be underneath the membrane surface, it is difficult to observe even under the SEM.

4.3.2 Performance of Sacrificial-layer stabilized GO membranes

In order to overcome the shrinkage of GO layer on hollow fibres, a sacrificial layer approach was implemented during the membrane synthesis. PMMA, a cheap and widely used polymer was used as the material for the sacrificial layer. A PMMA layer was coated on the ceramic hollow fibre substrate with dip coating and underwent a phase inversion process to form a porous PMMA structure. The porous PMMA layer acted like a permeable membrane enabling GO deposition using vacuum filtration. During the vacuum-facilitated flow directed deposition process, GO flakes self-assembled, in parallel to each other, on top of the PMMA sacrificial layer forming a GO membrane layer. After the GO deposition, the PMMA sacrificial layer was

washed off by immersing the hollow fibre in acetone. This could be done easily without affecting the quality of the GO layer due to the inert property of GO membranes in organic solvent. A gap was then created between the substrate and the GO membrane, allowing the GO membrane to shrink freely without introducing stress when drying.

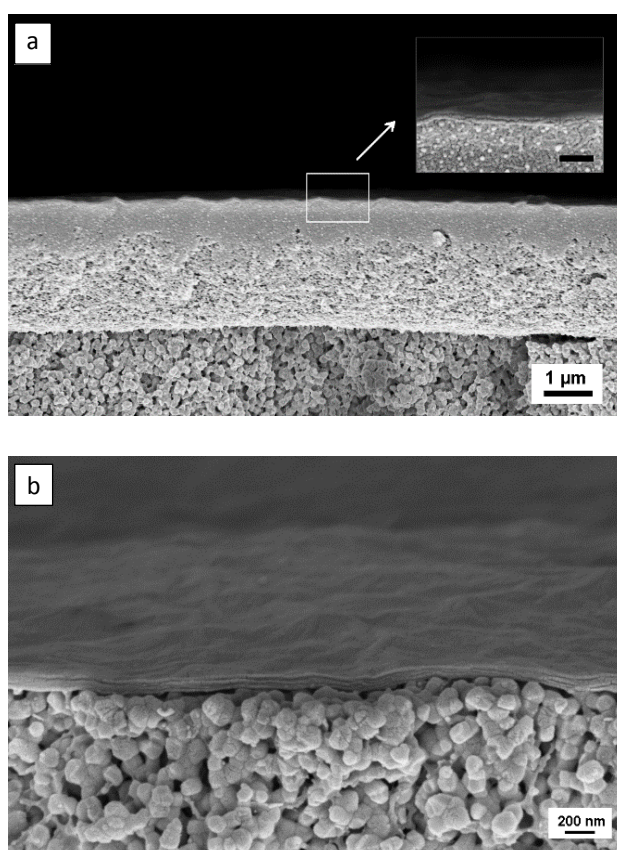


Figure 4.6: (a) An SEM image showing the GO/PMMA/YSZ tri-layer structure, where the sacrificial PMMA layer is sandwiched in the middle by the top GO layer and the bottom YSZ substrate. (Scale bar = 200 nm in the smaller image); (b) An SEM image showing the GO/YSZ structure after the PMMA layer was washed by acetone.

Figure 4.6 (a) shows a scanning electron microscope (SEM) image of a GO/PMMA/YSZ hollow fibre, it can be seen clearly that the PMMA sacrificial layer, about 3 µm thick, is sandwiched between the thin GO membrane and the YSZ substrate. As GO membranes would experience shrinkage of about 1% when drying, the optimum thickness of a PMMA layer for perfectly stress-free shrinkage is 5 µm for the hollow fibres (OD = 1 mm) used in this study. However, GO membranes can withstand a high tensile stress, up to a maximum fracture stress of 120

MPa, and has a maximum strain of 0.6% at the fracturing point [3]. Therefore, the minimum thickness of the PMMA layer required to avoid fracture is approximately 2 μm . In our study, PMMA thickness greater than 3 μm was sufficient to stabilise GO hollow fibre membranes, and wrinkles due to excessive space were observed when the sacrificial layer was thicker than 5 μm . Figure 4.6 (b) shows that the PMMA layer can be completely removed after leaching with acetone, and the GO membrane sits tightly on the YSZ substrate with a well-packed layered structure.

The gas-tightness property of the GO hollow fibre membrane was tested after the removal of the PMMA layer. For GO membrane with a thickness of 700 nm, the membrane was impermeable to various gases including N_2 , He and H_2 , as shown in Figure 4.7 (a). The test was run for 160 h in total and no leakage was observed, demonstrating that the GO hollow fibre membrane was very stable during the test for all different gases tested. The gas impermeability of GO membranes was similar to the results shown by Nair et al. where a free standing GO paper was tested [5]. Unlike their studies, we tested the GO membranes at a higher pressure, around 5 bar, which is closer to real gas separation operating conditions. We found that the membranes were still stable under such a high pressure. Similar GO hollow fibre membranes without a PMMA sacrificial layer allowed gases to leak quickly and the pressure drop result is also presented in Figure 4.7 (a) for comparison.

The PMMA sacrificial layer stabilised GO membranes was further tested for a longer period and the result is shown in Figure 4.7 (b). The GO hollow fibre membrane with a thickness of 150 nm was tested with O_2 for 1200 hours at a pressure of around 6 bar and the pressure did not decline throughout the entire test. The long-term test confirms that the sacrificial layer stabilised GO hollow fibre membrane was extremely stable, and did not degrade within the 50-day test under a high pressure. It also verifies that a defect-free GO membrane is impermeable to gases, given that the test was under the most stringent conditions so far.

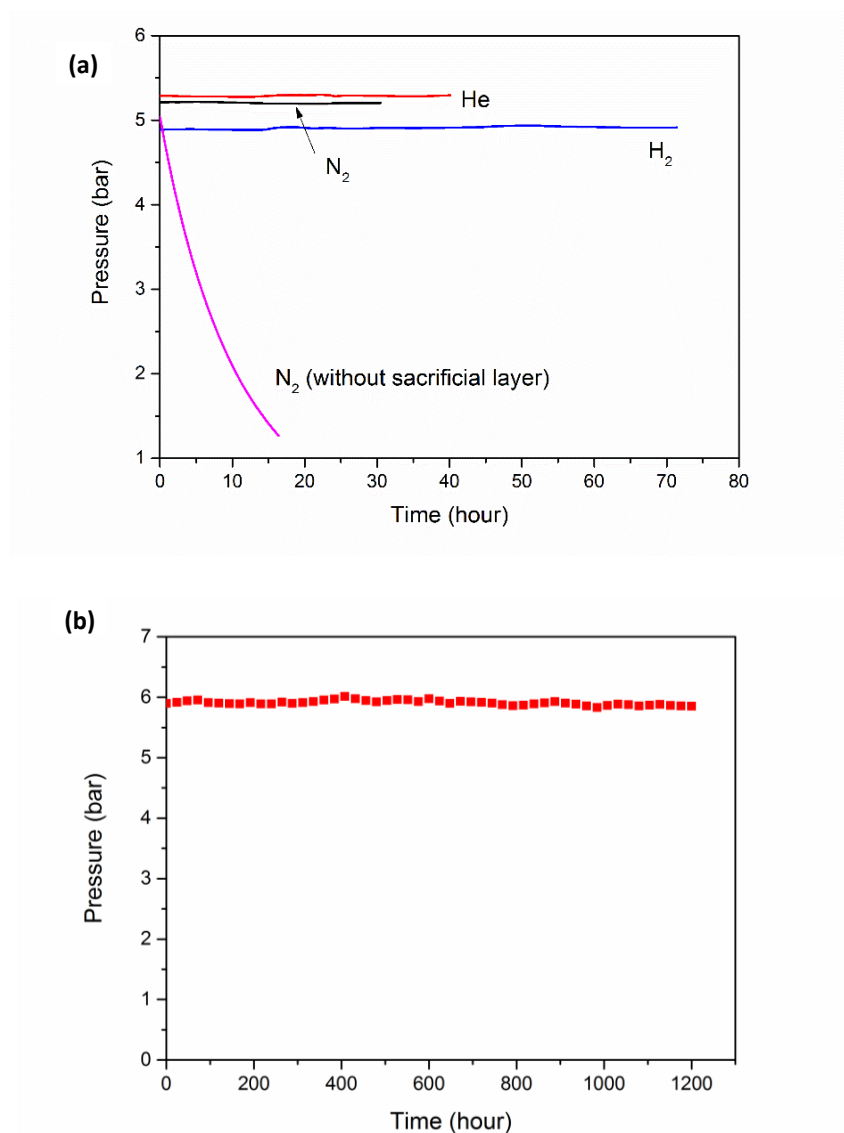


Figure 4.7: (a) The results of gas tightness tests of the GO/YSZ hollow fibre membrane prepared with a sacrificial layer. The tests were conducted with the sequence of N₂, He and then H₂. The test result of a GO/YSZ membrane without using a sacrificial layer is also presented for comparison. (b) The result of a long term stability test with O₂ on a sacrificial layer stabilised GO/YSZ hollow fibre.

The gas-tightness tests showed GO hollow fibre membranes can be stabilised in air after overcoming the shrinkage problem with a sacrificial layer. However, the resultant defect-free microstructure led to undesired performance changes in nanofiltration. The interlayer distance of GO membranes vary from 0.7 – 1.4 nm depending on the water content, and the larger interlayer distance in water enables them to be useful for nanofiltration [5, 13]. In a study in which GO membranes were stabilised by storing in water, water and acetone

permeated through the membranes, with a thickness of 1.5 μm , at a considerable flux of 1.04 and 6.35 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively, whilst completely rejecting dye molecules larger than 327.3 Da [15]. However, for the GO membranes stabilised by a sacrificial layer, the water permeation was extremely low, at only 0.074 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ through a 150 nm thick GO membrane. The permeability was two orders of magnitude lower than the membranes in our previous study. The acetone permeation of the stabilised GO membrane was also very low, only 0.14 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. The dramatic reduction of the permeability is believed to be the consequence of the elimination of microstructural defects in the GO membranes, which can act as shortcuts for the transport of liquids, and thus greatly reduces the permeation resistance in the non-stabilised membranes. However, the permeability of the stabilised GO membranes can be recovered or even further improved by post-treatments. In this research, UV radiation was used as an example to illustrate the possibility of tuning the property of the stabilised GO membranes.

4.3.3 Effect of UV post treatment on GO hollow fibre membranes

By using a sacrificial layer, stable GO hollow fibre membranes were successfully produced and these membranes can be post-treated in dry state to improve their performance. UV radiation was previously used to modify the properties of GO flakes and it could mildly reduce the functional groups on GO [19, 20]. In this study, UV radiation was used to post-treat the stabilised GO hollow fibre membranes, which led to similar changes to dry GO membranes in the air. Visually, the GO membranes turned from light brown to dark grey after UV treatment; it was close to the colour change of GO membranes reduced at elevated temperature under inert atmospheres.

To further confirm the reduction of GO membranes after the exposure of UV light, GO suspension was drop-casted on a quartz glass to form a thin GO layer. The GO layer coated on the quartz glass was exposed to UV light for 2, 5 and 8 h, and the change in functional groups of the GO was monitored using a UV-spectrometer. The UV spectrums are shown in Figure 4.8. Before the exposure to UV light, the UV spectrum of the GO coating showed a peak at wavelength ≈ 225 nm, which can be assigned to the $\pi \rightarrow \pi^*$ transition of aromatic C–C bonds, and a shoulder at ≈ 300 nm, which corresponds to $n \rightarrow \pi^*$ transition of C=O bonds [21,

22]. After the exposure to UV light, the shoulder was no longer observed and it could be due to the reduction of GO. The changes in the UV spectrums coincide with the UV spectrum of reduced GO (rGO) [23]. However, there was no obvious shift of the peak at ≈ 225 nm, compared to highly reduced rGO in which a peak shift to ≈ 270 nm was commonly observed, as the reduction of GO under the UV light could be relatively mild in our case.

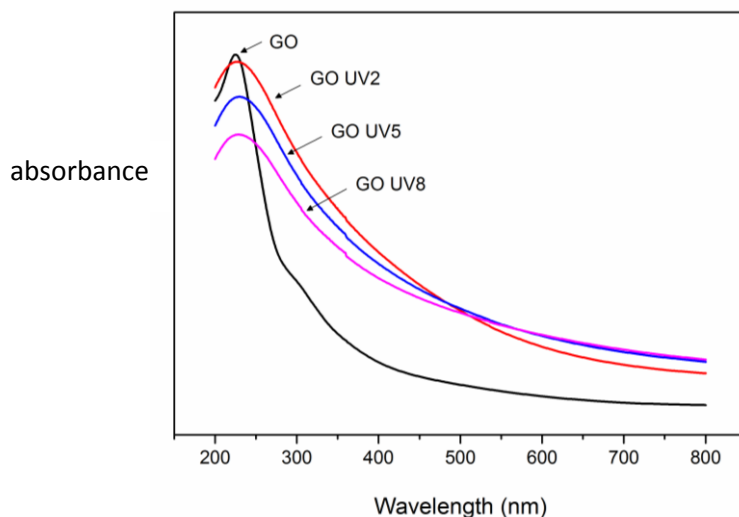


Figure 4.8: UV spectrums of thin GO layer coated on a quartz glass before and after UV-treatments.

Besides, the reduction of GO could also be observed when SEM images were taken. For GO membranes without the UV-treatment, metal plasma coating was required to observe the membrane surface. However, the electrical conductivity of GO membranes became higher after UV treatment and SEM images could be taken without metal plasma coating. As shown in Figure 4.9, the GO layer looked transparent and the hollow fibre substrate underneath could be observed. The higher conductivity can be attributed to the more conductive rGO area in the membranes after the mild reduction.

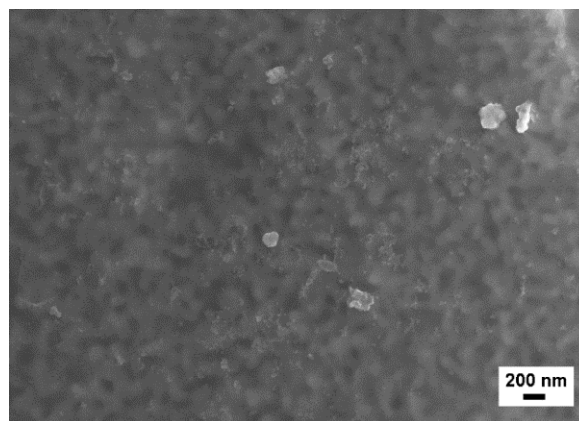


Figure 4.9: SEM image of GO membrane with 2 hours of UV treatment without plasma coating

The change in surface morphology was examined by AFM, and the images of the surface are presented in Figure 4.10 (a) and (b). It can be observed that after 2 h of UV treatment, many small features appeared intensively on the surface of the GO membrane. These features resembled small bumps on the membrane surface, and they were also observed on other UV-treated membranes with different exposure time (Figure 4.11). Phase analyses of the AFM images (Figure 4.11 (c) and (f)) revealed that these small bumps were of the same material as the rest of the surface, thus excluding the possibility that they are due to contamination from the environment during UV treatment, but originated from GO itself. These bumps on the surface could be created by local stress near the surface resulting from the mild reduction of GO.

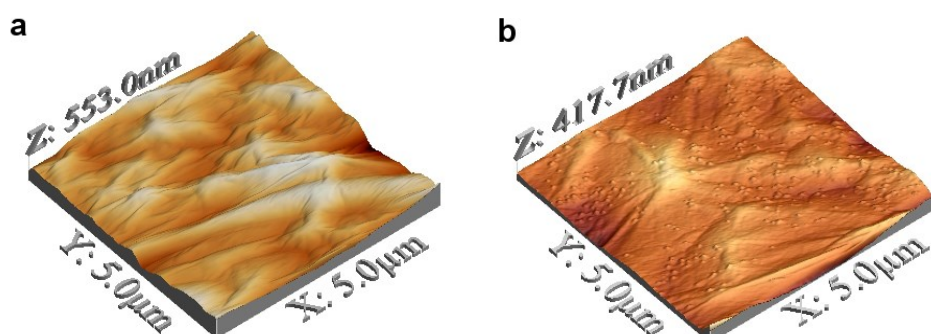


Figure 4.10: AFM images of GO membranes (a) before and (b) after 2 hours of UV-treatment.

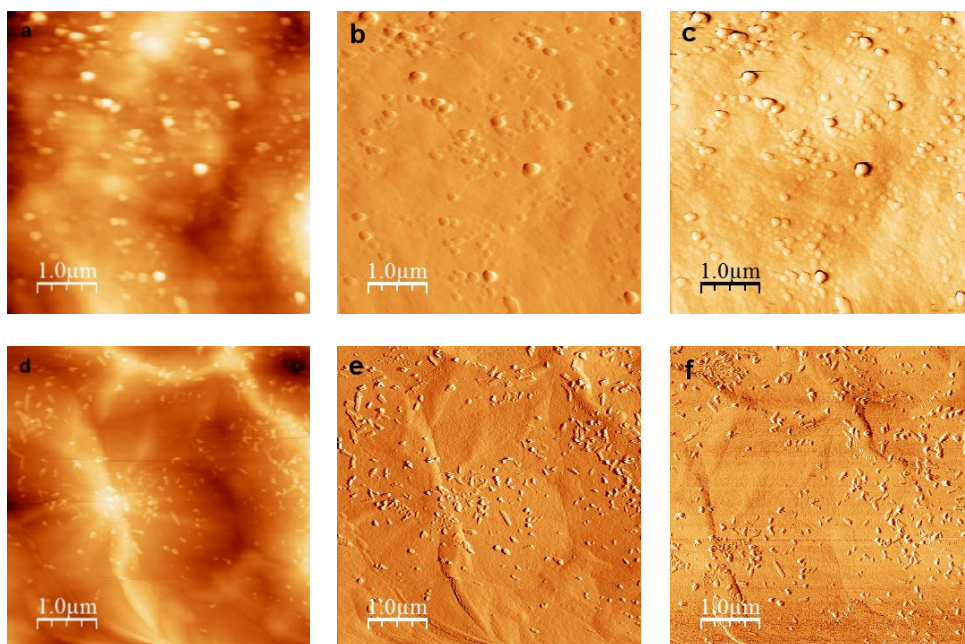


Figure 4.11: AFM images of the surface of GO membrane on PES substrate after (a-c) 5 and (d-f) 8 hours of UV treatment. (a,d) are the topology images, (b,e) are the gradient images and (c,f) are the phase images of the membrane surfaces.

The water contact angles of the GO membranes before and after UV treatment were measured (Figure 4.12). Before UV treatment, the GO membrane showed a contact angle of 39.5° , which was concurrent with the finding in other studies [24, 25]. The contact angle reduced to zero after UV treatments (2 h or longer).

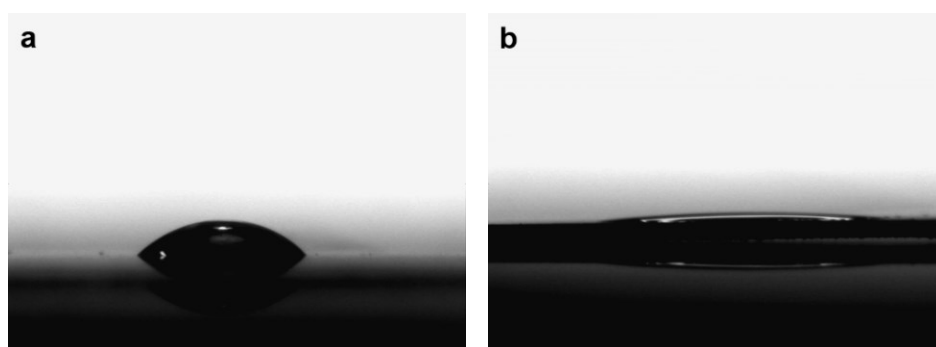


Figure 4.12: Water contact angles of GO membranes (a) before and (b) after UV treatment (2 h). GO membranes became very hydrophilic after UV treatment.

The decrease in the water contact angle of GO membranes after UV treatment was unexpected; the mild reduction of GO membranes should lead to a larger contact angle as reduced GO was more hydrophobic, but the experiments showed an opposite result. The smaller water contact angle observed could be due to the change in surface morphology. The effects of surface morphology on contact angle can be described using the Wenzel model [26]:

$$\cos \theta_W = r \cos \theta_Y \quad (3.3)$$

where θ_W is the apparent contact angle, θ_Y is the contact angle on a dense smooth surface (the Young's contact angle), and r is the roughness factor defined as the ratio of actual surface area over the projected area. The actual surface area of GO membranes after UV treatment was enlarged with the presence of the small features on the membrane surface, which subsequently led to a smaller apparent water contact angle.

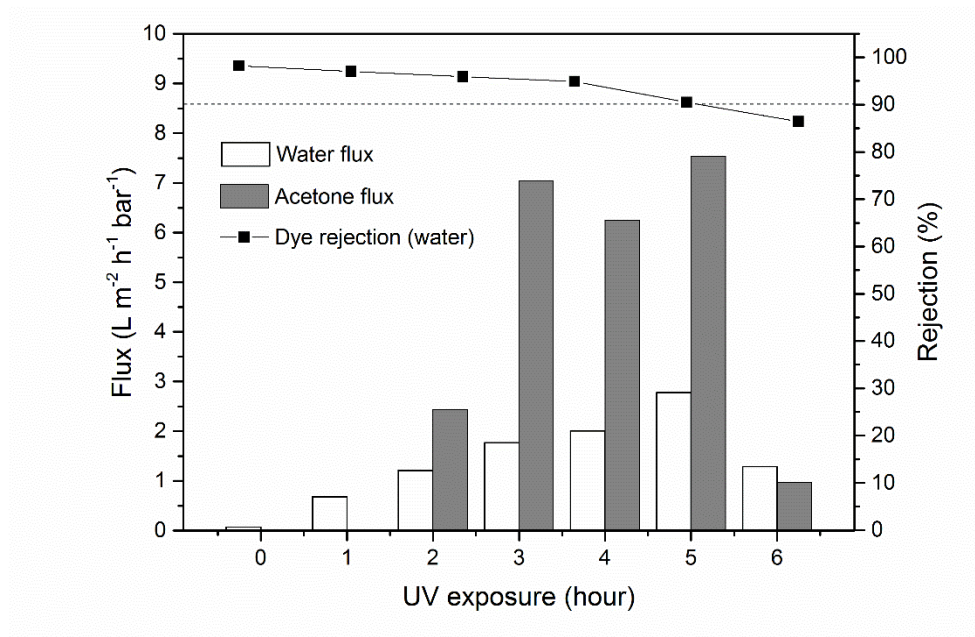


Figure 4.13: Nanofiltration performance of GO membranes with different UV exposure times. White columns: pure water permeation, Grey columns: permeation of acetone. The rejections of methyl red ($M_w = 269.3$ Da) in aqueous solution are shown with square dots.

