The potential of carbon nanomaterials for advancing high-performance membranes

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NANYANG
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**THE POTENTIAL OF CARBON NANOMATERIALS FOR
ADVANCING HIGH-PERFORMANCE MEMBRANES**

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NANYANG ENVIRONMENT AND WATER RESEARCH INSTITUTE

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LIST OF SYMBOLS

0-D	zero-dimensional
1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
A	pure water permeability coefficient
AFM	atomic force microscopy
ALD	atomic layer deposition
AL-facing-DS	active layer facing draw solution
Al-facing-FS	active layer facing feed solution
Al-facing-FW	active layer facing feed water
AO7	acid orange 7
AR	allura red
ATR FT-IR	attenuated Fourier transformed-infrared spectroscopy
B	salt permeability coefficient
CCG	chemically converted graphene
CNMs	carbon nanomaterials
CNTs	carbon nanotubes
CP	concentration polarization
CTA	cellulose triacetate
CVD	chemical vapor deposition
DWCNTs	double-walled carbon nanotubes
EDA	ethylene diamine

FE-SEM	field emission scanning electron microscopy
FO	forward osmosis
GO	graphene oxide
HI	hydroiodic acid
HR-TEM	high resolution transmission electron microscopy
ICP	internal concentration polarization
ID	inner diameter
IP	interfacial polymerization
<i>K</i>	mass transfer coefficient
LBL	layer-by-layer
MB	methylene blue
MPD	m-phenylenediamine
MWCNTs	multi-walled carbon nanotubes
MWCO	molecular weight cut-off
NF	nanofiltration
NMP	N-methyl-2-pyrrolidone
OD	outer diameter
OP	oxygen permeability
OTR	oxygen transmission rate
PA	polyamide
PAH	poly(allylamine hydrochloride)
PAI	polyamide imide
PAN	poly(acrylonitrile)
PEG	polyethylene glycol

PEI	polyethyleneimine
PES	polyethersulfone
PLA	poly(lactic acid)
PSB	poly(sulfobetaine)
PVDF	polyvinlidene fluoride
PVP	polyvinyl pyrrolidone
PWP	pure water permeability
QCM-D	quartz crystal microbalance with dissipation
rGO	reduced graphene oxide
RH	relative humidity
RhB	rhodamine B
RO	reverse osmosis
SWCNTs	single-walled carbon nanotubes
TEM	transmission electron microscopy
TFC	thin film composite
TMC	trimesoyl chloride
TMP	transmembrane pressure
UF	ultrafiltration
UV-vis	ultraviolet-visible spectroscopy
VDW	van der Waals
WVP	water vapor permeability
WVTR	water vapor transmission rate
XRD	x-ray diffraction
ZCNT	poly(zwitterionic) MWCNT

Greek

ΔD	dissipation shift of QCM-D
Δf	frequency shift of QCM-D
ΔP	transmembrane pressure
$\Delta \pi$	osmotic pressure difference
$\Delta \pi_{\text{eff}}$	effective osmotic pressure
$\Delta \pi_{\text{m}}$	real osmotic pressure
R_e	reynolds number
R_f	fouling resistance
γ	shear velocity
γ_{ave}	average shear rate
I_D/I_G	Raman intensity D to G ratio
J_s	salt flux
J_v, J_w	volumetric water flux
n	sampling size

ABSTRACT

Carbon nanomaterials (CNMs) are potential materials to be used as diffusion barriers for membrane-based separations. In particular, carbon nanotubes (CNTs) and graphene-based materials, such as graphene oxide (GO) and reduced graphene oxide (rGO) sheets, have displayed exceptional water transport properties and excellent molecular sieving capabilities owing to their unique structures and physicochemical properties. Presently, state-of-the-art CNM-based membranes exhibited extraordinary membrane performances but are challenging to fabricate. Mixed-matrix CNM-based membranes, on the other hand, are easier to fabricate. However, it is difficult to fully exploit the remarkable properties when CNMs are encapsulated. Therefore, the emphasis in this work is strategically focused on the fabrication of surface-modified CNM-based membranes in order to strike a balance between the two. The objective is to investigate the potential of CNMs as diffusion barriers with the purpose of advancing membrane performances to alleviate the global water scarcity challenge.