Nanofiltration performance of the UV-treated membranes was also tested. After exposure to UV for certain period of time, the permeability of the stabilised GO hollow fibre membranes

increased substantially, as shown in Figure 4.13. The water and acetone permeation fluxes increased along with the exposure duration, and reached the maximum values of 2.8 and 7.5 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively, after 5 h of UV treatment, whilst dye rejection tests showed these membranes remained highly selective with a rejection rate of >90 % to methyl red ($M_w = 269.3$ Da). However, when the GO membranes were exposed excessively to UV light, an adverse effect was observed. Instead of further increasing, the fluxes of water and acetone decreased when the UV exposure time was longer than 5 h. The permeation flux of water and acetone decreased to 1.3 and 1.0 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively, when the GO hollow fibre was exposed to UV light for 6 h. The water flux further decreased to 0.42 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ when the membrane was exposed to UV light for 8 h. Besides, the rejection of GO membranes to methyl red was also lower, only 86.4 % when the UV exposure time was 6 h, compared to above 90 % in cases where membranes with shorter hours of UV treatment. Besides that, rejection tests with multivalent cation Mg^{2+} were also conducted with the UV-treated GO membranes (5 h). The ion rejection rate was 78.4%, which indicated that the membranes could potentially be used to remove multivalent heavy metal ions in waste water.

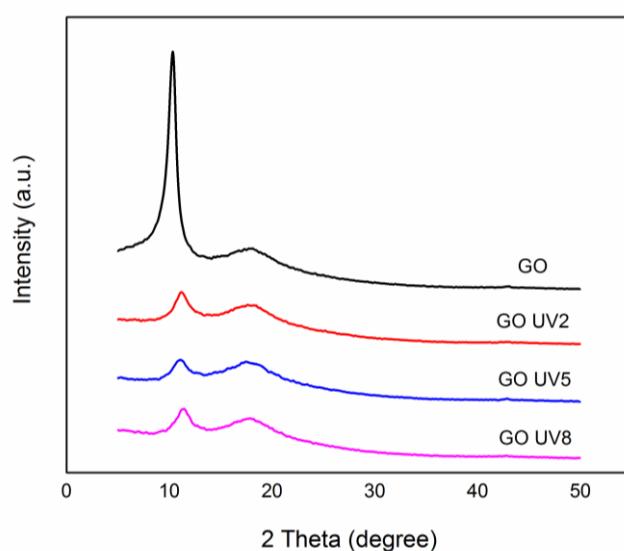


Figure 4.14: XRD patterns of flat-sheet GO membranes before and after UV treatments. The interspace between GO flakes in the membranes did not change at 0.8 nm. The broad peak around 18° is from the substrate, not from the GO membrane.

It is of great interest to investigate how the mild reduction of the GO membranes caused by UV treatment could cause a dramatic improvement in the permeability. XRD results (Figure 4.14) showed the interlayer distance of about 0.8 nm between the GO planes in the membranes was not affected by the UV treatment and only a marginal peak shift was observed. However, the intensity of the peak corresponding to the interlayer distance was considerably weaker after UV treatment, which could be due to the imperfection of GO laminar structure or defects generated in the GO membrane during the UV treatment. The formation of microstructural defects can be evidenced by the degradation of the dye rejection rate when the UV exposure duration exceeded 5 h. The change of microstructure of the membrane after UV treatment may have contributed to the enhanced permeability [15, 27].

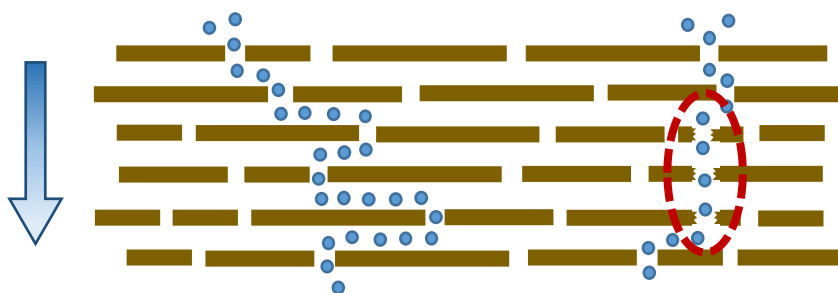


Figure 4.15: Microstructural defects in GO membrane formed as a result of reduction during UV treatment, serve as shortcuts for the liquid permeation process.

When liquid transports in the bulk of the membrane, the transport resistance is mainly affected by the length and the size/diameter of the pores. The permeability of GO membranes can be greatly affected by the presence of microstructural defects generated during the drying process for the membranes without using a sacrificial layer. The microstructural defects could serve as shortcuts for the permeation process (Figure 4.15), which reduced the length of the transport passage and therefore improved the membrane permeability. For the membranes prepared without using a sacrificial layer, defects are difficult to control, especially for very thin GO membranes. Fatal defects crossing over the membranes can be easily induced in a short time during drying, causing their lost in selectivity. But in this study, the process of producing microstructural defects by UV was much slower, and it stops once UV exposure is stopped, thus it is more controllable to avoid fatal defects.

Although UV exposure can lead to the formation of microstructural defects which improve the water permeation of GO membranes, the reduction of oxygen-containing surface functional groups may produce an opposite effect after prolonged UV treatment, causing a decrease in water flux after 6 and 8 h of UV exposure. The adverse effect can be interpreted as the result of locally increased hydrophobicity at pore entrances due to reduction, which hampers the entry of water into the pores, even when the wettability on the surface remains high. A similar situation was observed when GO hollow fibre membrane was annealed at elevated temperature in vacuum. Microstructural defects were generated in the membrane after thermal annealing due to further shrinkage of GO membranes [15] and the loss of oxygen containing surface functional groups from GO [28]. However, the water permeation of the annealed GO membrane was still very low, $0.13 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, as the loss of surface functional groups, especially near the pore entrances, may have had a larger effect in preventing water from entering the membrane.

4.4 Conclusions

GO membranes supported by ceramic hollow fibres are unstable primarily due to shrinkage during drying. This stability issue can be well addressed by using a sacrificial layer, which creates a gap between the GO membrane and the substrate, allowing the GO membrane to shrink freely in the absence of mechanical stress. The GO membrane fabricated with a sacrificial layer was stable in a long-term stability test over 1200 h in dry state. Possibility of post-treatments of the GO membranes in dry state was exemplified by UV treatment, which induced the formation of microstructural defects and greatly enhanced the permeability without losing the molecular sieving property. Such membranes showed high permeation fluxes of water and acetone compared to commercial nanofiltration membranes, and reject multivalent cations and molecules larger than 250 Da. Given the relatively large membrane thickness in this study, the performance of GO hollow fibre membranes can still be further improved if the membrane thickness can be reduced substantially.

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Chapter 5: Transport mechanism in graphene oxide membranes in pressure-driven filtration

Abstract:

Graphene oxide (GO) membranes have been reported to be a promising separation barrier that can retain small molecules and multi-valent ions. However, it is still puzzling that while many studies suggested fast liquid transport through the extremely tortuous transport path, contradictory observations have also been obtained. In this chapter, the water transport mechanism in GO membranes under pressure-driven filtration was studied, which were found closely related by the membrane microstructure. GO membranes prepared by varied methods and on different substrates presented a severe reduction in water permeability due to the compaction of their original loosely packed microstructure. The water flux dropped continuously and reached a steady state flux $<0.1 \text{ LMH bar}^{-1}$ after more than 10 h. This result demonstrated that the structure of GO membranes prepared by current approaches was far from the ideal laminar structure and the high permeability of GO membranes observed could be contributed by the disordered membrane microstructure.

5.1 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 to 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]. They have also been reported to 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, the water permeation flux of GO hollow fibres prepared by Aba et al. could only reach 1.04 LMH bar⁻¹. Chapter 4 showed that GO hollow fibre membranes prepared by using a sacrificial layer during membrane synthesis were impermeable to gases and they 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 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 ratios of GO flakes (width-to-thickness ratio up to few 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 thin 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 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 on 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 water and the pore wall. However, even with the advancement factor of 1000 times as predicted from some studies in a slip-flow condition, the calculated water flux is still far lower than what have been reported in many experimental studies. There has been another hypothesis suggesting that the defects on GO flakes could greatly shorten the effective passage for mass transport, therefore significantly enhance 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 magnitude lower than fluxes reported by many studies.

When trying to understand the transport mechanism, the stacking of GO flakes in GO 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 unsure to what extent the microstructure will affect the permeation flux, and this has hampered us from understanding the transport in laminar GO structures. It was shown in Chapter 4 that a pristine well-laminated GO membrane could be turned to 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 chapter, we systematically studied the change in permeation performance and microstructure of GO membranes during the pressure-driven filtration process. This study demonstrates 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 not be accurate.

5.2 Experimental

5.2.1 Preparation of GO membranes

GO suspension was synthesized using a modified Hummer's method, as described in Chapter 3. The GO suspension was centrifuged to control the size of GO flakes, which was determined to be 5 – 10 microns 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 (Figure 5.1 a-c).

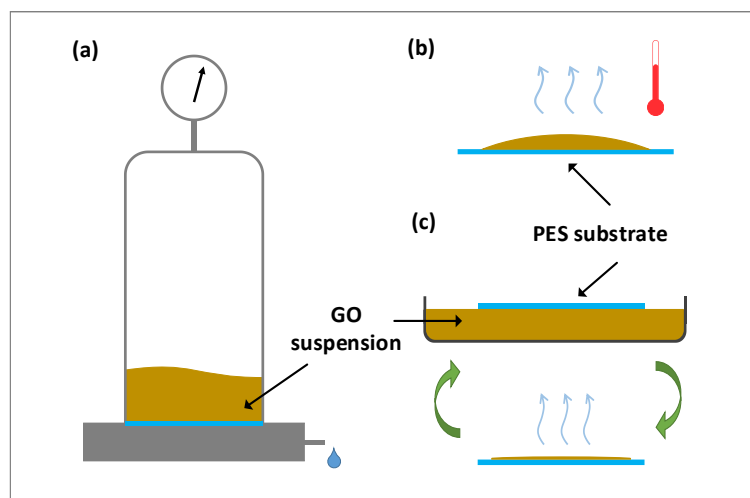


Figure 5.1: Schematics of GO membrane syntheses on PES flat sheet substrates: (a) high and low pressure filtration; (b) high temperature evaporation; (c) dip coating.

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 (Figure 5.1 b). 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 hour (Figure 5.1 c). 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, as described in Chapters 3 and 4 [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 hour before the next dip was taken place. The dip-coating process was repeated for 6 times to get a sufficient coating thickness and surface coverage.

5.2.2 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 Chapter 4. The filtration tests were conducted at 6 bar, or 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-charged molecule and is a good indicator for rejection tests as the molecular size is close to the molecular cut off of GO membranes. The permeate was collected in a test tube and the dye concentrations of the feed and the permeate were determined by using a UV-spectrometer (UV-2101PC, Shimadzu, UK).

5.2.3 Material characterization

The morphology of the membranes was observed by a scanning electronic microscope (LEO Gemini 1525 FEGSEM and Zeiss Auriga Crossbeam). XRD (X'pert Pro PANalytical) was used to determine the average interlayer space between the GO flakes in GO membranes. Only GO flat sheet membranes were used in XRD to ensure accurate diffraction angle measurements.

5.3 Results and Discussion

5.3.1 Water flux reduction in GO membranes

In this study, GO membranes were prepared by several commonly used methods. Besides the most used filtration method, GO membranes were also prepared using dip coating and evaporation/ drop casting. Two different pressures, 1 and 10 bar were applied in the filtration method as pressure could be an important variable affecting the compaction of GO membranes.

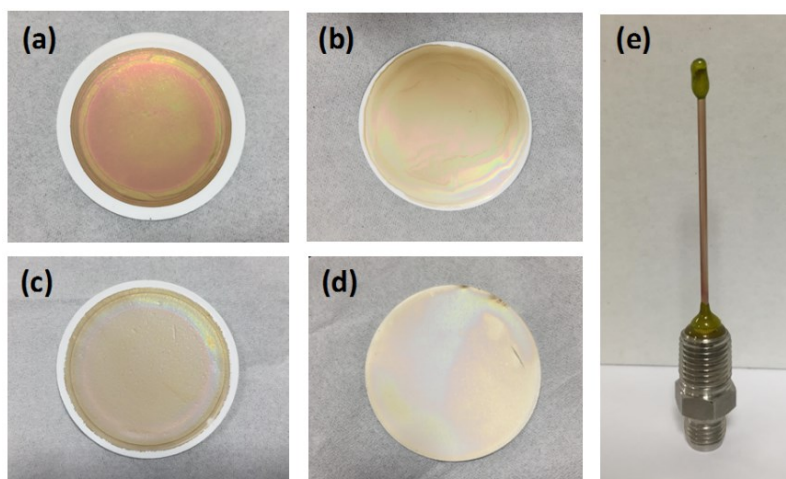


Figure 5.2: Pictures of GO flat sheet membranes prepared by 4 different methods: (a) low pressure filtration; (b) high pressure filtration; (c) high temperature evaporation; (d) dip coating. (e) A picture of GO hollow fibre membrane on a stainless steel holder.

Figures 5.2 (a-d) show the images of GO membranes on PES substrates. All of them had a smooth surface though GO membranes prepared by evaporation and dip-coating had slightly

uneven coatings which could be due to the uncontrolled evaporation or drying process. In a study reported by Tsou et al., peeling off of GO flakes was observed in GO membranes prepared by evaporation [24]. However, that did not happen in this study when GO membranes were prepared using the evaporation method at 80 °C. The high evaporation rate at high temperature may have enhanced the GO self-assembly process in forming continuous GO membranes. Besides flat sheet GO membranes, hollow fibre GO membranes were also successfully prepared and they showed very even coating, as illustrated in Figure 5.2 (e).

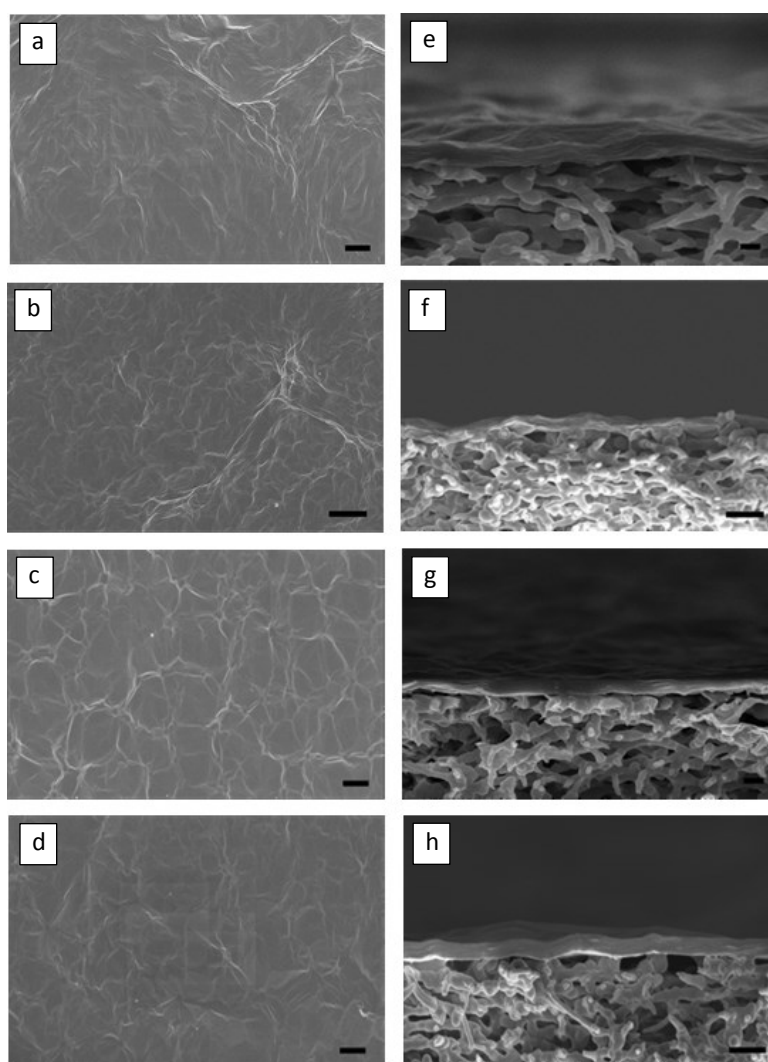


Figure 5.3: SEM images of the surfaces (a-d) and the cross-sections (e-h) of GO membranes prepared by 4 different methods: (a, e) 1 bar filtration; (b, f) 10 bar filtration; (c, g) evaporation; (d, h) dip coating. (Scale bar: (a) 2 μm (b) 3 μm (c) 1 μm (d) 1 μm (e) 300 nm (f) 1 μm (g) 500 nm (h) 1 μm)

Figures 5.3 (a-h) show the SEM images of the top surfaces and the cross-sections of the flat sheet GO membranes prepared by all these methods. They showed similar top surface morphology with wrinkles on the membrane surface, which were also commonly observed in GO membranes from previous studies [20, 21, 24]. From the cross-sections, GO membranes showed a uniform laminar structure attaching closely on the PES substrates. The thickness of the GO layers shown in Figure 5.3 ranged from 400 to 500 nm.

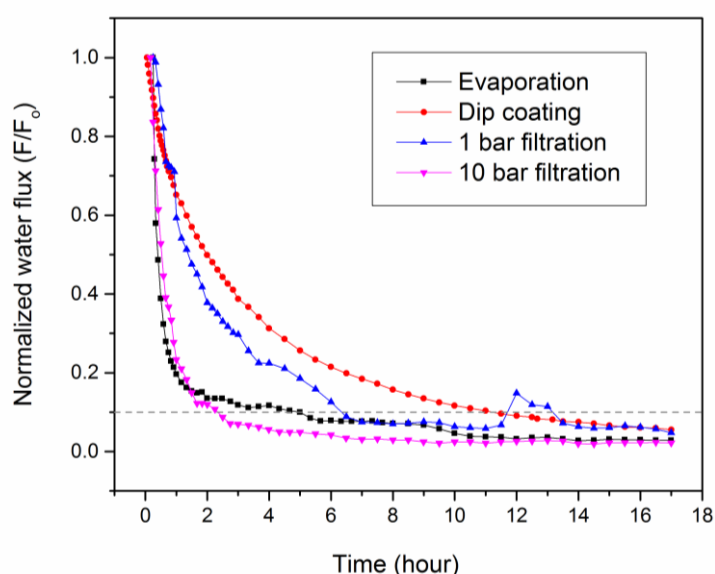


Figure 5.4: Normalized water flux of GO membranes prepared by 4 different methods. The steady state water fluxes were lower than 10% of the initial fluxes.

The water permeation fluxes of all the GO membranes were measured, and the membranes prepared by different methods showed a variation in the initial fluxes: 6.06 LMH bar⁻¹ for 1-bar filtration, 1.52 LMH bar⁻¹ for 10-bar filtration, 1.71 LMH bar⁻¹ for evaporation, and 8.56 LMH bar⁻¹ for dip coating. For easy comparison, normalized water fluxes based on their initial fluxes were plotted over time and shown in Figure 5.4. During the water permeation tests, all the membranes showed a decrease in water flux and the fluxes reached a steady state lower than 10% of their initial fluxes. GO membranes prepared by evaporation and 10-bar filtration showed very similar trends in the decrease in water fluxes and the fluxes reached a steady state faster compared to the other two methods.

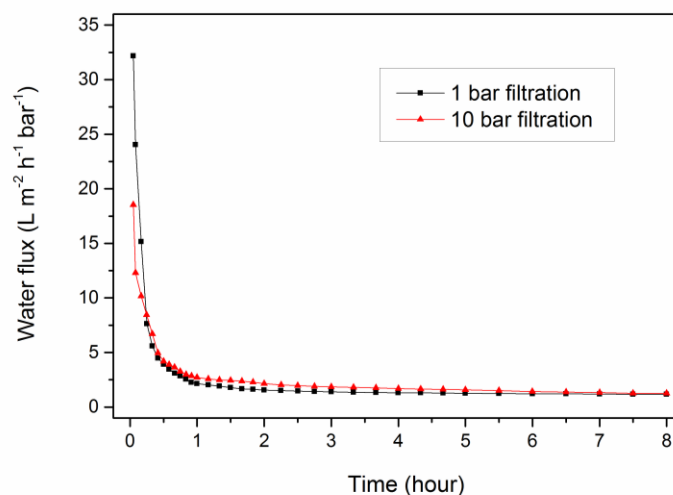


Figure 5.5: Water permeation flux of GO membranes as a function of time. The membranes were prepared using filtration at 1 bar and 10 bar, with thickness about 90 nm for the thin membranes and 450 nm for the thick membrane.

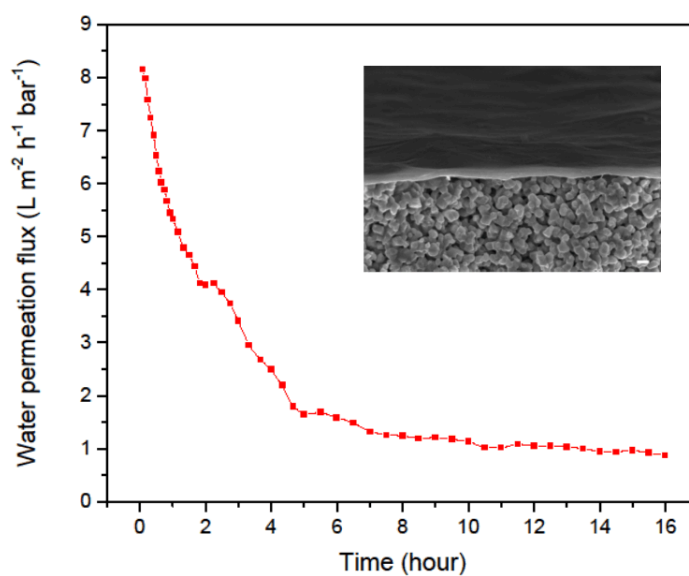


Figure 5.6: Water permeation flux of GO membrane prepared on YSZ ceramic hollow fibre. Insert: An SEM image of the cross-section of GO hollow fibre membrane. (Scale bar: 200 nm)

Aforementioned GO flat sheet membranes were relatively thick, but our study showed that the reduction in water permeation flux happened consistently regardless of the membrane thickness. As shown in Figure 5.5, thin GO membranes (thickness ≈ 90 nm) prepared by both 1-bar and 10-bar filtrations showed very high water fluxes, 32.2 and 18.5 LMH bar⁻¹,

respectively, in the beginning of the permeation tests. Such high water permeation flux was previously reported in some GO membrane studies [21, 26]. However, the membranes also showed a rapid decrease in water flux over time and reached a low steady state flux, lower than 10% of the initial flux. The decrease in water flux did not only happen in flat sheet GO membranes. For GO membranes coated on YSZ hollow fibre substrates, the membranes also showed similar decrease in water flux, as shown in Figure 5.6.