This study began with the demonstration of freestanding GO and rGO core barriers in sandwich-architected poly(lactic acid) (PLA)-graphene composite membranes. Micrometers-thick freestanding GO and rGO barriers exhibited high barrier properties towards oxygen and water vapor molecules. In particular, PLA-rGO showed a significant 87.6% decline in water vapor permeability with a reduction in oxygen permeability by two orders of magnitude. Mechanistic analysis attributed this to the extensive and tortuous diffusion pathway which can be up to 1450 times the thickness of the rGO barrier. To further demonstrate the effectiveness of graphene-based materials, the GO deposition on the surface of a hollow fiber substrate was engineered to only nanometers-thick. At this thickness, the GO deposition was found to serve as an effective selective barrier and achieved 86% higher

water permeability without sacrificing on membrane selectivity when used to substitute a part of the hollow fiber selective layer. The relatively lower hydrodynamic resistance of the GO sheets and their two-dimensional structures, which essentially fine-tuned the pore size distribution of the nanofiltration (NF) membrane, constituted the GO sheets as effective selective barriers. Next, functionalized multi-walled carbon nanotubes (MWCNTs) were explored as effective water nanochannels in the hollow fiber selective layer. The water permeability of the membrane was enhanced up to 44% in the NF process with inconsequential impact on the membrane selectivity. Correspondingly, the water flux was increased up to 29% in the active layer-facing-feed water orientation without compromising on the reverse salt flux when using 0.5 M MgCl_2 as the draw solution in the forward osmosis process. These empirical findings inspired the amalgamation of both MWCNTs and rGO sheets to give all-carbon nanoarchitectures. The nanoarchitectures utilized rGO as effective selective barriers and MWCNTs as water nanochannels to achieve a water permeability of $52.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and an almost 100% rejection rates towards methylene blue, acid orange 7 and rhodamine B solutes. Most importantly, the all-carbon nanoarchitectures demonstrated outstanding membrane stability towards turbulent hydrodynamic flow conditions up to 2000 mL/min cross-flow rate. Physicochemical characterization revealed that the inner graphitic walls of the MWCNTs can serve as anchors for the nanoscale rGO foliates on the outer walls of the MWCNTs to interconnect with the assimilated rGO sheets via van der Waals attractions and π - π stacking interactions.

In conclusion, this thesis presents a detailed study using graphene-based materials and MWCNTs as selective diffusion barriers on the membrane surfaces for NF and FO processes. The results suggested that the exceptional water transport properties of the CNMs can indeed be translated onto the membrane surfaces to enhance membrane performances under practical

membrane hydrodynamic operations. Fundamentally, this work contributes towards the development of surface-modified CNM-based membrane and facilitates the realization of practical, high-performance separations using CNM-based membranes.

1.1. Background

Water scarcity is a serious global issue which is projected to exacerbate with the ever growing population. This can be seen from the six-fold increase in global fresh water demand between the year 1900 and 1995 [1]. Such an increase in demand is more than twice the concurrent increase in the world's population [2]. In addition, fresh water is not geographically well distributed. More than a third of the world's population resides in water-stressed countries and this figure is projected to increase to nearly two-third by the year 2025 [3]. To further complicate the problem, emerging economies, rapid industrialization and the effects of climate changes are contributing towards the reduction in fresh water supplies. As a result, 1.2 billion people are deprived of clean drinking water and 2.6 billion people have little or no sanitation as of year 2002 [4]. Among them, many are poor people from developing countries [5]. Inevitably, this led to social, environmental and public health issues which will impede sustainable growth of the global population if remain unsolved.

Technological advancement has enabled solutions through utilizing membranes as diffusion barriers. Diffusion in membranes may either be retarded as in the case of packaging or protective coatings or be accelerated as in the instance of membrane-based separations. Fast and selective diffusion of water over other solutes is the key to achieve membrane-based separations for water purification or desalination [6]. Such membrane-based separations offer the advantages of energy efficiency, cost-effectiveness and affordability, smaller carbon footprints, robustness as well as safer operations when compared to conventional thermal

distillation or liquefaction [7]. Moreover, the steeper increment of the total desalination capacity using membrane-based separations over thermal processes as represented in Figure 1-1a and the vast improvements achieved for membrane-based separations in terms of increased salt rejection rates (decreased % salt passage), reduction in membrane cost and decreased energy consumption (Figure 1-1b-d) have revolutionized the conventional approach to water purification. At present, membrane-based separations are the preferred technology for providing sustainable solutions to address the global water shortages.

Figure 1-1. (a) Global water desalination capacity. Adapted from [8]. (b) Improved salt rejections of membrane-based separations. (c) Reduction in membrane cost. (b) and (c) Adapted from [9]. Decreased energy consumption of membrane-based separations. Adapted from [10].