The results showed clearly that all GO membranes prepared by varied methods and on different substrates presented a severe reduction in water permeability, and the flux dropped continuously from tens of LMH bar⁻¹ down to the range < 0.1 LMH bar⁻¹ after more than ten hours. The decrease in initial water flux was observed constantly in our lab but was seldom reported in previous studies. A decrease in the initial pure water flux of rGO membranes was reported by Han et al. [22] However, the water permeation of the membranes was shown reaching a steady state in less than an hour, and the extent of the flux reduction was not as severe as observed in our study on GO membranes. Besides, the cause of the flux reduction was not further examined in their studies. Similar decline in water flux in GO membranes was recently reported by Wei et al. [27] They attributed the observation to membrane compaction during filtration which resulted in narrower wrinkles and a flux decline in the membrane substrates.

5.3.2 Hierarchical microstructure of GO membranes

Membrane compaction or flux reduction is a well-known phenomenon in polymeric membranes due to their high elasticity and low mechanical strength [28]. During pressure driven applications, pressure applied would compact the membranes and change the microstructure in the membranes, and therefore lower the permeation flux. However, inorganic membranes such as ceramic membranes seldom experience compaction under high pressure because of their high rigidity [29]. GO membranes showed compaction consistently on both polymeric and ceramic substrates, and the compaction should not be contributed by the substrates. Ultrapure de-ionised water was used in the water permeation tests in our study and the reduction of membrane flux should not be due to fouling or concentration polarization, two common causes of drop in membrane permeability. During water

permeation, it is widely assumed that water molecules transport through the interlayer space between the GO flakes when pressure is applied on one side of the GO membranes [6]. The interlayer space was created by the hydrogen bonding formed between the GO flakes, and it is easy to estimate based on Lennard-Jones potential of hydrogen bonding that the equivalent interlayer space will not be affected by the filtration pressures applied during the tests. Therefore, the observed reduction in water flux should not be due to the change in the interlayer space either.

The assumption that water transports through the interlayer space may not reflect the actual structure of GO membranes. Under an ideal situation, GO flakes would stack flake by flake perfectly on top of each other, and this may be the case when GO membranes have only several layers of GO flakes. However, this is difficult to achieve in practice as sufficient number of GO layers are needed to ensure a full coverage on the substrate surface. In most of the situation, thicker GO membranes are fabricated and the laminar structure of the membranes is not perfect. Hierarchical structures of GO membranes/papers have been previously observed especially when the thickness is in a length scale of above 100 nm [30]. In these hierarchical structures, there are mainly two levels of structure formed by the stacking of GO flakes. The primary structure is from a highly ordered flake-by-flake stacking, which forms a GO lamina that may be thicker than 10 nm. The secondary structure is a looser stacking of the primary structures, but it may also mix with a certain extent of flake-by-flake structure to form a complete membrane structure.

The hierarchical structure is illustrated in Figure 5.7. Recently, the formation mechanism of the hierarchical structure in GO membrane was studied by Nandy et al. using a stop motion animation imaging technique to observe the evolution of membrane microstructures [31]. For GO membranes prepared using vacuum filtration, formation of interconnected proto-lamellar 3-D network was observed during the filtration process, which was slowly compressed into dense GO lamellae. Similar formation mechanism was also observed in the evaporation method but the growth of the dense lamellae started from the water-air interface at a lower rate. During the membrane formation process, GO flakes did not stack one by one from one end to the other, but started with forming proto-lamellar network. Therefore, the formation of imperfect stacking of GO flakes in GO membranes was inevitable.

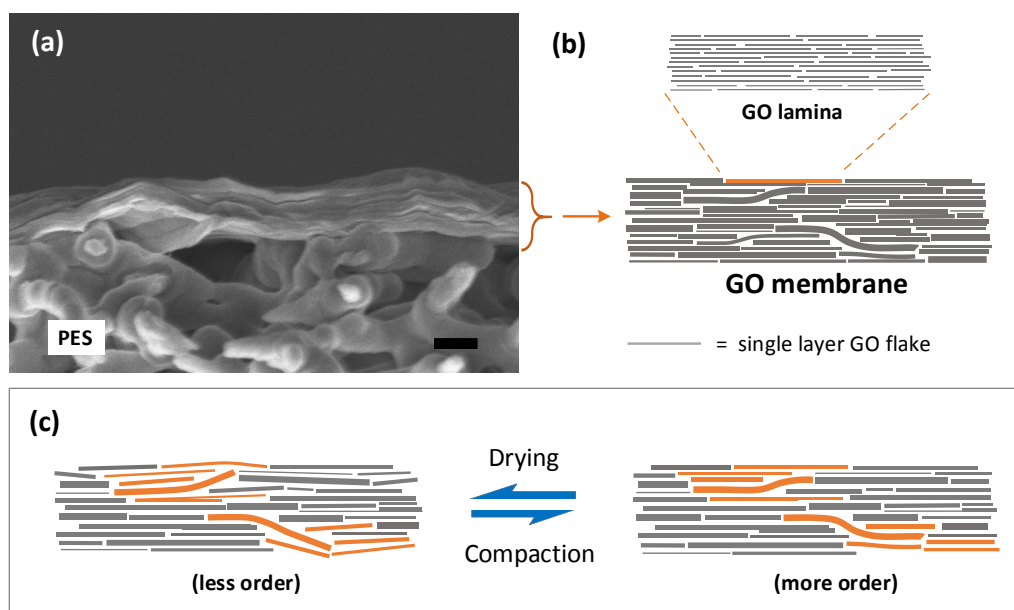


Figure 5.7: (a) SEM image of GO membrane on a PES substrate (scale bar: 300 nm). The stacking of lamina layers could be observed from the image. (b) Schematic of hierarchical GO membrane composed of GO lamina layers of different thickness. (c) Schematic of the change of GO microstructure under different conditions.

The spaces and cavities in the loosely stacked hierarchical structure create extra paths for water molecules to transport through the membranes and subsequently increase the water permeability of the membrane. However, when pressure is applied during water permeation, membrane compaction would happen to the loose and less ordered microstructure. The compaction may not have changed the interlayer distance of the membranes created by strong hydrogen bonds, but could compress the spaces and cavities between the laminae, leading to a more ordered microstructure in GO membranes. As the GO membranes are more densely packed and have minimum shortcuts in the more ordered microstructure, the effective transport path of water molecules in the membranes would become significantly longer, causing a drastic decrease in water permeability. It can also be expected that with the denser structure in GO membranes, the non-ideal flow passages that deviate from the theoretical interlayer space of the flake-by-flake stacking would be minimised or eventually eliminated, leading to a higher rejection rate to the probing molecules.

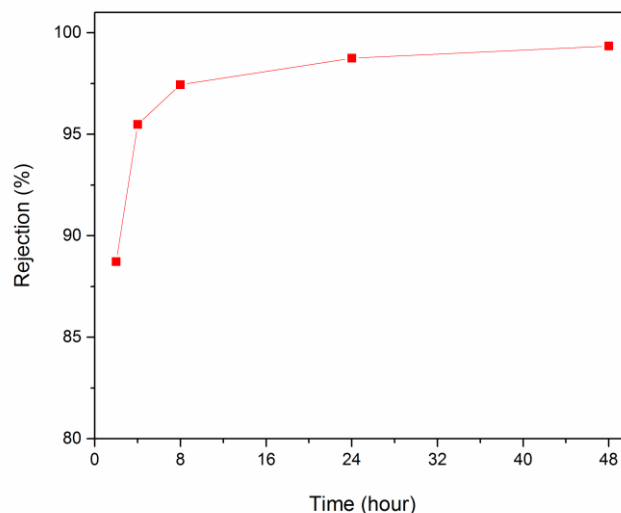


Figure 5.8: Rejection performance of GO membranes with methyl red ($M_w = 269.3$ Da) as the probing molecules.

This hypothesis was verified by the dye rejection experiment using methyl red ($M_w = 269.3$ Da) as the probing molecule (Figure 5.8). During the rejection test, the rejection rate was relatively low initially (88.7%), but improved after 4 h to above 95% accompanying the reduction of permeation flux. The improvement in rejection performance is additional evidence of the change in microstructure of GO membranes during pressure driven water filtration. Such improvement in rejection performance over time could only be observed when dyes with smaller size such as methyl red was used. When larger dye molecules such as tartrazine ($M_w = 534.3$ Da) and brilliant blue ($M_w = 792.9$ Da) were tested, GO membranes showed a high rejection rate (>95%) even at the beginning of the test, which indicated the cavities in the hierarchical structure were very small and still within the nanofiltration range. Though GO membranes may have a less ordered microstructure in the beginning of the compaction / water permeation tests, the less ordered laminar structure could still reject most of the molecules larger than 500 Da.

The permeation flux reduction shown in Figure 5.4 can be well explained based on the hierarchical structure model of GO membranes. The variation in the initial flux of the GO membranes prepared by different methods can be attributed to the initial level of disorder (e.g. the number of spaces and cavities between the GO laminae) in the membranes. GO membranes prepared by evaporation and 10-bar filtration had lower initial fluxes, 1.71 and 1.52 LMH bar⁻¹, respectively, which could be attributed to the more ordered microstructure

in the membranes. In contrast, GO membranes prepared by dip coating showed a much higher initial flux, $8.56 \text{ LMH bar}^{-1}$ as the GO membranes fabricated by this method could have a less ordered microstructure due to the relatively difficult control process especially for flat sheet substrates. The speed of coating, the thickness of wetted liquid film and the drying process could affect the integrity of GO coating. The disorder might happen not only at the laminar level, but the packing between the layers formed by each dip could also contribute to the less ordered microstructure. The more ordered microstructure in GO membranes prepared by evaporation and 10-bar filtration was also reflected by the shorter time taken to reach the steady state permeation flux, compared to membranes prepared by the other two methods.

Aforementioned evidence clearly shows that a more ordered microstructure can be achieved after the compaction of GO membranes. However, will the highly ordered microstructure in GO membranes be retained when the pressure is released after the permeation test? To answer this question and to further understand the dynamic microstructure of GO membranes, we ran the water permeation /compaction tests in several cycles. In the cycle test, two dry fresh GO membranes prepared by high pressure filtration were first tested for water permeation for 2 days. After that, the membranes were stored either in air (dry cycle run) or in water (wet cycle run) for 3 days before the second cycle tests were carried out. In both of the cycle runs (Figure 5.9), the fresh GO membranes experienced flux reduction, similar to other membranes tested in our study. However, different compaction behaviours were observed in the second and the following cycles. In the dry cycle run, flux reduction continued to happen in each of the following 5 cycles; the membrane showed a high initial water permeation flux in each cycle and reached to a very low steady water flux, below 0.1 LMH bar^{-1} eventually. It is apparent that the disordered microstructure of the membrane could be regenerated during drying, leading to the reoccurring of flux reduction in every cycle.

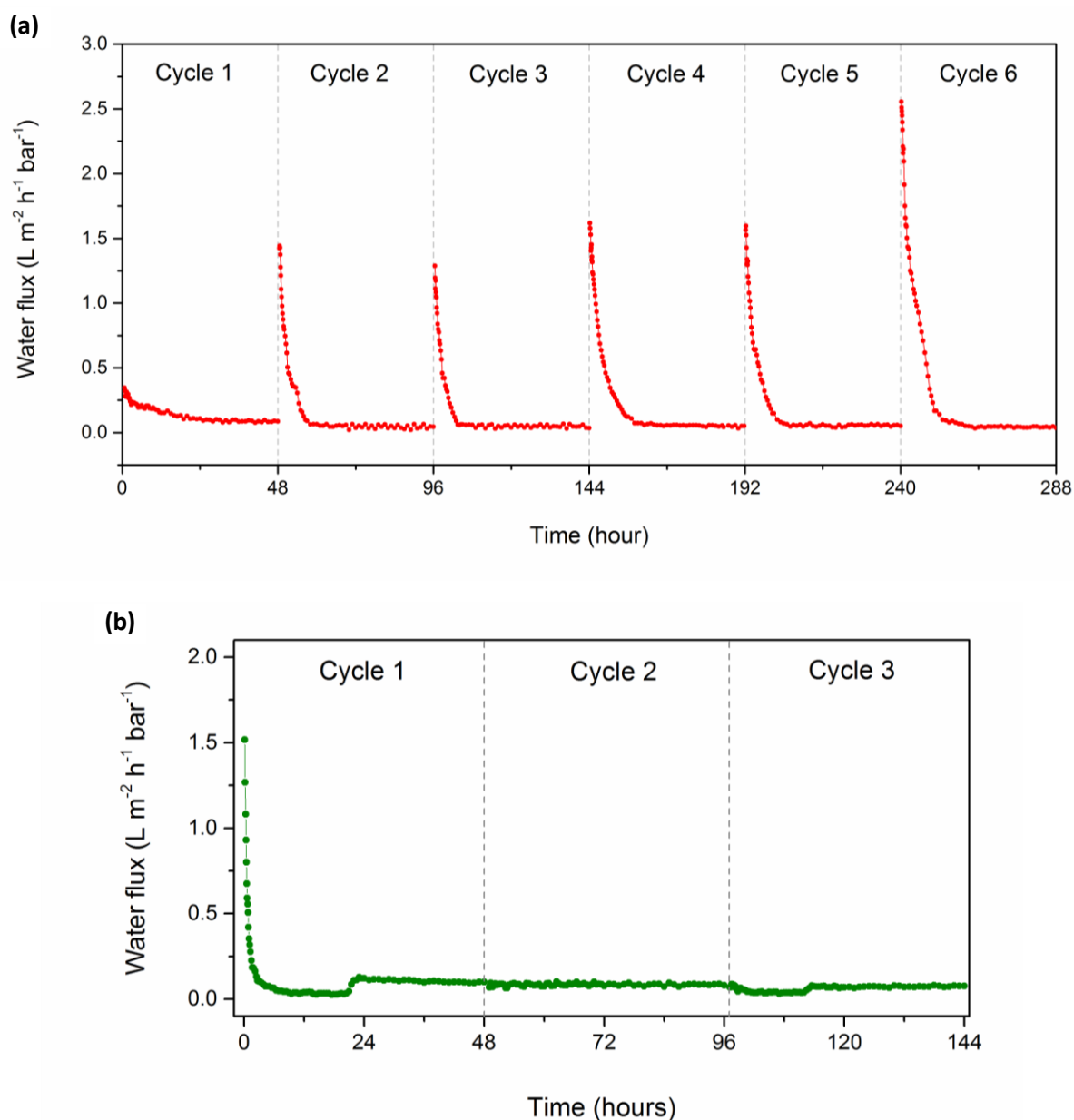


Figure 5.9: (a) Water permeation flux of GO membrane in a dry cycle run. The GO membrane was dried in the air for 3 days between cycles. (b) Water permeation flux of GO membrane in a wet cycle test. The GO membrane was stored in water for 3 days between cycles.

On the other hand, repeated membrane compaction was not observed in the wet cycle and the water permeation flux of GO membrane remained low in the second and third cycle. The highly ordered GO laminar structure may have been maintained when the membrane was stored in water continuously as there was no external force causing the disruption of microstructure like during the drying process. Correspondingly, GO membranes after the wet cycle showed a high initial dye rejection rate to methyl red (>97%) and other larger dye

molecules (Figure 5.10). This was expected from the water permeation tests as the more ordered microstructure was well preserved when storing in water.

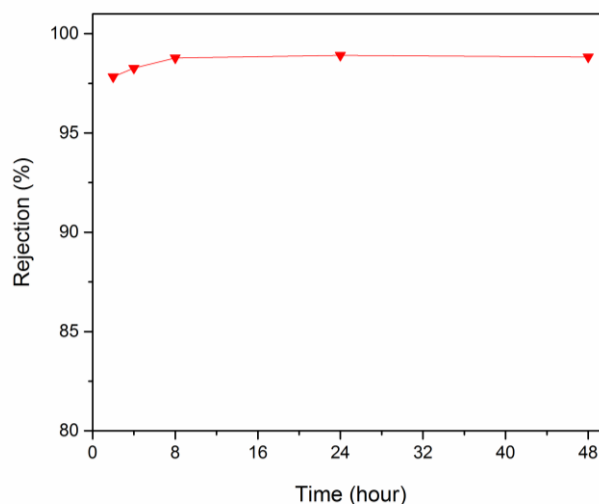


Figure 5.10: Rejection performance of GO membranes after wet cycle with methyl red ($M_w = 269.3$ Da) as the probing molecules.

The cycle tests provided an important clue for the understanding on the change in microstructure in GO membranes. The repeated membrane compaction in the dry cycle revealed that the disordered microstructure of GO membranes was restored when drying or storing in the air. The drying process could be critical for the microstructure of GO membranes and the disorder-to-order microstructure of GO membranes was reversible depending on the conditions where the membranes were stored (Figure 5.7 c). This result coincided with our previous study on the stability of GO membranes, where long duration of storage of GO membranes in air was shown to lead to a defective membrane due to excessive defects developed in the membranes [17]. By storing GO membranes in water, the microstructure and the performance of the membranes could be well preserved.

We further studied the effects of drying and storage condition on the microstructure of GO membranes by monitoring the change in XRD peak intensity over a longer period of time. GO membranes were stored in the air for 4 weeks and 1 year, and the same samples were scanned with XRD over the storage duration (Figure 5.11). The intensity of the peak ($2\theta=9-10^\circ$) corresponding to the interlayer space of GO membranes with the same thickness

decreased after 4 weeks and 1 year. The lower peak intensity indicated a change in microstructure of GO membranes, with increasing disorder over time when the membranes were stored in air even at room temperature. The big band at $2\theta=18^\circ$ was contributed by the PES substrate and it could be also used as a reference during the scan. It was revealed in our previous study that the shrinkage of GO membranes during drying was one of the apparent reasons to cause the generation of microstructural imperfections, but the underlying reason behind the destructive drying process was the high surface tension of water, which generated enormous capillary force in the sites of spaces and cavities in the hierarchical structure. Because of the size difference of the spaces and cavities, uneven capillary forces would be distributed in the GO membrane during drying, and thus intensifying the deviation from the ideal flake-by-flake stacking, and restoring the loose disordered membrane structure. It has also been demonstrated that by replacing water with low surface tension solvents, the disordered structure can be largely minimised, leading to a very low permeation flux [17].

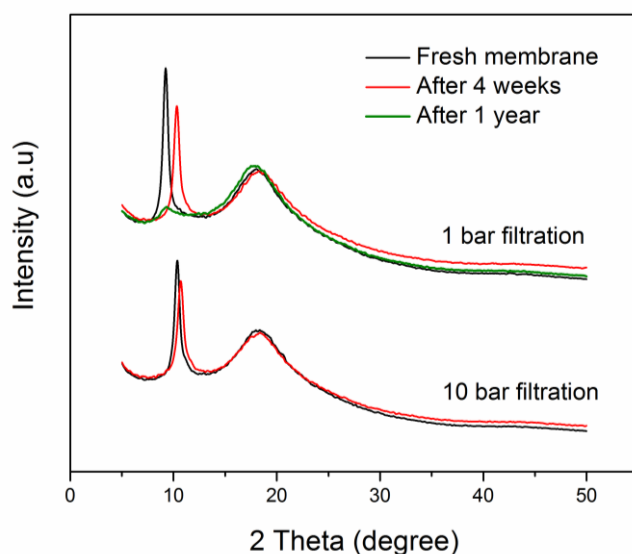


Figure 5.11: XRD diffractograms of GO membranes prepared by 1 bar and 10 bar filtration: Fresh membranes, after 4 weeks and after 1 year of storage in air.

5.3.3 Discussion of water transport mechanism in GO membranes

Water transport in GO membranes has been puzzling in the membrane field, and it has caused a theoretical problem to the researchers working on transport mechanisms. The classic

Hagen-Poiseuille equation is a starting point used to understand the water transport in GO membranes and the equation can be expressed as:

$$Q_{HP} = \frac{d^4}{12\mu L^2} \frac{\Delta p}{l} \quad (5.1)$$

where Q_{HP} is the permeation flux ($\text{m}^3 \text{s}^{-2}$), d is the pore size or the interlayer distance (m), μ is the viscosity of water (Pa s), L is the average lateral length of GO flakes (m), Δp is the pressure gradient (Pa) and l is the membrane thickness (m). As mentioned in the beginning of the chapter, the water permeation flux predicted using the equation was much lower than the water flux reported so far.

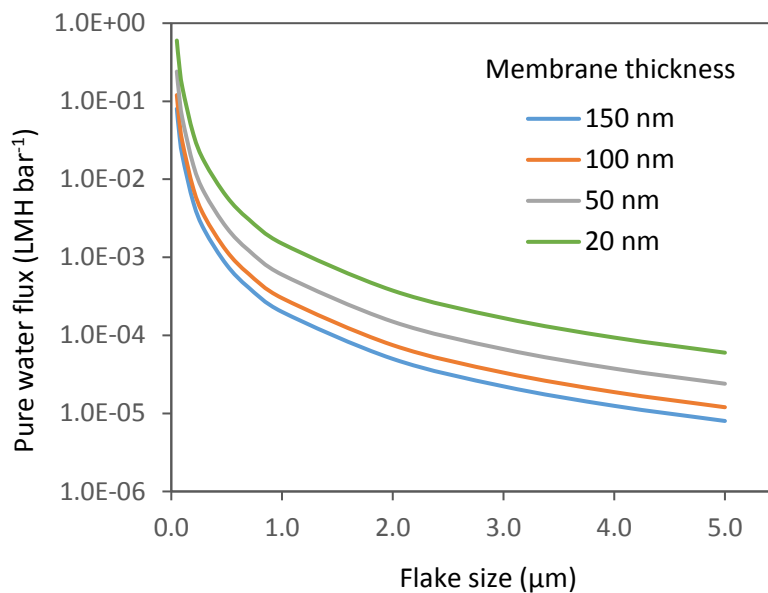


Figure 5.12: Pure water flux of GO membranes with thickness ranging from 20 to 150 nm calculated using the Hagen-Poiseuille equation

As shown in Figure 5.12, even by reducing the membrane thickness to 20 nm, GO membranes still could not achieve a high water flux. The flux might be greatly improved if GO flake size can be reduced to below 100 nm. However, a full coverage of GO on the substrates will be very difficult to attain with the small flake aspect ratio. This also showed that the high aspect ratio of GO flakes have very much contributed to the long transport path in GO membranes and water would transport at a very slow rate in an ideal flake-by-flake structure. In addition,

the large GO flake size also contributed to a low “effective porosity” on the membrane surface with less than 0.1% of the surface available for water molecules to enter the membrane [6].

Noticing the long transport path in GO membranes, many studies attempted to explain the reported high water permeation using the fast water transport hypothesis. Dynamic molecular simulation technique has been used to study the water transport in GO membranes and to support the fast transport hypothesis. Nair et al. showed that water molecules could have a low friction, ultrafast transport through the carbon hydrophobic network in GO membranes with a high effective capillary pressure [6]. However, their simulation study simplified the transport channels to an all-carbon network with no hydrophilic functional groups, which did not reflect the real situation in GO membranes. When including the surface effect, water molecules will interact with the hydrophilic functional groups and the side-pinning effect will slow down the transport of water in the carbon channel network in GO membranes due to the strong hydrogen bond interaction [32, 33]. Continuum theory was used in a recent study to predict the fast transport of water in GO membranes with low friction flow of water in carbon channels but the prediction again did not include the hydrophilic surface effects in the membranes [34]. Besides, the simulation by Nair et al. focused on the high capillary pressure in the interlayer space and water was set to be evaporated on the permeate side of the membrane. While the capillary pressure in the membranes could be high due to the small interlayer space, the driving force in evaporation was different from the pressure-driven filtration where water did not change to the vapour phase when exiting the pore.

This chapter demonstrated that the stacking of GO flakes was far from perfect and the membranes formed a hierarchical structure. The transport mechanisms proposed in previous studies assuming perfect GO laminar structure did not fully describe the water transport in GO membranes. The exceptional performance of GO membranes in water permeation reported has been explained by using the hypothesis of fast transport in GO membranes, but could be contributed by the loosely packed membrane microstructures. Besides, the experimental data in this study also suggested that the permeation tests should be conducted for at least 12 h in order to have an accurate measurement of the performance of GO membranes.

5.4 Conclusions

GO membranes showed a low steady state water permeation flux in pressure-driven filtration due to the extremely high tortuosity in the membranes. The high water flux observed was not an intrinsic property of GO laminae but could have been attributed to the disorder of GO flakes and the loosely packed hierarchical microstructure in GO membranes. GO membranes showed a serious reduction in water flux during the permeation test, which could be due the change in the membrane microstructure. The transport mechanisms assuming perfect laminar structure in GO membranes are inaccurate and the low friction flow proposed by previous studies may not fully describe the water transport in GO membranes under a pressure-driven condition.

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Chapter 6: Transport of water through graphene oxide membranes in pervaporation

Abstract:

Graphene oxide (GO) membranes have shown excellent performance in pervaporation for dewatering of organic solvents. However, the adsorption–diffusion model adopted by many did not fully describe the water transport in the interlayer space of GO membranes. In this chapter, GO membranes were tested under pressure-driven filtration and pervaporation. The water permeation was found 1-2 orders of magnitude higher in pervaporation, and a pore flow model was used to explain the higher permeation flux. The chapter also discussed how the large capillary pressure in the interlayer space could enhance the water permeation in pervaporation. Besides that, GO membranes were tested with water-liquid mixture in pervaporation. A stable interface due to a steep concentration difference was observed at the pore entrance of the membranes. This surface phenomenon has enabled the measurement of effective interfacial tension between miscible liquids using GO membranes.

6.1 Introduction

Graphene oxide (GO) membranes can be fabricated by assembling two dimensional GO flakes layer-by-layer on top of each other. The membranes form a uniform laminar structure with a well-defined interlayer space [1, 2]. In an early study by Nair et al., GO membranes were shown impermeable to all gases including helium. However, the same membranes demonstrated a fast transport of water molecules [3]. When a GO membrane was sealed at the opening of a container in their study, water in the container evaporating through the membrane resulted in a weight loss in the container. The weight loss was observed to be almost as fast as when the container had an open aperture. However, when water in the container was substituted by other solvents such as ethanol and hexane, they could not evaporate through the membrane sealed at the opening. The observations of fast evaporation of water through GO membranes was attributed to a low-friction flow of a monolayer of water through the two-dimensional capillaries formed by the closely spaced GO sheets, while diffusion of other molecules was blocked by the narrow capillaries [3].

The fast water vapour permeation has enabled GO membranes to separate water from other organic solvents by pervaporation [4, 5]. Different from pressure-driven membrane filtration, the permeate side of membrane is under vacuum in pervaporation; the permeate is evaporated from membrane surface due to a low partial pressure on the permeate side, and the permeation is driven by the chemical potential gradient across the membrane. GO membranes were tested in dehydration of organic solvents such as alcohols and dimethyl carbonate, and they showed excellent performance with a very high separation factor, >1000 especially when the solvents had a molecular weight larger than ethanol [6-8]. Though with a well-defined interlayer space, the separation of water from the water-solvent mixtures was not completely due to the molecular sieve property of GO membranes. For instance, GO membranes showed a separation factor of above 200 when a water-ethanol mixture was separated under the pervaporation mode, even though both water and ethanol were able to permeate through GO membranes at rates of same magnitude under a pressure-driven filtration mode, as their molecular sizes were smaller than the membrane interlayer distance [9]. The separation of water in pervaporation was not possible if molecular sieving was the main separating mechanism.

In this case, solution–diffusion or adsorption–diffusion models have been adopted by many to explain the good performance of GO membranes in pervaporation [5, 6, 10]. In these models, the permeability coefficient of the individual liquid is the product of the sorption coefficient and the diffusivity. GO membranes were found having a high water adsorption capacity and this was shown by Huang et al. in a direct measurement of water adsorption using the quartz crystal microbalance technique [5]. The preferential water adsorption was due to the large amount of hydrophilic functional groups in GO membranes and the low water condensation partial pressure resulted by the fine laminar structure. Because of the selective adsorption, water molecules had a much higher permeability than other solvents, leading to an effective water separation from a water-solvent mixture. To further demonstrate the importance of water adsorption, Huang et al. improved the surface hydrophilicity of GO membranes by coating a thin layer of hydrophilic polymer, N-deacetylated derivative of chitin [11]. The separating factor of dewatering of butanol was considerably improved, but interestingly, the higher surface hydrophilicity did not increase the water permeation flux.

While the adsorption of GO membranes was well studied, the diffusion of water in GO membranes was not much discussed in the adsorption–diffusion model. In the adsorption–diffusion or solution–diffusion models, a phase transition has to occur at the feed-side membrane surface so that water will turn from continuous bulk liquid phase to individual molecules or clusters. An apparent difficulty for the adsorption–diffusion model to explain the pervaporation performance in GO membranes is that the molecular diffusion is unlikely to be fast in the long and tortuous transport path in GO membranes [12], which is opposite to high water flux observation from the experimental results.

To explain the high water permeation flux, fast transport hypothesis proposed by Nair et al. has often been adopted by researchers to explain the transport mechanism in the interlayer space [3, 6, 8]. However, the hypothesis suggested that water molecules condensed and permeated through the interlayer space in a bulk phase with one to three layers of water. If this hypothesis is adopted, the adsorption–diffusion model will no longer be suitable, as the transport of water in the interlayer space will follow a pore flow model instead. Different from the solution–diffusion or adsorption–diffusion models, the driving force for water permeation in the pore flow model is not concentration gradient but the pressure difference in the membranes. Therefore, two important questions have been raised if the pore flow model is applied to explain the transport mechanism in the interlayer space:

1. Where and how did the liquid phase water in the nanochannels turn to the vapour phase in the scenario of pervaporation? In Chapter 5, we revealed that water permeation through GO membranes under the pressure-driven mode is actually very slow. However, in the pervaporation mode, it was suggested that when water on the permeate-side was evaporated swiftly, the liquid-vapour interface created in the nanochannels will produce a huge capillary pressure that will drag the condensed water to pass through GO membranes quickly [3]. Therefore, it is crucial to locate the liquid-vapour interface as it relates the water transport in the membrane and thus the determining steps in permeation. However, this question has not been properly answered in the literature and has hindered researchers from explaining their experimental observations.
2. How did the selectivity occur and how was it maintained in pervaporation? In the pore flow model, it is assumed that no concentration gradient exists in the membrane nanochannels, and the transport is driven by the pressure gradient in the membrane. The

selectivity is determined as soon as water enters the membrane nanochannels. In that case, there will be a sudden concentration jump at nanochannel entrances on the feed side rather than a gradual change in concentration across the membrane. Such concentration jump is understandable for the solution–diffusion model, or in a pore flow model if the pore size is smaller than the solutes. However, would it still be possible in the pore flow model if the pore size is bigger than all species in the solution, such as the ethanol-water mixture?

In this chapter, the two key questions are answered. To answer the first question, pure water permeation flux of GO membranes were tested using two different modes: pressure-driven filtration and pervaporation. It was revealed that the water permeation flux through GO membranes during pervaporation was 1 - 2 orders of magnitude higher than when tested in filtration, and the flux was comparable to the free evaporation rate of water. The experimental results suggested that the driving force for water permeation through GO membranes in pervaporation was much larger due to the high capillary pressure maintained by evaporation, and the rate-determining step should be the evaporation steps on the permeate side surface. To answer the second question, we further tested GO membranes in pervaporation using an ethanol-water mixture. The membranes showed a good separation of water from the liquid mixture due to the preferential water adsorption of GO membranes. We propose that when the selective adsorption occurs, a thin transition layer with sharp concentration gradient, which resembles the interface between two immiscible liquids, is formed at the entrance of nanochannels in GO membranes [13-15]. This type of interface leads to an effective interfacial tension (EIT), also described as Korteweg stress, which hinders the water-ethanol mixture from entering the membrane under a pressure-driven condition. We demonstrate the existence of the EIT experimentally using high-pressure permeation experiments with ethanol-water mixtures; conversely, the results can be used to measure the EIT between two miscible liquids like water and ethanol and to determine the pore size distribution in GO membranes. The EIT data obtained is of great physical importance and useful for studies such as viscous fingering and microfluidic processes where transient interfaces of miscible liquids may occur.

6.2 Background

Interface between two immiscible liquids such as water and oil can be observed easily in many daily-life phenomena. The interfacial tension between immiscible liquids is an equilibrium thermodynamic property, where the liquids are mutually saturated, with no net inter-diffusion taking place. Similar interface can also exist between miscible liquids such as water and alcohol, due to a sharp concentration gradient between two liquids, immediately after they are in contact. However, the interface between miscible liquids is temporary and will eventually disappear after sufficient diffusion or mass transfer. The transient effective interfacial tension (EIT) between miscible liquids has been described as Korteweg stress [13-15].

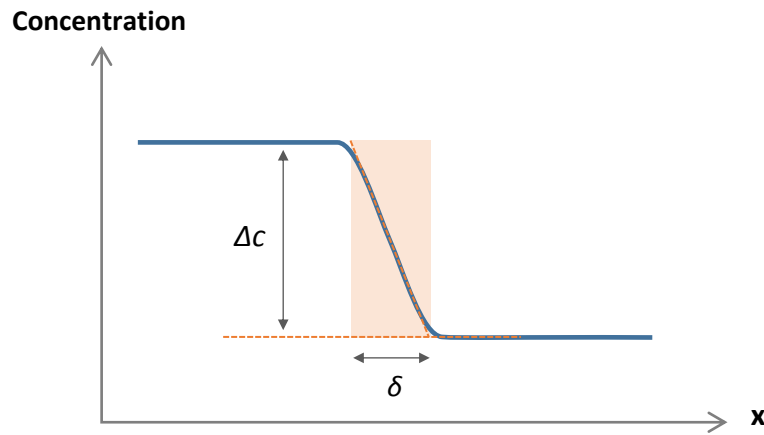


Figure 6.1: Schematic of transient interface of two miscible liquids.

Figure 6.1 illustrates an example of a concentration gradient at the transient interface and the EIT, σ_e , is related to the concentration gradient at the interface:

$$\sigma_e = \kappa \frac{(\Delta c)^2}{\delta} \quad (6.1)$$

where κ is the Korteweg constant, Δc is the change in concentration and δ is the width of the transition zone.

Though the property of miscible interface is difficult to quantify, the existence of EIT is relevant in many practical applications such as solvent exchange in microporous structures, viscous fingering, membrane surfaces and microfluidic processes [15, 16]. It is also important in numerical simulation of miscible liquids like Rayleigh-Taylor instability and Hele-Shaw flows

[17]. Methods such as light scattering and spinning droplet tensiometry have been used to study miscible interfaces and their dynamics [13, 14]. However, these measurement techniques are limited by the time required to reach quasi-steady state for accurate measurement, which can be longer than the diffusion time, especially for the liquid pairs with high affinity and low viscosities.

When an ethanol-water mixture with a small amount of water comes into contact with a GO membrane, water molecules are preferentially adsorbed on the GO membrane due to the high hydrophilicity of the membrane. The adsorbed water will condense in the interlayer space, this results in a water-rich phase in the GO membrane in contrast to the ethanol-rich bulk solution, as illustrated in Figure 6.6 later on. The steep difference in concentration will form an interface at the entrance of the hydrophilic nanochannels, which is analogous to the interface formed between immiscible liquids. In the case of GO membranes, the interface could remain stable at the pore entrance due to the preferential water absorption of GO membranes. This pseudo-equilibrium surface phenomena can be used to measure the EIT between two miscible liquids. The measurement method is similar to the liquid-liquid displacement porosimetry [18], where the liquid in the pores is replaced by another liquid under a pressure to overcome the interfacial tension.

At the membrane pore entrance, the meniscus of the interface will curve towards the water side in the membrane as water is preferentially adsorbed on the wall of the interlayer space. Therefore, the interfacial tension will be against the pressure outside the membrane. The interlayer space is similar to the space between two flat plates, and the Young-Laplace equation can be used to determine the EIT:

$$\sigma_e = \frac{P \cdot r}{\cos \theta} \quad (6.2)$$

where P is the pressure applied to overcome the interfacial tension, r is the radius of the interlayer space and θ is the contact angle. The interlayer space and the wetting angle are the intrinsic properties of GO membranes. During the EIT measurement, the pressure on the feed side will be slowly increased. At low pressure, the EIT is larger than the pressure applied and no liquid flux is expected to be observed. However, when the pressure applied is sufficiently high to overcome the EIT, the liquid mixture will start to permeate through the membrane. The EIT can be determined from the pressure required for the liquid to permeate through.

6.3 Experimental

6.3.1 Preparation of GO flat sheet membranes

GO suspension was synthesized using a modified Hummer's method, as described in Chapter 3. Flat sheet GO membranes were fabricated using the filtration method as described in Chapter 5: GO suspension was filtered on polyethersulfone (PES) or polyacrylonitrile (PAN) substrates at 10 bar in a dead-end filtration cell (Sterlitech HP4750 Stirred Cell). PAN flat sheet membranes were used as the substrates due to their strong resistance to various solvents as PES substrates would swell in solvents such as ethanol. The PAN substrates were supplied by the Livingston's lab and they were prepared by knife casting on a polyester nonwoven layer. After filtration, GO membranes were dried in air for 2 days before being sealed in a filtration cell for further testing.

6.3.2 Water permeation and pervaporation

GO membranes were sealed in the same filtration cell used in membrane fabrication with an extra PTFE sheet as sealant. The pure water flux of GO membranes was tested using two different modes: pressure-driven filtration and pervaporation. The pressure-driven mode was similar to what described in Chapter 5, where pressure was applied on the feed side during the water permeation test. However, in pervaporation, the permeate side of the membrane was connected to a vacuum system. The experimental setup is shown in Figure 6.2. The vacuum level was maintained at 1.3 mbar and a cold trap filled with liquid nitrogen was used to condensate the permeate. The permeation flux was determined by weighing the amount of permeate collected. For high temperature pervaporation, the membrane cell was immersed in a water bath to maintain the temperature.

In addition to the pure water flux, GO membranes were also tested in pervaporation with a water-ethanol mixture. During experiments, deionized water in the membrane cell (the feed solution) was substituted with a water-ethanol mixture a weight ratio of water:ethanol = 5:95. The concentration of ethanol in the permeate was determined by gas chromatography (GC) (Varian 3900). For all experiments, the membranes were compacted with pure water under 6 bar for at least 24 h to ensure the water flux and membrane structure reached its steady

state, as described in Chapter 5. The same membrane samples were used in both pressure-driven permeation and pervaporation tests.

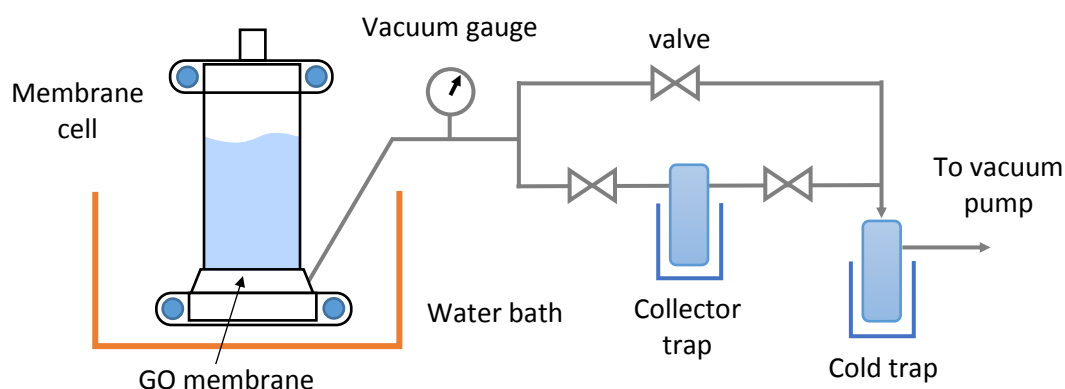


Figure 6.2: Schematic illustration of pervaporation set-up

6.3.3 Permeation of ethanol-water mixtures through GO membranes/ measurement of effective interfacial tension

The same membrane cell used in filtration and pervaporation was used for the EIT measurement. Before the measurement, GO membrane was first tested for pure water permeation under a pressure-driven mode for several reasons. Firstly, it was to compact the GO membrane to ensure liquid predominantly permeated through the interlayer space in the membrane during the EIT measurement, instead of passing through the microstructural defects. Besides, the water permeation flux could be a good guideline to predict the final liquid permeation flux during the measurement. A higher than usual water permeation could also indicate the presence of large number of the microstructural defects in the membrane. Most importantly, the water permeation test ensured the interlayer space in GO membranes was prefilled with water molecules. This was to ensure the formation of a large water-ethanol concentration gradient at the pore entrance.

During the ethanol-water EIT measurement, ethanol with a low water concentration (20 and 30 wt%) was used as the feed solution. The experimental set-up was similar to the filtration test, as shown in Figure 6.3. The filtration cell was pressurized by nitrogen supplied from a

gas cylinder. The amount of the liquid permeated through the membrane was monitored by measuring the mass of the liquid collected and the real time measurement data was recorded by a computer. The pressure was increased after at least 2 ml of permeate was collected. In the case where there was no permeation or the permeation was too low, the same pressure was maintained for at least 24 h before it was increased. The pressure was increased with a 2-5 bar interval until the permeance reached a constant value. Due to the limitation of the test-cell, the highest pressure used in this study was 67 bar.

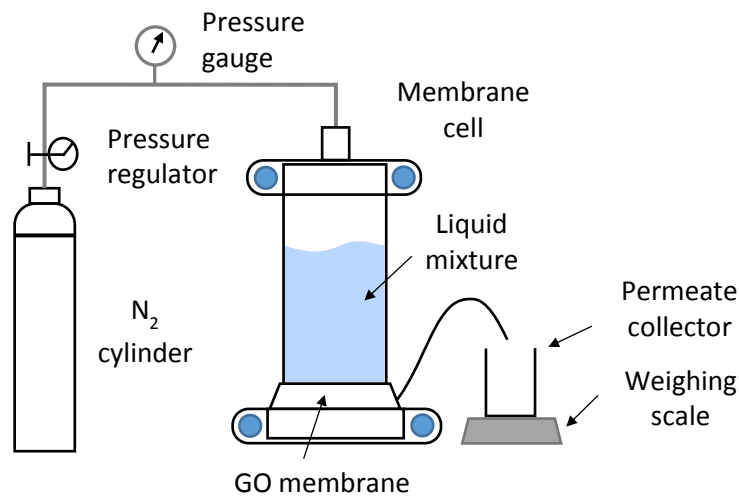


Figure 6.3: Experimental set-up for effective interfacial tension measurement

From the flux data collected, the flow distribution at different pressure was calculated based on the equation:

$$\text{Flow percentage at } \bar{P}_n = \frac{J_{n+1} - J_n}{J_T} \times 100\% \quad (6.3)$$

where $\bar{P}_n$ is the mean pressure, $\bar{P}_n = 0.5 \times (P_n + P_{n+1})$, J_n is the liquid permeance at pressure P_n , and J_T is the total liquid permeance, which is the highest permeance achieved during the measurement. The EIT value between the liquids could then be calculated based on Equation 6.2, using the pressure where the flow percentage was the highest. The flow distribution was also used to determine the pore size distribution of GO membranes by calculating the corresponding pore size at each pressure point.

6.4 Results and Discussion

6.4.1 Pure water flux through GO membranes in pressure-driven permeation and pervaporation

Flat sheet GO membranes were fabricated on PES and PAN substrates using the filtration method. The GO membranes fabricated on PES substrates were same as those prepared in Chapter 5. The SEM image of the GO membranes on PAN substrates was shown in Figure 6.4. The surface of GO membranes looked smooth and with some wrinkles, which were also commonly seen when other types of substrates were used. Since the PAN substrate surface was very smooth, it was difficult to observe using the SEM due to the low contrast during scanning. AFM scan was carried out and the topology image of the PAN substrate surface was shown in Figure 6.4 (c). The surface had a uniform morphology with very fine pores. As the PAN layer had a low mechanical strength, polyester nonwoven (Figure 6.4 d) was used as a support to the substrate.

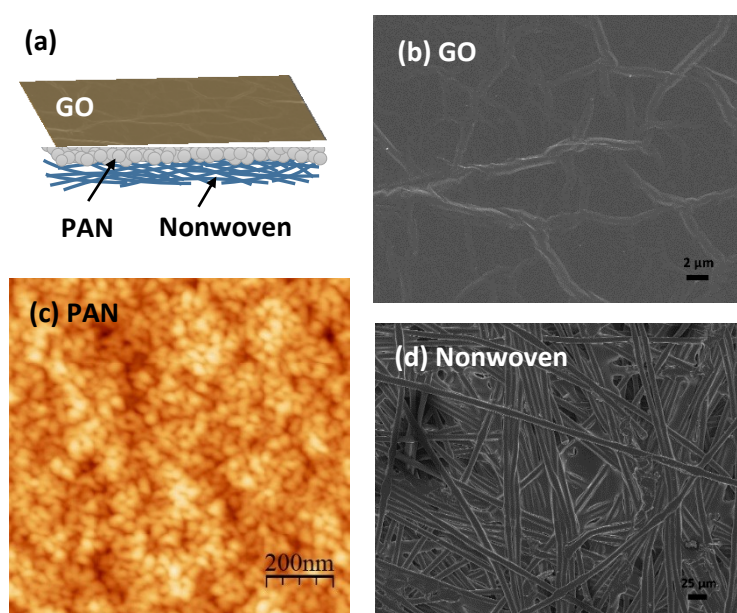


Figure 6.4: (a) Schematic of GO membranes on PAN substrates. (b) SEM image of the surface of GO membrane on a PAN substrate. (c) AFM topology image of the PAN substrates. (d) SEM image of the nonwoven support

Table 6.1: Pure water flux of GO membranes supported by PES and PAN substrates tested using pressure-driven filtration and pervaporation

Substrates	Pure water flux		
	Filtration (L m ⁻² h ⁻¹ bar ⁻¹)	Pervaporation (L m ⁻² h ⁻¹)	
		Room temperature	70°C
PES	0.059	1.74	8.83
PAN	0.056	1.50	8.31

GO membranes synthesized on both substrates were tested for pure water permeation using two different modes: pressure-driven filtration and pervaporation. Pressure-driven filtration was first carried out so that the membranes were compacted and a steady state flux was obtained. GO membranes showed similar permeation fluxes even though two different substrates were used, as shown in Table 6.1. The membranes had a low permeance, lower than 0.1 LMH bar⁻¹ under the pressure-driven condition, which was similar to what observed in the previous chapter. Due to the high tortuosity in GO membranes, the long transport path of water molecules was unlikely to yield a high permeation flux.

However, when tested under the pervaporation mode, the pure water flux of GO membranes was 1.50 – 1.74 LMH, with an apparent 1 bar pressure difference. The higher permeation flux was mainly due to the difference in driving force in the membrane. When vacuum is applied on the permeate side, water on the permeate side surface is evaporated quickly due to a low partial pressure. Whenever the evaporation is faster than the permeation of liquid water, the liquid-vapour interface may move and locate at the entrance or even inside the nanochannels. When the interface reaches the nanochannels, a large capillary pressure can be generated as a result of the extremely small pore size, and will drag water from the feed side to the permeate side swiftly. As reported by Nair et al., the capillary pressure in GO membranes could be as large as 1000 bar [3]. However, the capillary pressure does not exist under the pressure-driven mode as there is no phase change on the permeate side. Water permeation only relies on the hydraulic pressure applied, which is much smaller than the capillary pressure.

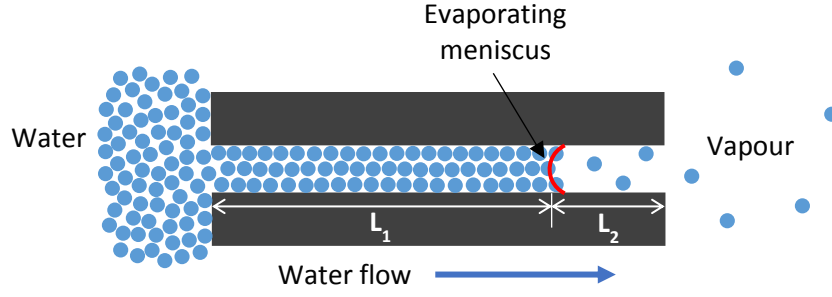


Figure 6.5: Illustration of water transport mechanism in GO membranes in a pervaporation mode

Figure 6.5 illustrates the water transport in the interlayer space of GO membranes during pure water pervaporation. Water enters the nanochannels due to the hydrophilic nature of the membranes, and then permeates through the interlayer space driven by the capillary pressure generated by the evaporating meniscus on the other side. The permeation flux in the interlayer space before the evaporating meniscus (Q_1) is proportional to the capillary pressure (P_c) but inversely proportional to the passage length (L_1):

$$Q_1 \propto P_c / L_1 \quad (6.4)$$

At the evaporating interface, water evaporates and diffuses through the interlayer space if the interface is in the membrane. The vapour pressure at the interface could be assumed to be the saturated pressure and the permeation rate (Q_2) could be determined by the diffusivity of water in the interlayer space (D), the pressure difference between the vapour pressure at the meniscus (P_l) and the vacuum pressure (P_v), and the passage length of the water vapour L_2 :

$$Q_2 \propto D \times (P_l - P_v) / L_2 \quad (6.5)$$

In a steady state, $Q_1 = Q_2$, and the position of the evaporating meniscus moves to attain the steady state permeation flux, which will then determine L_1 and L_2 . Since the transport of the condensed water through L_1 is much faster due to the high capillary pressure, it is reasonable to predict that the evaporating meniscus would be close to membrane downstream surface, and evaporation steps determine the overall water flux.

As shown by Nair et al., the water vapour permeation rate through GO membranes was close to the evaporation rate of a free water surface with the same area of the membrane [3]. To

verify if it is the case for pervaporation, we carried out a simple experiment to measure the evaporation rate of free water surface in vacuum at room temperature. A glass cylindrical bottle half filled with water was connected to a vacuum system and the evaporation rate of water was determined from the change in the mass of the bottle. The water evaporation rate was found to be 1.67 LMH, which was very close to the water permeation flux of GO membranes in pervaporation. The experimental results from pervaporation would be difficult to explain if the water transport only followed the model illustrated in Fig. 6.4. As the surface porosity of GO membranes was very low ($<0.1\%$), the water evaporation would be very slow if water evaporated only via the liquid-vapour interface in the nanochannels.

To match the experimental results, the evaporation area has to be extended to the whole membrane surface rather than staying inside the pores. Such extension of the evaporation area can be realised due to the high surface hydrophilicity of GO membranes, where water molecules can migrate to the whole permeate side membrane surface via surface diffusion before desorption. Such full coverage by surface diffusion is very likely since the required diffusion distance from the entrances of nanochannels to the centre of each GO flake is only a few micrometres, which can be easily covered if the desorption is relatively slow. Since water molecules on the GO surface are bonded by hydrogen bonds, their desorption from the membrane surface would have a similar energy requirement to evaporation from bulk water, which is also to break the hydrogen bond. Therefore, the water flux through GO membranes in pervaporation showed similar value as free evaporation. We note that the water flux through pervaporation can be slightly higher than the evaporation of free water surface, which could be contributed by the larger effective surface area of the membrane due to the surface roughness.

To further study the effect of evaporation rate on the water permeation flux of GO membranes, the pervaporation test was also carried out at $70\text{ }^{\circ}\text{C}$. The pure water flux increased to about 8.31 – 8.83 LMH, which was more than 5 – 5.5 times higher than the flux at room temperature. However, the evaporation rate of free water surface increased to 13.3 LMH at $70\text{ }^{\circ}\text{C}$, which was about 8 times higher than that at room temperature. Such different trends between the pervaporation and free evaporation indicated the change in rate-determining step at higher temperatures. It is known that surface diffusion normally has very low activation energy ($<20\text{ kJ mol}^{-1}$) [19, 20], while the activation energy for desorption could

be higher (latent heat of vaporisation of water is higher than 40 kJ mol^{-1} between room temperature and 70°C [21, 22]). When temperature increases, the rate of desorption increases more than surface diffusion, and consequently, the centre of GO flakes will not be covered by water molecules as they leave the surface before reaching the centre. This leads to the reduction of effective evaporation area and hence the water flux of pervaporation will be lower than free evaporation. Besides the competition between surface diffusion and desorption, another possible reason for the lower water flux could be due to the relatively slow water permeation driven by the capillary force compared to the much higher evaporation rate at high temperature. However this is not very likely considering the huge capillary pressure could be generated in the nanochannels ($>1000 \text{ bar}$).

6.4.2 Pervaporation of ethanol-water mixture through GO membranes

The previous section revealed the water transport mechanism in GO membranes in pervaporation, focussing on the permeate side membrane surface as pure water was used as the feed in the experiments. To have a complete picture of the transport mechanism, the performance of GO membranes in pervaporation was also tested with ethanol-water (95:5 weight ratio) as the feed solution. This is to understand how GO membranes can have high water selectivity even though water permeates through the membrane in a pore flow. Since the PES substrates swelled in ethanol, only GO membranes fabricated on the PAN substrates were tested. The membrane showed a total flux of $0.47 \text{ kg m}^{-2} \text{ h}^{-1}$, with 91.4 wt% of water in the permeate, giving a separating factor of 202. The results were comparable to previous studies though a feed solution with a lower water concentration was used in this study [4, 7]. Both water and ethanol had molecular sizes smaller than the interlayer distance in GO membranes. The good separation of water from the liquid mixture was mainly contributed by the selective adsorption of water molecules on GO membranes.

Figure 6.6 illustrates the water transport in GO membranes when tested for water-ethanol pervaporation. The water transport mechanism was similar to the pure water pervaporation, but with an extra selective adsorption step on the feed side surface. During pervaporation, water molecules were preferentially adsorbed to the membrane surface and then condensed in the interlayer space, forming a condensing meniscus. The condensation of water can be

calculated using the Kelvin equation as shown by Abo, and only a small amount of water was required in the water-ethanol mixture, 1–1.3 ppm, in order for condensation to occur [23]. However, as the concentration of water was very low in the liquid mixture, the permeation flux was therefore affected by adsorption and was lower than the pure water flux.

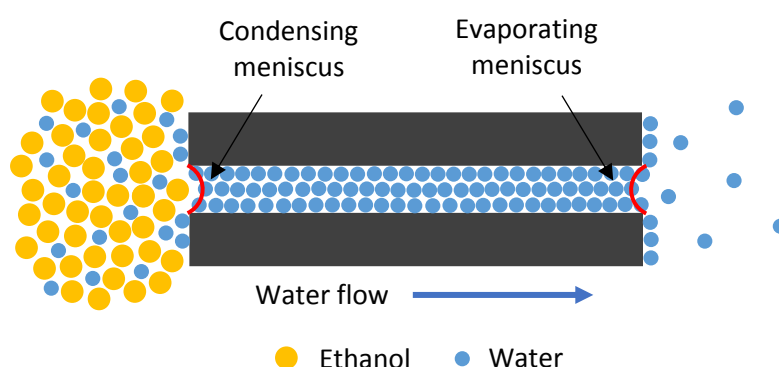


Figure 6.6: Illustration of water transport mechanism in GO membranes in water-ethanol pervaporation

The preferential water adsorption and condensation has enabled the separation of water from the solvent mixture even when the concentration of water was very low. During pervaporation, the concentration of water in the membrane was much higher than the concentration in the bulk solution. The concentration discontinuity must be distinct in a pore flow model to maintain the selectivity, and an interface therefore formed at the entrance of the pores as a result of the steep water concentration gradient. The interface was verified later and used for measurement of EIT of miscible liquids.

6.4.3 Measurement of effective interfacial tension using GO membranes

In order to have an accurate measurement of EIT using GO membranes, it is important to ensure the liquid will predominantly permeate through the interlayer space in the membranes. However, as discussed in Chapter 5, GO membranes could form hierarchical structure due to imperfect stacking of GO flakes [24]. Large spaces or microstructural defects formed could provide extra transport paths for the liquid to permeate through the membrane.

Therefore, GO membrane was first tested for water permeation under a pressure-driven condition to compact the membrane and to eliminate most of the microstructural defects. It was also to fill the membrane interlayer space with water molecules so that an EIT would form when contacting with a water-solvent mixture.

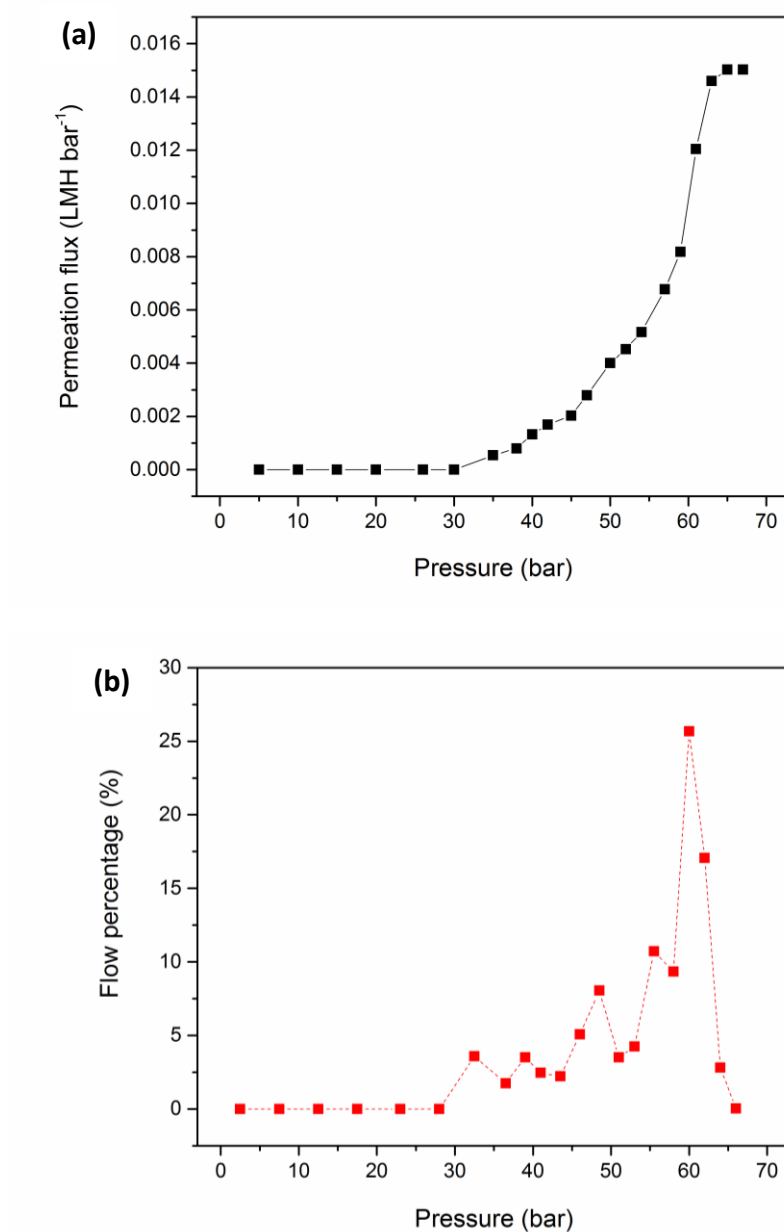


Figure 6.7: (a) The permeance of ethanol-water (80:20) mixture at increasing pressure
(b) Flow distribution of GO membrane at different pressure

An ethanol-water mixture with a weight ratio of ethanol:water = 80:20 was used for the EIT measurement. During the experiment, the pressure of the membrane cell was increased gradually and the permeance at different pressures is shown in Figure 6.7 (a). At relatively low pressures less than 35 bar, the liquid mixture did not permeate through the membrane at all. The impermeable GO membranes at the low pressures showed an evidence of the formation of a resistant interface at the membrane surface, which could only be overcome by applying a higher pressure. The observation was similar to the porometry tests where gas-liquid and immiscible liquid-liquid interfacial tensions were used to measure the pore sizes of membranes [25, 26]. At the pressure when the gas or the replacing liquid started to push the replaced liquid through the membrane, the bubble point or the largest pore size in the membrane was determined.

When the pressure was higher than 35 bar, the permeance (permeation flux normalised by pressure, $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$) increased with the increasing in pressure. The permeance increase showed an “S” type curve, which was a typical break-through curve observed in gas-liquid or liquid-liquid displacement measurements. It was interpreted as a step-by-step opening of pores at increasing pressure; the EIT at more pore entrances was overcome when the pressure increased, contributing to more transport channels and the increase in permeance. The membranes reached a constant permeance at about 65 and a further increase in pressure to 67 bar did not change the permeance. At this point, the EIT at the smallest pore was overcome and all pores were open for liquid permeation. As the filtration cell used in the experiment could only withstand a maximum pressure of 69 bar, the experiment did not proceed with a higher pressure. The constant liquid mixture flux was $0.015 \text{ LMH bar}^{-1}$, which was comparable to the pure water flux, $0.019 \text{ LMH bar}^{-1}$, measured before the EIT measurement.

Figure 6.7 (b) shows the flow percentage of the GO membrane at different pressure and the flow percentage was the highest at 60 bar. At this pressure, the EIT at the entrance of the interlayer space was overcome and large amount of liquid could permeate through the interlayer space, which was the main transport path in the membranes. However, the flow percentage distribution was not very sharp though majority of the flux, 66% was in the pressure range between 57 to 65 bar. The distribution of flux at lower pressures indicated that the interlayer space in the GO membrane was not uniform even after high pressure

compaction, which was concurrent with the nanofiltration results and could be explained by the hierarchical structure model described in Chapter 5.

By using the pressure with the highest flow percentage and the properties of GO membranes, the EIT between water and the ethanol-water (80:20) mixture could be calculated using the Young-Laplace equation (Equation 6.2). The interlayer space of GO membranes enlarged when immersing in water but unfortunately the XRD machine we used could not measure the interlayer distance of wet samples accurately. From the literature, hydrated interlayer space of GO reported ranged from 13 to 14 Å [9, 27, 28]. After deducting the thickness of graphene ≈ 3.4 Å [3], the interlayer distance available for water permeation was assumed to be about ≈ 10 Å and 5 Å was used as the pore radius in the calculation. The contact angle was assumed to be zero as the water molecules were adsorbed on the wall of the interlayer space. Using these parameters, the EIT between water and the ethanol-water (80:20) mixture is calculated to be 3.0 mN m^{-1} . The measurement of the EIT between ethanol and water is very challenging using other methods due to their high diffusivity and there is currently no experimental data in the literature can be used to compare the value obtained in our experiments. Quincke attempted to measure the EIT between alcohol and water using a fluid mechanic approach more than a century ago but the value was not obtained [29]. However, the interface between water and ethanol was indeed observed by Sugii et al. in a microfluidic device [30]. The liquids showed a shear stress difference of more than 1.1 N m^{-2} in the device, which was attributed by the Korteweg stress. However, their experimental data could not be translated directly into EIT. The EIT between water and 1-butanol was measured by Pojman et al. using a spinning-drop tensiometer [13]. As water and 1-butanol were semi-immiscible, the technique may still give a reasonably accurate measurement. The EIT obtained was about 17 mN m^{-1} , which was much higher than the EIT of water/ethanol+water obtained in our study. The EIT of water/1-butanol is also higher than the interfacial tension between mutually saturated water-rich phase (92.3 wt% water) and isobutanol-rich phase (20.1 wt% water) in the water/1-butanol system, which is only 1.8 mN m^{-1} . The lower interfacial tension at equilibrium could be due to the lower concentration gradient across the interface [13].

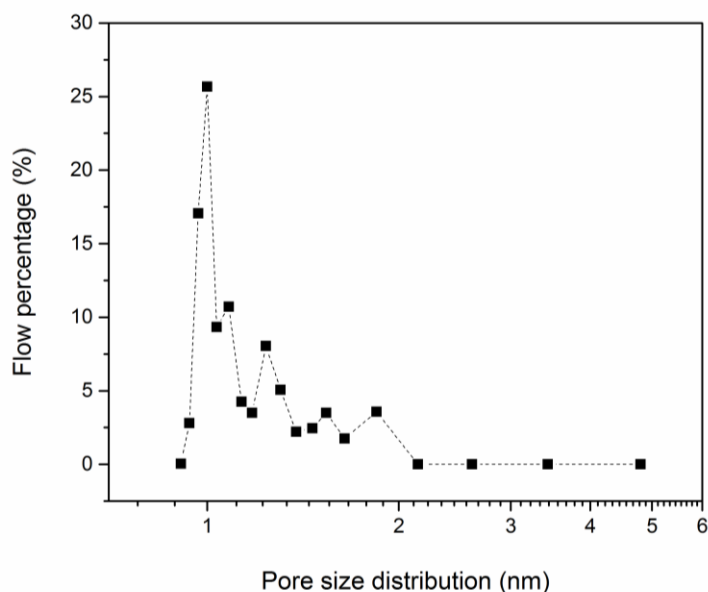


Figure 6.8: Pore size distribution of GO membranes

By using the calculated EIT, the pore distribution in GO membranes can be estimated by using the flow percentage, as shown in Figure 6.8. The corresponding pore size at each pressure point was calculated using Equation 6.2. The pores in GO membranes showed a distribution ranging from 0.9 nm to 2.1 nm though most of them were in the range of 0.9 to 1.15 nm, which was mainly contributed by the interlayer spaces in GO membranes. Such distribution of interlayer space was quite commonly observed especially when GO membranes were in a hydrated form [27]. Pores larger than the interlayer space can be due to the imperfect stacking in the hierarchical membrane pore structure, as discussed in the previous chapter. Though the membrane was compacted before the EIT measurement and was under high pressure for more than a week during the measurement, the bigger pores still could not be completely eliminated. These bigger pores could not be easily detected using other characterization techniques such as XRD, as shown in Chapter 5. The bigger pores, albeit only occupy a small proportion of all pores, could be the reason of non-perfect rejection rates in nanofiltration and pervaporation even after membrane compaction.

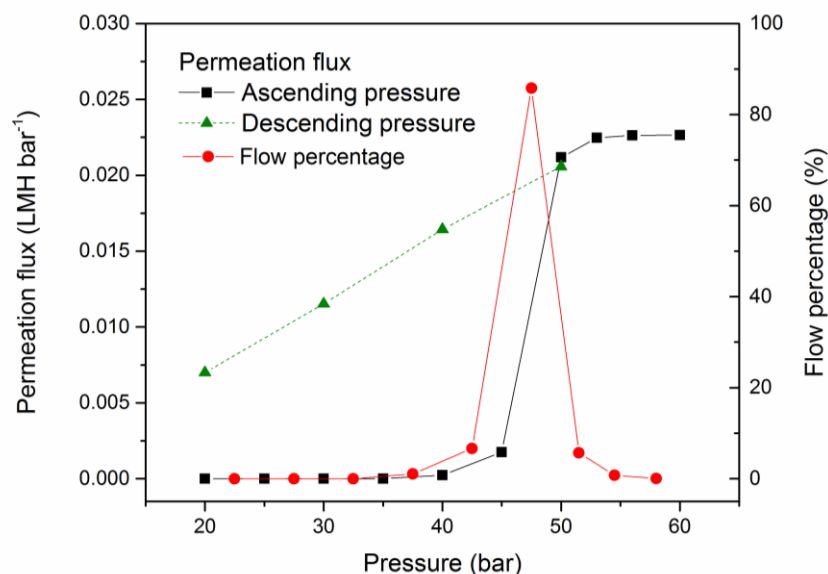


Figure 6.9: The permeation flux of ethanol-water (70:30) mixture at ascending and descending pressure, and the flow distribution at different pressure

The EIT of water-ethanol at a higher water concentration (30 wt%) in the ethanol mixture was also measured. Figure 6.9 shows the permeation of the GO membrane at increasing pressure. Same as what observed previously, the membrane was impermeable at low pressure and the liquid only started to permeate through the membrane at 40 bar, which was slightly higher than the case with a lower water concentration (20 wt%). The liquid mixture was expected to permeate through the membrane at a lower pressure as the concentration difference at the interface was lower, which resulted in a lower EIT. The higher bubble point pressure could be due to the larger pressure increase step used in the experiment or the change in pore distribution after long period of measurement. The liquid permeance reached a constant value at 53 bar and a further increase in pressure until 60 bar did not change the permeance.

After the pressure-increasing cycle, the pressure was stepped back to pressures lower than the break-through pressure of 40 bar. The permeance decreased with the pressure but it was still maintained at a high level, demonstrating that most of the pores were kept open when the pressure was withdrawn. Such result indicated that the resistance to the external pressure was not from possible osmosis pressure, otherwise the permeation should have stopped when the pressure was reduced below the break-through pressure. Additional evidence to exclude the effect of osmosis pressure was the composition in the permeate, which was the

same as the feed, while it would give a selectivity between ethanol and water if the permeation was against an osmosis pressure. The reduction in permeance could be due to reformation of the miscible interfacial tension at some pore openings, as a result of the competing effect from preferential adsorption.

The permeance showed the largest increase when the pressure was increased from 40 to 45 bar, which accounted for 86% of the total flux. The sharper distribution in the flow percentage could be due to the larger pressure increase step. An EIT of 2.38 mN m^{-1} was obtained by calculating using the pressure at the highest flow percentage. EIT is proportional to the square of the concentration difference, as shown in Equation 6.1, and both of the obtained EIT agreed with the theoretical relationship. Using the data obtained, the EIT between water and pure ethanol was estimated to be 4.8 mN m^{-1} . However, more points with varied concentration need to be further measured to obtain a more accurate EIT value. We also attempted to measure the EIT using a higher ethanol concentration, 95 wt%, but the attempt failed because the pressure required to overcome the EIT was higher than the maximum pressure the filtration cell could withstand. But it was apparent that the higher ethanol concentration increased the concentration gradient across the interface and thus the EIT, which again was concurrent with the theoretical trend according to Equation 6.1.

6.5 Conclusions

GO membranes showed higher pure water permeation in pervaporation compared to the pressure-driven filtration due to the difference in driving force. Water molecules condensed in the interlayer space and permeated through the membranes at a very high speed due to the high capillary pressure in GO membranes. The high water adsorption capacity of GO membranes also yielded a good selectivity in dewatering of ethanol in pervaporation. In addition, a stable interfacial tension due to a steep concentration gradient formed at the pore entrance was verified. This surface phenomenon has enabled the measurement of EIT between miscible liquids using GO membranes. The EIT of water-ethanol was successfully measured in this study and the result further demonstrated the pore size distribution of GO membranes as a result of the hierarchical microstructure of the membranes.

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Chapter 7: Development of graphene hollow fibre membranes

Abstract:

Graphene is an attractive material for membrane applications due to its one-atomic thickness and excellent mechanical properties. However, it is still challenging to fabricate large area of graphene for membrane applications. In this chapter, graphene membranes were synthesized on ceramic hollow fibres using a CVD approach. Nickel layer was first coated on the outer surface of hollow fibres via electroless plating, which served as a catalyst layer for graphene growth. Multi-layer graphene membrane was successfully synthesized on the nickel layer. However, leaching of the nickel layer after graphene synthesis still remained challenging. Graphene membranes are exceptional inert, which can serve as an excellent protection layer against corrosive chemicals.

7.1 Introduction

Graphene, as a single layer of sp^2 -bonded carbon atoms packed in a hexagonal lattice, is an attractive material for thin film and membrane applications. As the permeability of membranes is inversely proportional to the thickness, ultrathin graphene membranes are predicted to have a superior membrane performance [1]. Sub-10 nm membranes have been successfully fabricated using material such as graphene oxide, polyamide and two dimensional metal organic framework (MOF), and these membranes showed exceptional performances in gas separation and nanofiltration [2-4]. For example, the sub-10 nm polyamide nanofilms showed a very high acetonitrile permeance up to $112 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which was more than 10 times higher than most of the reported nanofiltration membranes [3]. Graphene as a material with an atomic thickness and excellent mechanical strength demonstrates a great potential to prepare ultrathin membranes with a high permeability [1].

There are several methods to synthesize graphene such as mechanical exfoliation, chemical exfoliation, chemical vapour deposition (CVD) and epitaxial growth. As discussed in the previous chapters, large amount of graphene oxide (GO) can be synthesized easily by using the chemical exfoliation approach. GO produced can be reduced to reduced graphene oxide (rGO) by using methods such as chemical and thermal reductions [5]. Though the number of

surface functional groups can be very much reduced, the properties of rGO is still very different from graphene; for example, the electrical conductivity of rGO is much lower compared to pristine graphene [6]. While for membrane application, thin rGO membranes with thickness 22–53 nm were successfully fabricated by Han et al. using the method similar to preparing GO membranes [7]. However, further reduction in the membrane thickness can be very challenging using the self-assembly method as a full coverage of rGO nanosheets on the substrates is difficult to achieve. Furthermore, the microstructural defects formed as a result of imperfect stacking of rGO nanosheets may degrade the membrane performance.

Single layer graphene can be obtained using mechanical exfoliation as demonstrated in the scotch-tape experiment [8]. Though high quality graphene can be produced, the area of the graphene obtained using this method was still in the micron range [9], constraining their practical applications. In the last decade, CVD has been much explored to synthesize large area of graphene for various applications [10-14]. In this method, metals such as nickel and copper are used as a catalyst surface for graphene synthesis at high temperature. Light hydrocarbon such as methane and solid polymers can be used as the carbon precursor for graphene growth. The area of graphene synthesized will be determined by the area of the catalyst surface and graphene can be transferred to various types of substrates for various thin film applications [10, 12, 14, 15]. Graphene has been successfully transferred to flat porous substrates and tested for gas separation and water filtration [16-18]. Pristine graphene is impermeable to all types of gas including helium [19]. However, defects may form during the synthesis and transferring of graphene and these defects can act as intrinsic pores, allowing molecules to permeate through the membranes. Besides, tiny pores can also be created in the graphene layer to improve the permeability.

In this study, graphene membranes were developed into a hollow fibre geometry for scaling up purposes. The graphene transferring method used in flat sheet substrates may not be feasible as rolling graphene on hollow fibre substrates is technically challenging. Besides, the edge of the graphene layer has to be sealed to form a continuous layer on the hollow fibre substrates. Therefore, graphene membrane was proposed to be synthesised directly on the hollow fibre surface using the CVD method. To do so, a continuous, dense metal surface on the hollow fibres is required and metal hollow fibres such as copper or nickel can be used, as illustrated in Figure 1. The metal hollow fibres act like a metal foil, providing an active surface

for graphene growth. However, as the metal hollow fibres will then serve as the substrates of the graphene membrane, the metal hollow fibres have to be partially etched to create a porous structure after graphene synthesis. This is to enable fluid transport through the substrate in the final membranes while the graphene serving as the separating layer.

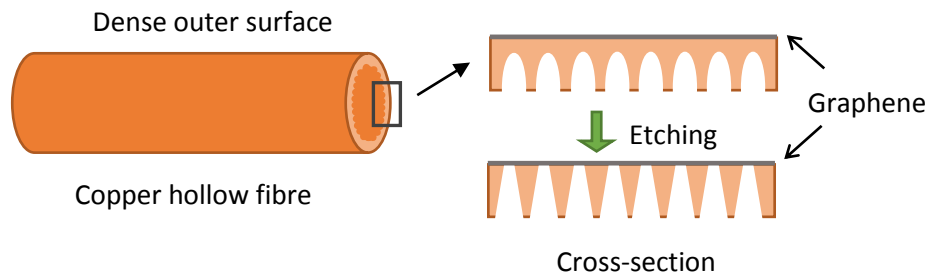


Figure 7.1: Example of how graphene hollow fibres can be synthesized on metal hollow fibres

To implement this idea, the metal hollow fibres have to have a dense outer surface to determine a continuous graphene layer. At the same time, they also need to have a controllable porosity with a sufficient mechanical strength after etching. Metal hollow fibres made of a single component are unlikely to meet such criteria during etching. Dual-layer metal hollow fibres with two different types of metal (e.g. copper/stainless steel hollow fibres) can be explored to determine a dense surface for graphene synthesis while maintaining their mechanical strength after etching if the leaching is selective to only one phase.

Instead of using metal hollow fibres, metal surface was coated on ceramic hollow fibres in this study to provide a catalytic surface for graphene membrane synthesis. Yttria-stabilized zirconia (YSZ) hollow fibres were used as the substrate and they were fabricated in large batch using the phase inversion-sintering method [20]. YSZ hollow fibres are excellent substrates for ultrathin membranes due to their smooth surface, high mechanical strength and excellent chemical resistance.

Figure 7.2 shows the working principle of the synthesis of graphene hollow fibre membranes in this study. YSZ hollow fibres are first plated with nickel using the electroless plating method. Electroless plating of nickel is commonly used in the industry and similar technique has been used to coat metals such as palladium on ceramic surfaces [21-23]. After that, the nickel layer

is annealed at high temperature to create a smooth surface for graphene growth. Right after the annealing, graphene is grown using the CVD approach in the same furnace. The nickel layer can then be washed off after the synthesis, leaving the graphene layer sitting on the YSZ substrate.

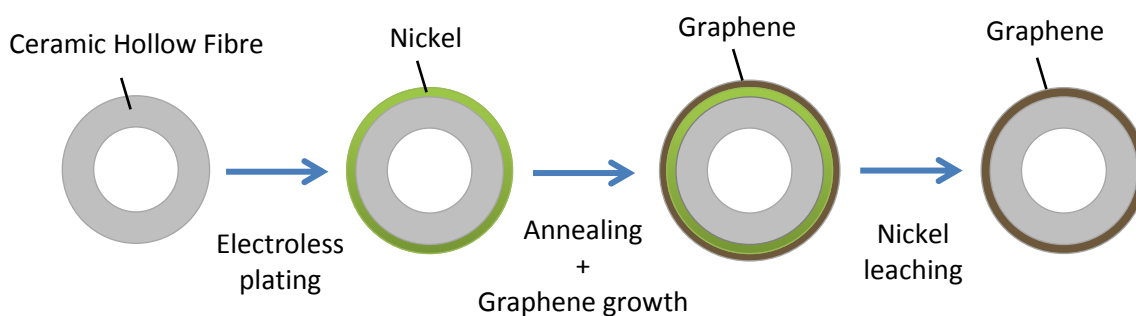


Figure 7.2: Working principle of synthesis of graphene membrane on ceramic hollow fibres

7.2 Preparation of graphene hollow fibre membranes

7.2.1 Nickel electroless plating

Tin (II) chloride (>99.99 %, Sigma-Aldrich), palladium (II) chloride (99.999 %, Sigma-Aldrich) and hydrochloric acid (37%, AnalaR NORMAPUR) were used to prepare the sensitisation and activation solutions. The plating solution was prepared using nickel (II) acetate tetrahydrate (99.998 %, Sigma-Aldrich), EDTA (IDRANAL®III, Riedel-de Haen), anhydrous sodium hydroxide (>98%, Sigma-Aldrich), DL-lactic acid (90%, Fluka Analytical) and hydrazine hydrate (Sigma-Aldrich). The same YSZ hollow fibres described in Chapter 4 were used here in this chapter as the substrates to synthesize graphene hollow fibre membranes. The YSZ hollow fibre were fabricated through a combined phase-inversion/sintering process, and the green fibres were sintered at 1150 °C to gain the mechanical strength [20].

Nickel was coated on the outer surface of the YSZ hollow fibre substrates using electroless plating and the procedure was modified from a previous study [24]. Seeding or activation of hollow fibres with Pd nuclei was first carried out and the procedure of the seeding step is shown in Figure 7.3. YSZ hollow fibres were immersed in an acidic SnCl_2 solution for 5 min, followed deionised water for 5 min, acidic PdCl_2 solution for 5 min, diluted HCl solution for 2

min and finally deionised water for 3 min. The procedure was repeated 6 times to ensure a good coverage of Pd nuclei. The compositions of the solutions are shown in Table 7.1. To ensure uniform seeding on the hollow fibre surface, all the chemical baths were homogenised by air bubbles.

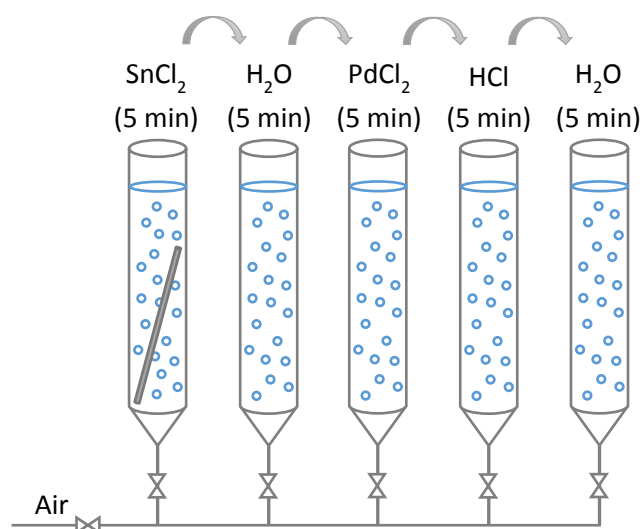


Figure 7.3: Activation of YSZ hollow fibre substrates before nickel plating

Table 7.1: Compositions of solution used in the activation and the electroless plating

Step	Compound	Concentration
Sensitisation	SnCl ₂	1 g L ⁻¹
	HCl	0.01 M
Activation	PdCl ₂	1 g L ⁻¹
	HCl	0.01 M
Rinsing	HCl	0.01 M
	Ni(Ac) ₂ ·4H ₂ O	0.09 M
Electroless Plating	Na ₂ EDTA·2H ₂ O	0.016 M
	CH ₃ COCOOH	0.15 M
	NaOH	7.5 g L ⁻¹
	N ₂ H ₄	0.8 M

The activated hollow fibres were plated with Ni by immersing in a plating solution and the chemical composition of the plating solution is listed in table 7.1. The nickel electroless plating was carried out at 80 °C and the plating solution was immersed in a water bath to maintain the temperature. Different plating temperature, 75 and 85 °C, was also used to study the effect on the plating rate. The solution was homogenised by air bubble to determine a more uniform coating. The thickness of the nickel layer was controlled by the plating time.

7.2.2 Nickel annealing and CVD growth of graphene

After nickel plating, the hollow fibre was annealed at 900 °C to create a smooth surface for graphene growth. The hollow fibre was placed in a tubular furnace and the setup of the furnace is shown in Figure 7.4. The furnace was heated at a rate of 5 °C min⁻¹ and the annealing was done for 30 min in flowing hydrogen and helium at a ratio of 1:1.

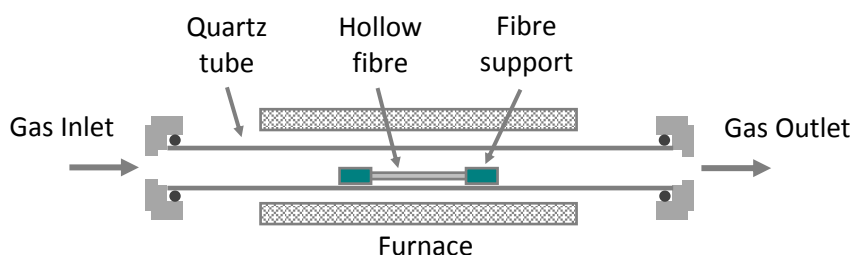


Figure 7.4: CVD setup for nickel annealing and graphene growth

Graphene synthesis was carried out in the same furnace right after the annealing. To start the synthesis, methane was supplied to the quartz furnace tube, serving as the carbon precursor of the synthesis. The CVD process was carried out for 20 min at atmospheric pressure. At the end of the synthesis, the methane flow was stopped and the quartz tube was withdrawn from the furnace to cool the sample down rapidly. In the meantime, the flow rate of helium was increased to aid the cooling. The rapid cooling step was particularly important for graphene growth on nickel surface as graphene formed during the cooling through precipitation on the metal surface. The temperature profile of the annealing and CVD is shown in Figure 7.5.

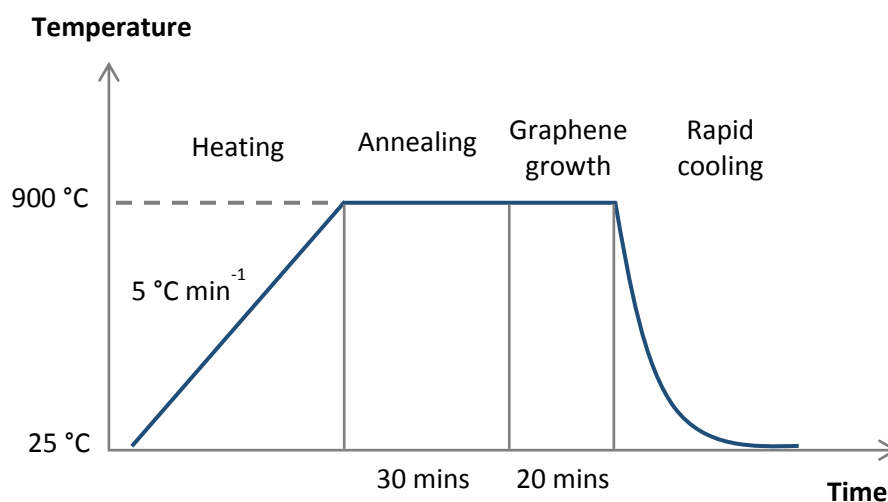


Figure 7.5: Temperature profile of the annealing and CVD

7.2.3 Post treatment and nickel etching

After graphene synthesis, the nickel coating in between the graphene and the hollow fibre substrate was leached by immersing the hollow fibres into a 1M nitric acid solution overnight. As graphene can act as a protective layer, leaching of the nickel layer can be very slow. Pore creation in the graphene layer was carried out to accelerate the nickel removal. The graphene/nickel/YSZ hollow fibres were immersed in a solution with gold nanoparticles (diameter = 5 nm, Sigma Aldrich) for 1 h and then treated at 200 °C for 2 h. The adsorbed nanoparticles acted as a catalyst for the oxidation of graphene during the heat treatment.

7.2.4 Characterization

The morphologies of the nickel coating and the growth of graphene were characterized by using a scanning electron microscope (LEO Gemini 1525 FEGSEM and Zeiss Auriga Crossbeam). Raman spectrometry (WITec solid state, diode pumped 532 nm laser) was used to determine the quality of graphene synthesized.

7.3 Results and discussion

7.3.1 Nickel electroless plating and annealing

YSZ hollow fibres were activated by seeding with palladium nuclei on the surface before plating. The YSZ hollow fibres turned brown after the seeding step as shown in Figure 7.6. The SEM images of the YSZ hollow fibres before and after the activation step are shown in Figure 7.7. Most of the palladium seeds were very small, with diameter smaller than 50 nm and they were well dispersed over the hollow fibre surface. Some agglomerations were also observed though they were generally smaller than 200 nm.



Figure 7.6: Photo of a YSZ hollow fibre after the Pd seeding step (Scale bar: 5 mm)

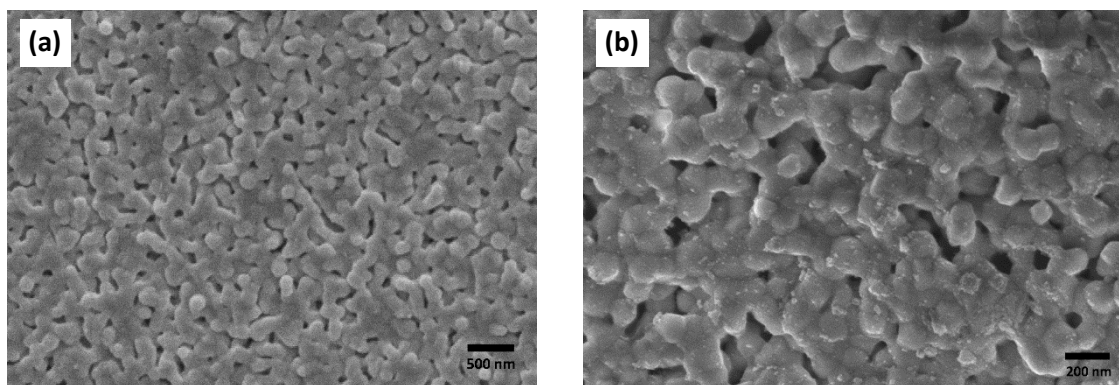
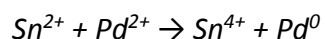


Figure 7.7: SEM images of YSZ hollow fibres (a) before and (b) after the Pd seeding step

During the activation step, YSZ hollow fibres were first immersed into the acidic SnCl_2 solution and Sn^{2+} ions were adsorbed on the hollow fibre surface. Palladium nuclei formed when the hollow fibres were immersed in the acidic palladium solution.



The activation method was similar to the method used in palladium and silver electroless plating [22, 23]. Though nickel will be plated in this study, the palladium nuclei on the hollow fibre surface can still serve as a catalyst during the plating step.

Figure 7.8 shows the nickel plated on the YSZ hollow fibres. Two types of nickel morphology were observed; when the plating was well controlled, nickel formed small particles and they were packed densely on the hollow fibre surface as shown in Figure 7.8 (a). However, the sharp morphology shown in Figure 7.8 (b) was observed when the plating rate was too high at high temperature or when the air bubbling was insufficient. Similar sharp morphology was observed in previous studies when the temperature used was higher than 85 °C [25]. This type of morphology was not favourable for nickel coating in our study as the coating layer normally could not reach a large thickness. The coating layer peeled off easily when the coating time was prolonged for thicker coating.

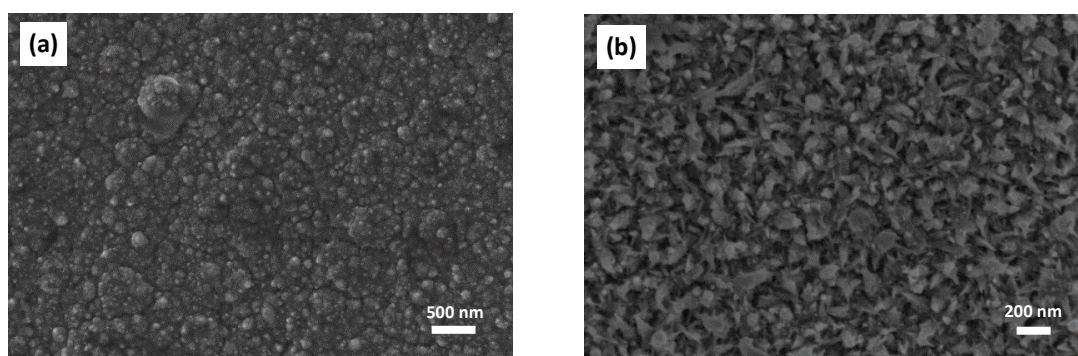
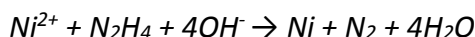


Figure 7.8: SEM images of nickel coating on the hollow fibre substrates

Plating temperatures ranging from 75 to 90 °C were studied by Hagg et al. and found not to affect the plating rate significantly, especially when the plating solution was bubbled with nitrogen [24]. However, we found in our study that the plating rate was too low at 75 °C; the plating was not successful in most of the batches even after 2 h where no metal crystal was formed on the hollow fibre surface as observed under the SEM. The lower plating rate could be due the different types of substrates, the fewer number of cycles in the activation step, and the solution bubbling condition used in our study. Therefore, 80 °C was used in our experiment as plating at a higher temperature was difficult to control and the undesirable sharp morphology was obtained.

Hydrazine was used as the reducing agent in the nickel plating to determine a pure nickel layer. The overall reaction of the plating is:



Hydrazine is a strong reducing agent and it is also commonly used for electroless plating of palladium and silver [22, 23]. Reducing agents such as sodium hypophosphite was widely used in nickel plating in the industry and other studies [21, 26, 27]. However, nickel-phosphorus alloy will be deposited and the presence of phosphorous in the nickel coating may affect the graphene growth later on.

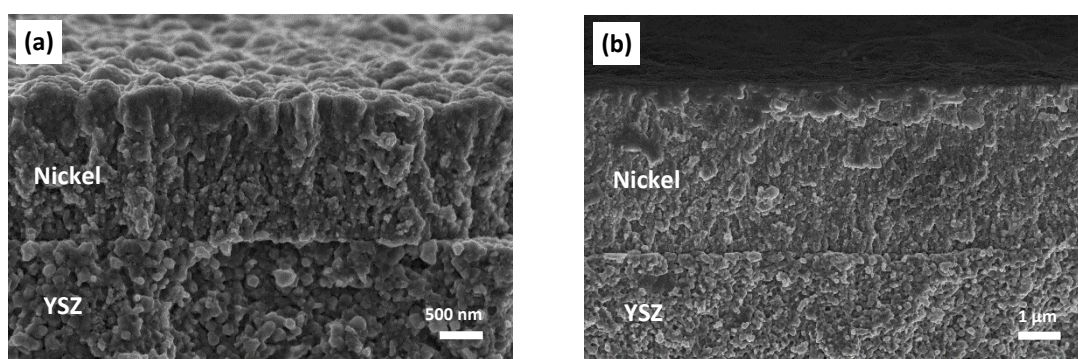


Figure 7.9: SEM images of nickel plated hollow fibre with different plating time at 80 °C. Plating thickness: (a) 1.7 micron. (b) 4.0 micron)

Figure 7.9 shows the SEM images of the cross-section of nickel plated YSZ hollow fibres. The nickel layer looked very dense and had a good integration with the YSZ substrates. The thickness of nickel could generally be controlled by the plating time and nickel layer with a thickness as thin as 250 nm was obtained by having a minimum plating time of 1 h. By increasing the plating time to 6 h, the thickness of nickel can be increased to about 4 µm. However, due to the use of strong reducing agent at high temperature, the plating solution can be unstable [21]. This could cause variation in the nickel thickness sometimes. Therefore the plating solution was not reused in this study and fresh solution was prepared all the time to ensure repeatability.

The gas tightness of the nickel plated hollow fibre was tested using the gas-permeation set-up described in Chapter 4 to evaluate the coating of the nickel layer. The N₂ permeation result is shown in Figure 7.10 and the hollow fibre had a low gas permeability of about 1.5-2 GPU (1

Gas Permeation Unit (GPU) = $10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} = 3.35 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$). This was much lower than the hollow fibre substrates which had a gas permeation flux higher than 1000 GPU. The plated nickel layer was very dense though it was not totally gas tight as gaps may still exist between the nickel particles. Thermal annealing was carried out to determine a dense and a smooth nickel layer for graphene synthesis.

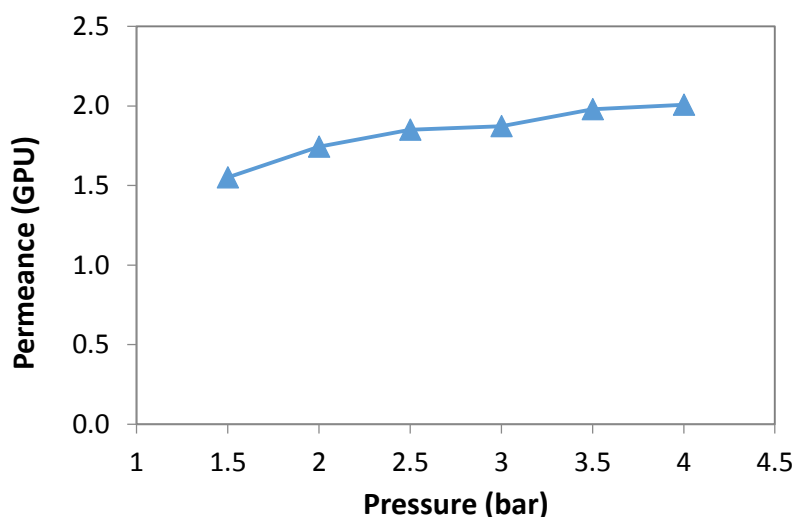


Figure 7.10: Gas tightness test of nickel plated hollow fibre membrane before annealing. N_2 was used as the feed gas

The hollow fibres were annealed at 900°C under the H_2 and He environment for 30 min. Figure 7.11 shows the photograph of an annealed nickel-coated hollow fibre. The surface was very shining after annealing, indicating a dense smooth surface. The surface of the nickel layer looked very dense indeed under the SEM, as shown in Figure 7.12. During the heat treatment, the nickel nanoparticles merged into large metal particles with grain size larger than $1 \mu\text{m}$ and any gaps between the nanoparticles were closed. At a tilted angle (Figure 7.12 (b)), the nickel surface looked slightly uneven with a height deviation smaller than $1 \mu\text{m}$, which is roughly same as the grain sizes. The nickel surface on the hollow fibre with such roughness should not hinder the graphene synthesis as graphene was successfully grown on 3D nickel foam and nickel particles in previous studies [28-30]. Figure 7.13 shows the cross-section of the nickel coating on YSZ hollow fibre before and after the annealing. The nickel layer formed large grains throughout the cross-section after annealing and the thickness did not change significantly as observed from the SEM images.



Figure 7.11: Photograph of an annealed nickel-coated YSZ hollow fibre

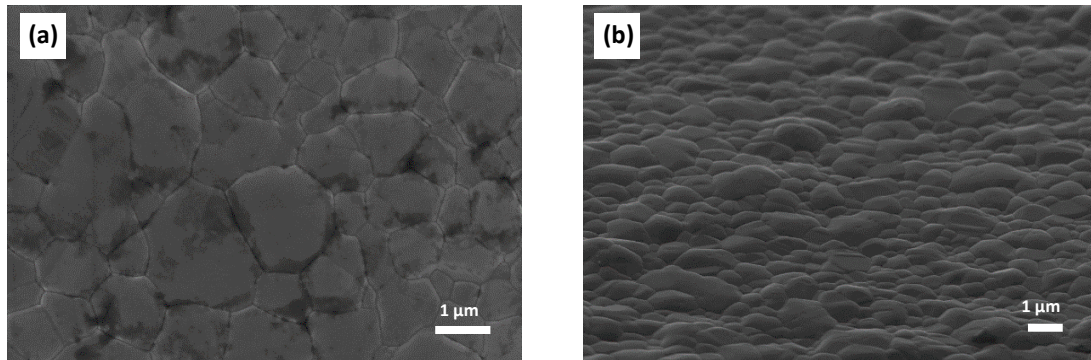


Figure 7.12: SEM images of nickel plated YSZ hollow fibres after thermal annealing at 900 °C (a) top view (b) tiled view

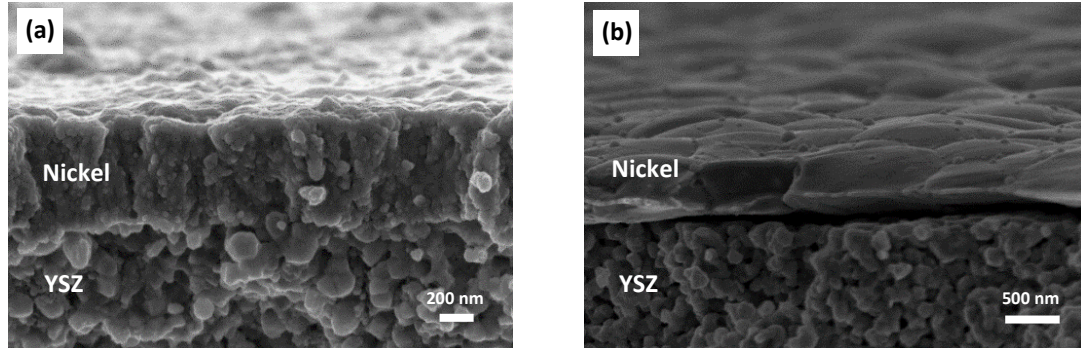


Figure 7.13: SEM images of the cross-section of the nickel coating on YSZ hollow fibres (a) before and (b) after thermal annealing.

Though large nickel grains formed in most part of the surface, defects were observed sometimes, as shown in Figure 7.14 (a). Some of the areas were not covered by nickel coating after annealing though such defects were not observed before the annealing. The formation of defects could be due to an uneven coating in the plating step but it could also be caused by an insufficient coating thickness overall. Submicron electroless plated metal coating was difficult to achieve especially on porous ceramic substrates. The thickness of coating was

normally larger than 5 times the diameter of the surface pore size of the substrates to ensure a continuous coating and a strong mechanical strength of the coating layer [22]. The surface pore size of the hollow fibre used in this study was about 80 nm and a coating thicker than 400 nm should be sufficient to ensure a good coating layer. However, defects were observed in the sample with a nickel coating of 600 nm. As the diameter of the defects could reach the micron size, they may not be eliminated by further annealing. On the other hand, defects with different morphology were also observed in some samples, as shown in Figure 7.14 (b). This type of defects could be due to an uneven surface plating where large agglomerations may form and caused defect-free surfaces difficult to achieve even after annealing.

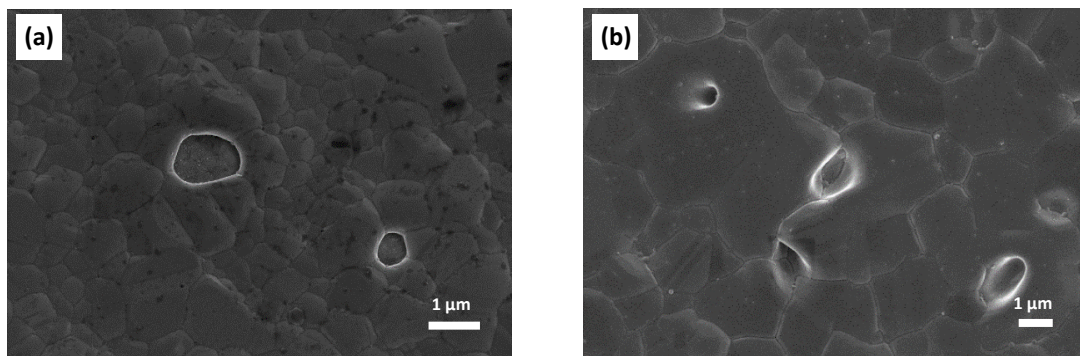


Figure 7.14: SEM images of nickel coating on YSZ hollow fibre after thermal annealing

The effect of plating thickness could be noticed more clearly when the coating was thinner than 500 nm. As shown in Figure 7.15, nickel did not cover the entire surface of hollow fibre after annealing even though the hollow fibre surface was completely plated with nickel. The discontinuous nickel coating could be due to insufficient coating of nickel from electroless plating. As the nickel nanoparticles were densely packed together after electroless plating, a minimum volume change in the nickel layer was expected during the annealing. However, the annealing of nickel could be very fast and nickel formed large grains with diameter bigger than 1 µm after annealing for 30 min. The growth of nickel grain did not only happen in the two dimensional direction but also in the vertical direction. Each nickel grain may grow up to a certain diameter-to-thickness aspect ratio and further annealing will cause mobilization of metal to form a larger grain. This could happen more easily in the case in this study as the coating of nickel was done on a ceramic surface. The adhesion between ceramic and metal was minimum, and metal could move on the ceramic surface at high temperature during the

annealing. Nickel grains or crystals also formed spherical structure as the structure could have a lower surface energy (Figure 7.15 (b)). The success of the annealing was very much dependent on the thickness of the nickel plating. In this study, nickel coating with thickness larger than 1 μm generally gave a good surface coverage after annealing.

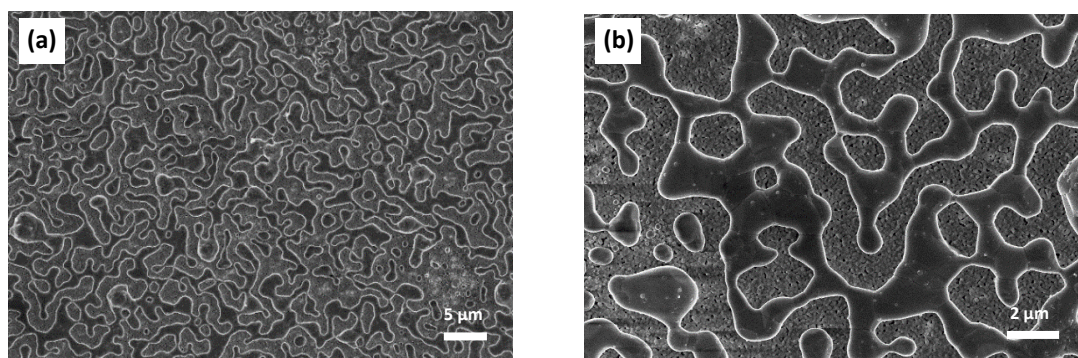


Figure 7.15: SEM images of the surface of hollow fibre after thermal annealing. The surface was not entirely covered by nickel due to the insufficient coating of nickel.

Though requiring multiple steps, electroless plating is a simple technique to create a good nickel coating on ceramic hollow fibre substrates, which can be scaled up easily. Nickel vaporization was used in some graphene synthesis studies to obtain a nickel layer, but the technique required a more complicated experimental set-up and it may not be easy to determine an even coating on the hollow fibre substrates due to the round geometry. Considerable work has been carried out in this study to ensure a good coating of nickel layer. The nickel coating on ceramic hollow fibre is not only useful for graphene synthesis, but can also be applied for hydrogen permeation as hydrogen is soluble in nickel at high temperature. Though the solubility of hydrogen in nickel is not as high as in palladium, a commonly used metal for hydrogen permeation, the cost of using nickel can be much lower [31].

7.3.2 Graphene synthesis on nickel-coated YSZ hollow fibres

Graphene was grown on the nickel surface using methane as the carbon precursor and the synthesis was carried out in the same furnace right after the annealing by changing the flow rate and the composition the feed gas. A flow ratio of $\text{He:H}_2\text{:CH}_4 = 8:1:1$ was used in this study and it was based on the growing conditions reported previously [14, 32]. The CVD was run for 20 min before the sample was cooled rapidly. Figure 7.16 shows the photographs of the hollow fibre before and after the graphene synthesis. The hollow fibre still looked very shiny after the CVD though it turned slightly darker due to the carbon layer formed.

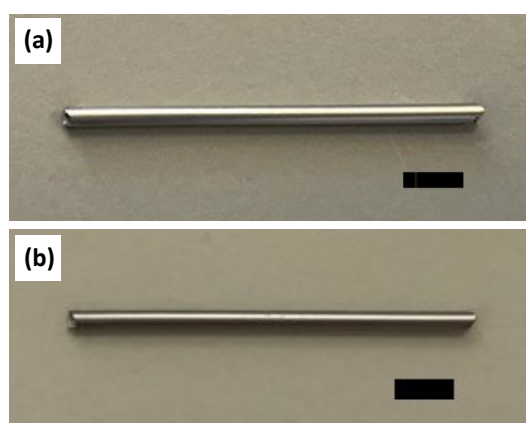


Figure 7.16: Photograph of annealed nickel/YSZ hollow fibre (a) before and (b) after the CVD graphene growth. (Scale bar: 5 mm)

Figure 7.17 shows the SEM images of the nickel surface after the graphene growth. The success of graphene synthesis can be indicated by the wrinkles formed on the nickel surface. Different from the grain boundary, the wrinkles formed on the grains and could be extended from one grain to another. Graphene wrinkles were commonly observed when synthesis was done using nickel as the catalyst and the formation of wrinkles was due to the difference in thermal expansion coefficient between graphene and nickel [32-34]. The height of the wrinkles could vary from 10 - 75 nm from a measurement using AFM by Kim et al. [14] Some round particles were observed on the surface in our study, which could be due to contaminations in the furnace tube [35].

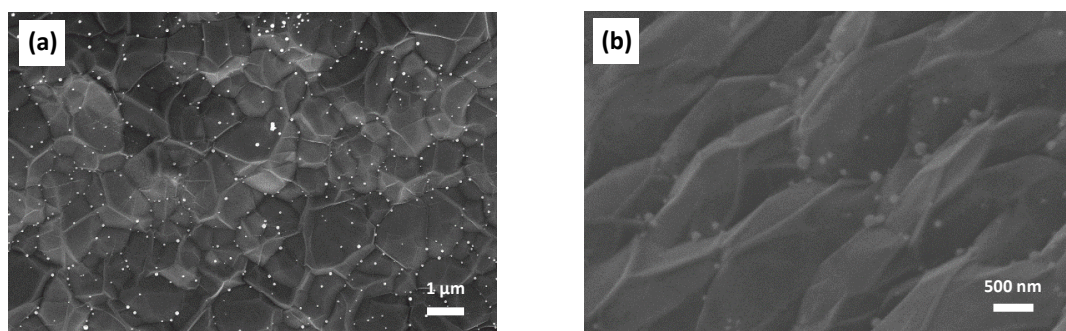


Figure 7.17: SEM images of graphene on the surface of the Ni/YSZ hollow fibre

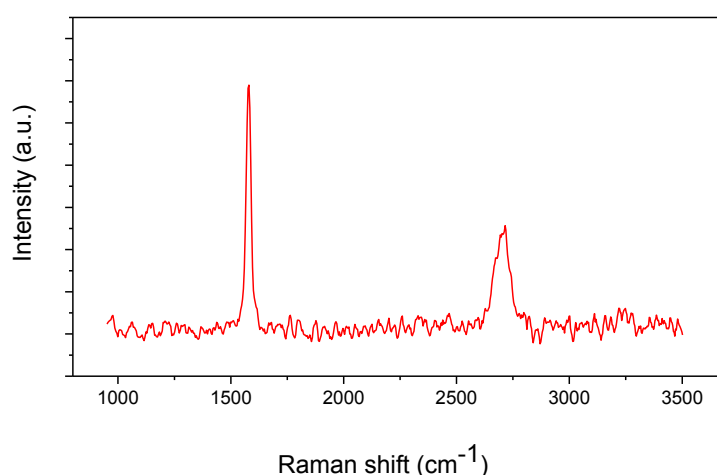


Figure 7.18: Raman scanning spectrum of graphene on nickel/YSZ hollow fibre

Though the wrinkles observed from the SEM scanning gave a good indication of the graphene growth, it was difficult to evaluate the quality of the graphene, for example the number of graphene layers. Raman spectrometry was used to scan the graphene/nickel surface. From the spectrum shown in Figure 7.18, G and 2D peaks were observed at about 1600 and 2700 cm^{-1} , respectively, confirming the growth of graphene on the nickel surface [14, 32]. The intensity ratio of 2D to G peak was about 0.5, indicating the presence of a multi-layer graphene layer. A typical 2D to G peak ratio of 2 will be observed for a single layer graphene and the ratio decreases when the number of graphene layer increases [36]. As defect-free single layer graphene was difficult to determine, multi-layer graphene was not undesirable and can be more practical for membrane applications. No D peak (1350 cm^{-1}) was observed from the Raman spectrum, indicating the presence of defects in the graphene layers was rare.

Rapid cooling is an important step to synthesize graphene on the nickel substrate. During the CVD, methane decomposed at the nickel surface and the carbon atoms diffused into the bulk nickel phase due to their high solubility in nickel. At the end of CVD, the methane flow was stopped and the hollow fibre was withdrawn from the furnace to induce rapid cooling. During this process, the carbon atoms diffused back to the nickel surface as the solubility of carbon in nickel decreased with the rapid drop in temperature [37]. Graphene then formed as a result of carbon precipitation on the metal surface. Yu et al. found that medium fast cooling rate at $\sim 10\text{ }^{\circ}\text{C s}^{-1}$ yielded a good quality graphene with less than 4 layers. When the cooling rate was too fast at $\sim 20\text{ }^{\circ}\text{C s}^{-1}$, large amount of carbon atoms was found segregated at the surface. The insufficient time to attain a good crystallinity resulted in the formation of multi-layer graphene [32]. In addition, Kim et al. revealed that the large thickness of nickel may also result in the formation of multi-layer graphene due to the high concentration of carbon absorbed. [14].

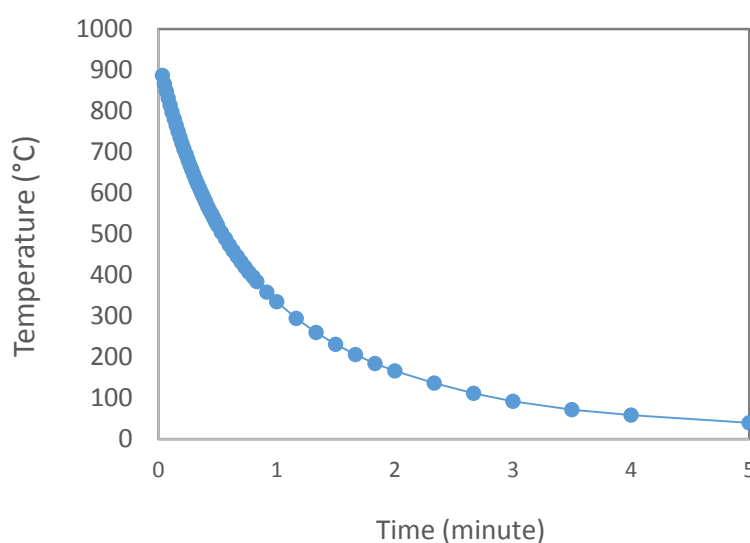


Figure 7.19: Temperature in the furnace tube during rapid cooling

Rapid cooling was done in this study by withdrawing the furnace tube out of the furnace and the temperature change was measured with a thermocouple, as shown in Figure 7.19. The cooling rate started at about $20\text{ }^{\circ}\text{C s}^{-1}$ but decreased to about $10\text{ }^{\circ}\text{C s}^{-1}$ after 25 seconds at around $570\text{ }^{\circ}\text{C}$. The multi-layer graphene obtained in our study could be due to the fast cooling

rate in our experiment and the thick nickel coated as thin sub-micron nickel was difficult to obtain as discussed earlier.

7.3.3 Challenges in nickel leaching

After the graphene growth, the nickel layer should be leached so that the graphene layer would sit on the porous YSZ substrates, serving as a membrane separating layer. The leaching step was first done by immersing the graphene/nickel/YSZ hollow fibres in a 1M nitric acid solution overnight. As the outer surface of the hollow fibre was covered by the graphene layer, the leaching could be difficult as graphene was very inert and could act as a protective layer to the nickel layer. Therefore, in the initial trials to leach the nickel layer, the acid solution needs to go through the lumen of the hollow fibres to get into contact with the nickel layer, as shown in Figure 7.20.

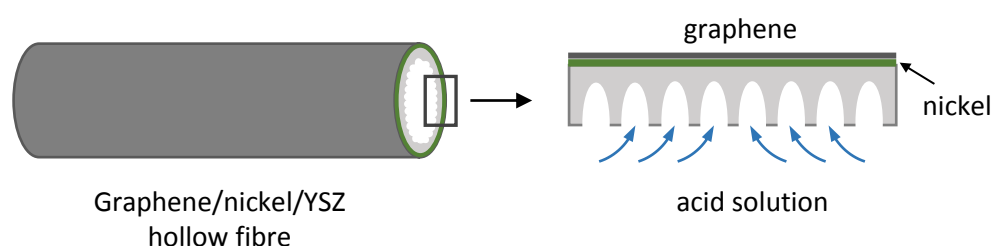


Figure 7.20: Leaching of nickel coating after the synthesis of graphene

Unfortunately the leaching of nickel was very slow and the nickel layer did not dissolve even after immersing in the acid solution for more than 1 day. A higher concentration nitric acid solution, 2 M was tried but it did not improve the leaching process. Other etching agent such as iron chloride was also tried but the nickel layer did not dissolve in the solution. The results suggested that the graphene layer might be formed on both sides of the nickel layer, which is reasonable following the solution-precipitation graphene growing mechanism. The difficulty to leach off the nickel layer was mainly due to the highly inert nature of graphene. Therefore, in order to have a more effective leaching, defects may need to be created in the graphene layer so that the acid solution can come in contact with the nickel layer more easily.

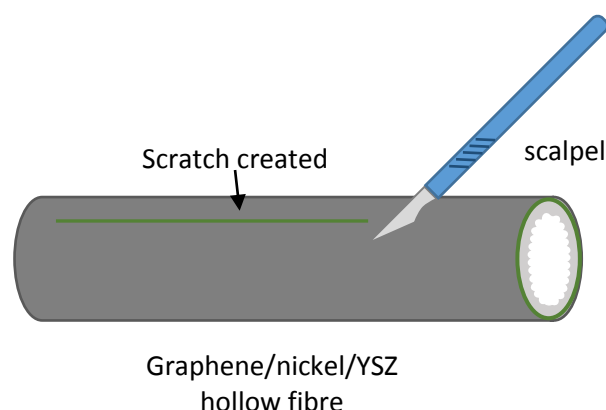


Figure 7.21: Defects were created on the graphene/ nickel/ YSZ hollow fibre surface

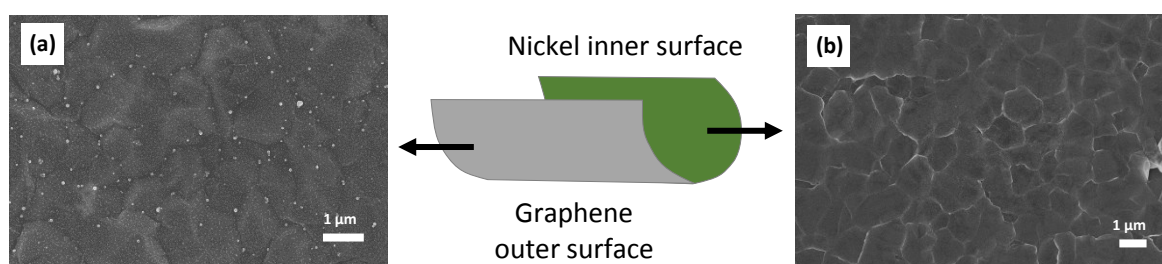


Figure 7.22: SEM images of the outer and inner surfaces of the graphene/nickel layer peeled off from the hollow fibre substrates

To study the role of defects on the graphene layer, a large defect was first created by scratching the graphene surface using a scalpel, as shown in Figure 7.21. When the hollow fibre was immersed in the acid solution, instead of leaching slowly, the whole nickel layer peeled off after a few minutes. The defects created on the surface may be too large and the nickel layer exposed near the defect could have dissolved very easily. However, the graphene/nickel layer peeled off from the hollow fibre remained in the acid solution even after a few days. The peeled layer was very fragile and broke into pieces when it was fished out of the solution. Figure 7.22 shows the SEM images of both surfaces of the graphene/nickel peeled layer. Graphene can be observed on the outer surface and it looked similar to the graphene/nickel surface on the hollow fibre before the leaching process. On the inner surface, uniform nickel grains were observed and most of them were not dissolved in the acid solution. This further indicates that graphene may have also grown on the inner surface of the nickel layer and acted as a protective layer, though it could not be observed from the SEM scanning.

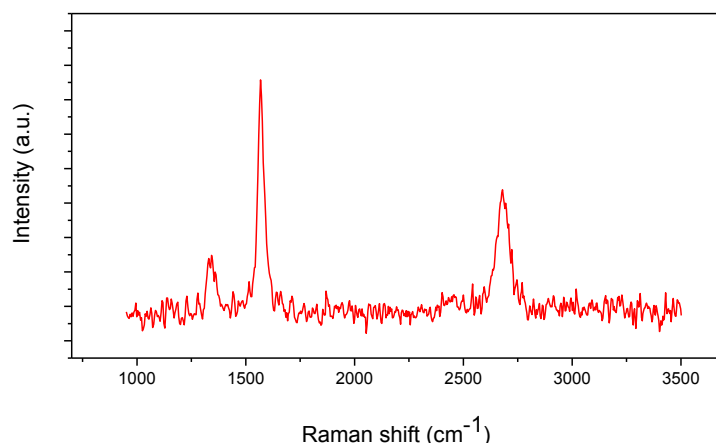


Figure 7.23: Raman spectrum of surface of the hollow fibres after peeling of the nickel layer

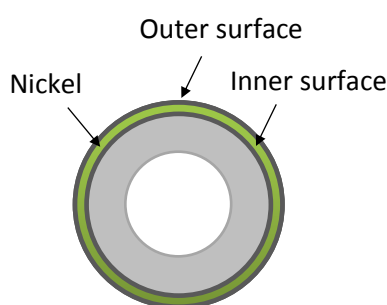


Figure 7.24: Graphene grown on the outer and inner surfaces of the nickel coating layer

The other interesting finding from this experiment was that some graphene material was found on the hollow fibre substrates even after the removal of the nickel layer. Though it could not be observed from the SEM scanning, the Raman spectrum (Figure 7.23) showed that the hollow fibre substrate was covered by multi-layer graphene, with the presence of 2D to G peaks. However, defects were present in the graphene layer as a significant D peak was observed. Though the graphene layer on the YSZ substrate was not defect-free, it supports our speculation that the graphene did not only grow on the outer surface of the nickel coating but also on the inner surface between the nickel coating and the YSZ substrate, as illustrated in Figure 7.24.

This could happen due to the growing mechanism of graphene on nickel substrates. As discussed earlier, carbon dissolved in the nickel layer during the CVD process and the graphene layer only formed on the nickel surface through precipitation during the rapid

cooling. Though the cooling on the other layer was much faster, the cooling rate in the inner layer might also be sufficient to induce the precipitation of graphene. The growth of graphene on the inner layer of nickel was observed previously by Peng et al. [38] Bilayer graphene was obtained between SiO₂ substrates and the nickel coating due to fast carbon diffusion in the nickel layer. The graphene growth on the inner layer of the nickel layer could explain the reason why the leaching of graphene was very difficult even though the acid solution may get in contact with the nickel layer from the lumen of the hollow fibre; the nickel layer was sandwiched in between two graphene layers which were highly protective and resistant to acid. The leaching of the nickel might be easier by avoiding graphene growth on the inner surface of the nickel layer. However, this can be difficult to achieve as fast carbon diffusion from the outer surface can provide a sufficient amount of carbon to form graphene in the inner layer.

Controlled fine pores in the graphene layer can be created to help the leaching of the nickel layer. The small pores or defects in graphene membranes can also serve as pores in graphene membranes for permeation. Many studies have looked into methods to create pores in graphene. Fine pores with diameter of about 4 Å was successfully created by using ion bombardment [17]. Besides, Agrawal et al. showed that by introducing a small amount of oxygen in the presence of hydrogen to the graphene surface (H₂:O₂ ratio of 13 to 7600), pores with size varying from a few nanometres to a few hundred nanometres could be created, depending on the amount of oxygen fed [39]. Uniform size nanoparticles were also used to create pores but the pores size was relatively large, with a diameter of about 50 nm [40]. Pores with small sizes are desirable as graphene can be potentially used in reverse osmosis or nanofiltration to reject small ions and molecules.

An experiment was carried out to create fine pores in the graphene membrane using gold nanoparticles as the catalyst. The catalyst was adsorbed on the graphene surface to oxidise some of the carbons at high temperature. Gold nanoparticles have shown excellent catalysis performance in CO oxidation [41], and therefore was chosen for graphene pore creation. However, the post-treatment did not solve the nickel leaching problem as the heat treatment might not be effective to create pores in graphene. Besides, gold nanoparticles were found inactive when the particle size was larger than 2 nm [42]. Therefore, more effective pore creation methods need to be further explored.

Though the graphene grown in the inner layer may have hindered the leaching of nickel in our study, it can also be useful as a graphene membrane. However, in order to use it as a membrane, the defects in the layer has to be minimized and this can be done by increasing the carbon concentration during the CVD [38]. Besides, the nickel layer has to be etched using a more destructive method like creating large pores and defects on the surface. On the other hand, the use of other types of metal catalyst such as copper can be further explored to avoid graphene growth in the inner surface. Copper has a lower carbon solubility and the diffusion of carbon from one surface to another will be limited [43]. The growth of graphene in the inner surface can be avoided, which will ease the leaching of the catalyst surface after the CVD.

7.4 Conclusion

Graphene membrane was fabricated into a hollow fibre geometry for scaling up purposes. Nickel was coated on YSZ hollow fibres using the electroless plating to provide a catalytic surface for graphene growth. Multi-layer graphene was successfully synthesized on the nickel surface using the CVD method. However, the leaching of nickel layer after the graphene synthesis remained challenging as graphene served as a protective layer to the nickel surface. Pore creation in graphene was explored to aid the leaching of nickel but more work has to be conducted to develop a more effective pore creation method. Nevertheless, graphene has shown an exceptional inert property, which can serve an excellent protection layer.

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Chapter 8: Conclusions and Future work

8.1 Overall conclusions

The thesis focused on two main topics: (1) Fabrication of graphene-based hollow fibre membranes and (2) Understanding of the water transport mechanism in GO membranes. High performance stainless-steel/ceramic hollow fibres were also developed in the process of developing graphene-based hollow fibre membranes. GO and graphene membranes were fabricated on ceramic hollow fibres using two different approaches. Since large amount of GO suspension could be synthesized easily using the modified Hummer's method, solution-processing methods were used to fabricate GO membranes on the hollow fibre substrates. On the other hand, large area graphene membranes were fabricated on the hollow fibre substrates through a chemical vapour deposition (CVD) method. Multi-layer graphene membranes were successfully synthesized on the nickel-plated ceramic hollow fibres.

Chapter 3 aimed to improve the mechanical strength of inorganic hollow fibre substrates for graphene-based membrane synthesis. This chapter extended the phase inversion-sintering technique used in fabricating ceramic hollow fibres to fabricate stainless steel (SS) hollow fibres. By controlling the sintering conditions, ductile SS hollow fibres with a high porosity were fabricated. The surface pore size was further reduced by incorporating yttria-stabilized zirconia (YSZ) nanoparticles around the SS particles. Dual-layer SS/SS-YSZ hollow fibres with a pore size of approximately 300 nm were successfully fabricated using a one-step co-extrusion method. The composite hollow fibres showed an improved mechanical strength and a high water permeation flux, exhibiting great potential for microfiltration application. However, they were not suitable for thin film coating due to the dual-phase uneven surface.

In Chapter 4, GO hollow fibres were fabricated on YSZ hollow fibres using vacuum filtration. However, GO membranes were found unstable on hollow fibre substrates, as shown by the degrading gas permeation performance over time, primarily due to a drying-related shrinkage problem. This stability issue was addressed by introducing a poly(methyl methacrylate) sacrificial layer, which created a gap between the GO membrane and the substrate, allowing the GO membrane to shrink freely. The GO membranes were stable in a long-term stability test for over 1200 hours. However, the defect-free GO membranes showed a low water permeation flux due to the long transport path length in the membranes. Microstructural

defects were created by using UV-treatment, which served as shortcuts for the permeation process. The water and acetone permeation fluxes of the UV-treated GO membranes were greatly enhanced.

Chapter 5 and 6 studied the water transport mechanism in GO membranes. According to Hagen-Poiseuille equation, GO membranes should have a low water permeation flux under a pressure-driven filtration due to the long transport path length in the membranes. However, fast water transport hypothesis has been widely used to explain the high permeation flux observed in the experiments. In Chapter 5, flat sheet GO membranes fabricated by high-pressure filtration, vacuum filtration, evaporation and dip-coating were tested for water permeation under a pressure-driven mode. Serious membrane compaction was observed where the water permeation flux decreased considerably over time and reached a low steady stated flux $<0.1 \text{ LMH bar}^{-1}$. The high water flux observed may not be an intrinsic property of GO laminae; it could be contributed by the disorder of GO flakes and the loosely packed hierarchical microstructure in GO membranes. The transport mechanisms assuming perfect laminar structure in GO membranes were inaccurate, and the low friction flow proposed by previous studies may not fully describe the water transport in GO membranes under a pressure-driven condition.

In Chapter 6, GO membranes were tested under two different modes: pressure-driven filtration and pervaporation. The pure water permeation was 1-2 orders of magnitude higher in pervaporation due to the difference in driving forces. A pore flow model was proposed to describe the high water permeation in pervaporation, as opposed to the solution-diffusion model used by many studies. When water evaporated on the permeate side surface of GO membranes, the high capillary pressure induced could drive the water molecules to permeate through the interlayer space quickly in a bulk phase. This phenomenon did not happen in pressure-driven filtration as evaporation did not take place on the permeate side surface. Besides that, the high water adsorption capacity of GO membranes also yielded an excellent performance in dewatering of ethanol in pervaporation. A stable interfacial tension due to a steep concentration gradient formed at the pore entrance was verified and this surface phenomenon has enabled the measurement of effective interfacial tension (EIT) between miscible liquids using GO membranes. The EIT of water-ethanol was successfully measured in this study.

In Chapter 7, CVD was shown to be a promising approach to synthesize large area graphene membranes on substrates of different geometry. Nickel was coated on YSZ hollow fibres using electroless plating to provide a catalytic surface for graphene growth. Graphene membranes were then synthesized on the nickel-plated YSZ hollow fibre substrates without a transferring step. Multi-layer graphene was successfully synthesized on the nickel surface. However, the leaching of the nickel layer after graphene synthesis remained challenging as graphene served as an excellent protective layer to the nickel surface.

8.2 Future work

8.2.1 Graphene oxide membranes

GO membrane modifications

Though GO membranes showed excellent molecular sieve properties in nanofiltration, they had a low water permeation flux under a pressure-driven process, mainly due to the long water transport path in the membranes. More studies can be done to improve the membrane performance by reducing the transport path length. For example, systematic approaches to generate microstructural defects and robust methods to preserve the loosely packed microstructure in GO membranes can be investigated.

The water permeation of GO membranes in pervaporation was found limited by the evaporation rate on the permeate side surface. In order to further increase the permeation flux, GO membranes with a larger effective surface area can be synthesized. This may be done by using wrinkled and patterned GO flakes [1]. Besides that, the surface diffusion was found limiting the water permeation at high temperature. Membrane modifications to enhance surface diffusion can be carried out, for example by grafting hydrophilic chains on the permeate surface, between GO membranes and the substrates.

The stability of GO membranes is a major concern for scaling up applications. Cross-linking methods have been widely explored to improve the stability of GO membranes especially in water filtration application [2]. However, long term stability of GO membranes needs to be further investigated, for example by testing the membranes in a cross-flow and with feed solutions similar to the industrial environment.

Extension of the EIT measurement

This study successfully demonstrated the use of GO membranes in measuring the effective interfacial tension (EIT) of miscible liquids. Currently, only ethanol-water system was tested and the measurement method can be extended to other liquid pairs. As the EIT between water and butanol was previously measured by using the tensiometer technique [3], it can be used to verify the value obtained from GO membranes. Other types of molecular sieve membranes can also be explored for EIT measurement. Besides that, EIT might be used to measure membrane pore sizes <2 nm, which cannot be measured easily using the current liquid-liquid displacement method as a very high pressure is required.

Energy related applications

Due to the large interlayer space, small ions could still permeate through GO membranes, limiting their application in desalination. However, ion permeation in GO membranes can be utilized in other applications where selective ion permeation is required. For example, GO membranes can be used as an effective barrier in the lithium-sulphur battery system. Lithium ions were found could transport through GO membranes easily, while the polysulphides were effectively confined in the cathode side [4]. The use of GO membranes could potentially avoid rapid capacity degradation and solve the poor cycling stability of lithium-sulfur cells. Besides that, GO membranes could also be potentially used for energy harvesting while having ion separations [5]. By effectively preventing the permeation of source ions, an electrochemical dialysis equilibrium can be established, which generates a Donnan potential. The understanding gained from GO membranes in fluid separations, such as the effect of microstructure on permeation flux, could be useful in fabricating GO membranes required for energy related applications.

8.2.2 Graphene membranes

Graphene membrane synthesis methods

Though graphene layer was successfully synthesized on the nickel-plated ceramic hollow fibres in this study, there were still some challenges in the current synthesis method. The leaching of nickel after the graphene synthesis was difficult as graphene grew on both inner and outer surfaces of the nickel plating layer. Graphene synthesis using different types of

catalyst such as copper can be investigated to overcome the problem. Graphene grows on copper substrates through surface nucleation, which is different from the precipitation method on nickel [6]. By isolating the inner surface from the carbon source, graphene will only grow on the outer surface of copper-plated hollow fibres, as carbon diffusion across the copper layer is unlikely. This will enable the leaching of copper from the inner surface.

Metal layer coating using other methods can also be explored. Electroless plating was used in this study due to the simplicity of the method. However, the plating process can be difficult to control due to the instability of the plating solution. The plating time can also be long to achieve a thick layer. Methods such as sputtering can be explored to achieve a more efficient metal coating. Besides that, hollow fibres made of copper can be designed so that graphene can be synthesized on the hollow fibre directly without any prior coating.

Pore creation in graphene membranes

Defect-free graphene is impermeable to all molecules and it can be an ideal protective layer. Graphene membranes were successfully synthesized on the nickel-plated ceramic hollow fibres in this study. However, the leaching of the nickel catalyst after CVD was difficult due to the protective nature of graphene. In addition, in order to apply in membrane separations, fine pores with a narrow distribution in graphene membranes are desirable. Effective pore creation in graphene membranes can to be further explored to enable the leaching of nickel catalyst and to introduce pores for permeation. Agrawal et al. showed that pores with size varying from a few nanometres to a few hundred nanometres could be created by introducing a small amount of oxygen in the presence of hydrogen to the graphene surface at high temperature [7]. Pore creation methods involving controlled oxidation can be further studied as they can be potentially scaled up.

Applications in membrane separations

The molecular sieving properties of graphene membranes can be further explored after pore creation. Depending on the pore size, graphene membranes can be applied for various separation processes. For pore size smaller than 1 nm, graphene membranes can be potentially applied in reverse osmosis to reject salts in water, or for gas separation. Ideally graphene membranes can separate most of the gas pairs such as H_2/CH_4 , H_2/CO_2 and N_2/O_2 through size exclusion if the characteristics of pores can be well controlled. While for bigger pores, graphene membranes can be used for nanofiltration or ultrafiltration. Graphene

membranes can also be applied in more challenging separation processes involving harsh environments such as organic solvent nanofiltration and organic solvent reverse osmosis, as they have excellent chemical resistance.

Beyond membrane separations

The application of graphene membranes can also be extended beyond water treatment and gas separation. For example, large-scale graphene devices for DNA sequencing can be designed if well-defined pores can be created [8]. The inert nature of graphene can also be further studied for protective layer against corrosion, especially in highly corrosive chemical reactions.

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1. N.F.D. Aba, J. Y. Chong, B. Wang, C. Mattevi, K. Li, Graphene oxide membranes on ceramic hollow fibres - microstructural stability and nanofiltration performance, *Journal of Membrane Science*, 484 (2015) 87-94.
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6. J. Y. Chong, B. Wang, K. Li, Water transport through graphene oxide membranes: the roles of driving forces, *Chemical Communications*, Accepted.

List of Conference Presentations:

1. J. Y. Chong, N.F.D. Aba, B. Wang, C. Mattevi, K. Li, Graphene based ceramic hollow fibre with poly(methyl methacrylate) sacrificial layer, 13th International Conference on Inorganic Membranes, Brisbane, July 2014. (Oral)
2. J. Y. Chong, N.F.D. Aba, B. Wang, C. Mattevi, K. Li, UV-enhanced sacrificial layer stabilised GO hollow fibre membranes for nanofiltration, Euromembrane 2015, Aachen, September 2015. (Oral)
3. J. Y. Chong, N.F.D. Aba, B. Wang, C. Mattevi, K. Li, Graphene oxide hollow fibre membranes: Stability, modifications, and challenges, 2015 American Institute of Chemical Engineers Annual Meeting, Salt Lake City, November 2015. (Oral)
4. J. Y. Chong, B. Wang, C. Mattevi, K. Li, Dynamic microstructure and compaction of GO thin film membranes in nanofiltration, 14th International Conference on Inorganic Membranes, Atlanta, July 2016. (Oral)
5. J. Y. Chong, B. Wang, C. Mattevi, K. Li, On transport mechanism and dynamic microstructure of GO thin film membranes, 2016 American Institute of Chemical Engineers Annual Meeting, San Francisco, November 2016 (Oral)
6. J. Y. Chong, B. Wang, K. Li., Ceramic/ stainless steel composite hollow fibre membranes for water treatment, Chem Eng Day UK 2017, University of Birmingham, March 2017. (Oral and Poster) - Excellent Poster award by IChemE Water Special Interest Group

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22, 31, 34	Figure	R.R. Nair et al., Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes, Science, 335 (2012) 442-444.	The American Association for the Advancement of Science (2012)	4/10/2017	4201980609869
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