1.2. Challenges in membrane-based separations

Despite the numerous advantages offered by membrane-based separations, there exist many challenges yet to be overcome. The first challenge, which is also the greatest one, is to make clean drinking water affordable to the poorer countries. Currently, the bulk of the expenses of membrane-based separations is spent on electricity [11]. Comparing Figure 1-1(d) and Figure 1-2, the energy consumption of membrane-based desalination has been optimized close to the theoretical minimum energy of 1.06 kWhm^{-3} at 50% recovery for seawater at 35 g/L NaCl salt [3]. This suggests that the operating conditions are reaching their thermodynamic limit. Further optimization would not impact in a significant reduction in energy consumption and certainly not able to reduce the cost of producing clean water [12].

Figure 1-2. Theoretical minimum energy required for desalination as a function of percent recovery. Adapted from [3].

The second challenge is to improve the selectivity of the membrane-based separations. At the present moment, the percentage removal of boron and chlorides from a single pass membrane-based separation has yet to meet the required standards of various applications [1, 13]. Moreover, higher rejection rates of salts and low molecular weight compounds are desired to reduce the number of passes needed to produce the necessary water quality for desalination and water reuse [3]. Ultimately, improving the selectivity is also correlated to reducing the total energy consumption to make clean water production more cost-effective.

The third challenge is membrane fouling problem which can cause serious inefficiencies in membrane-based separations. Fouling occurs by deposition of a layer on the membrane surfaces or by blockage or partial blockage of the membrane pores during the separation process [14]. It affects membrane performances by decreasing the flux, leading to premature replacement of the membranes. Strategies to mitigate fouling include changing the hydrodynamic flows across the membrane surfaces and chemical backwashing to clean the fouling layers [1]. However, all these efforts consume energy which incurs additional costs.

1.3. Carbon nanomaterials as a solution

There are many approaches to address the above challenges. These include engineering membrane processes and developing novel membranes with desired properties and added functionalities [15]. Considering that the operating conditions of membrane processes are near their thermodynamic limits, the latter approach is embarked upon to try to tune the diffusion rates of water in membranes using carbon nanomaterials (CNMs) to achieve higher water permeability and enhanced membrane selectivity.

An ideal membrane should possess key qualities such as excellent membrane selectivity with high throughput, good processability and superior membrane stability to handle the necessary hydrodynamic conditions required by the membrane-based separations [7]. Currently, most of the membranes used for separations are synthetic and polymeric in nature. Polymeric membranes possess several of the key qualities and their fabrications are already well-established and highly developed. However, they exhibit a near universal trade-off between flux and selectivity which has yet to be overcome [16]. Therefore, there is an urgent need to research into new materials to overcome this fundamental hurdle.

Recently, the use of CNMs such as carbon nanotubes (CNTs) and graphene-based materials in membrane fabrications has attracted significant attention owing to their uniquely defined structures which allow the creation of nanochannels that are sufficiently small to facilitate water transport and yet sieve out ions and low molecular weight compounds [16-20]. The hydrophobic and non-oxidized surfaces of the CNMs also provide a near frictionless region to promote ultrafast transport of water molecules across the surfaces [21, 22]. Hence, CNMs are deemed as promising materials with the potential to alter diffusion rates of water to overcome the trade-off phenomenon hindering polymeric membranes.

1.4. Research objectives

In this research, the overarching objective is to enable CNMs as diffusion barriers to demonstrate their potential in water purification. Specifically, the study aims to address the first two challenges of membrane-based separations and hopes to achieve the following primary objectives:

- **Tailoring and engineering CNMs for development of novel membranes** with focus on solution-based processing of CNMs to enhance better compatibility with membrane modification methods.
- **Architecturing and leveraging on CNMs to realize high performances in water purification** with special emphasis placed on achieving key qualities such as high water throughput with enhanced membrane selectivity, good processability and good membrane stability under practical hydrodynamic conditions.
- **Elucidating the mechanisms and understanding the roles played by the CNMs in realizing high performances in water purification** through physicochemical characterizations of the nanomaterials and the ensuing membranes and providing theoretical perspectives to explain the experimental results.
- **Drawing comparisons and references to latest existing studies in the literature** in an effort to benchmark the results and to determine the relevance of this study from a broader perspective.

1.5. Thesis outline

The thesis comprises seven chapters. A brief highlight of the rationales and key findings of each chapter is summarized as follows:

Chapter 1: Introduction. The background of membrane-based separations together with the existing challenges, motivations of using CNMs and the research objectives of this study are encapsulated in this chapter.

Chapter 2: Literature review. The review starts off with a brief synopsis of the CNMs. In particular, the focus is on the unique structures and properties of graphene oxide (GO), reduced graphene oxide (rGO) and CNTs. Subsequently, the theoretical background of osmotically-driven membrane-based separations, notably nanofiltration (NF) and forward osmosis (FO), the challenges they faced and the different strategies currently adopted to resolve these challenges are provided. This is followed by highlighting the competitive edge offered by these CNMs in membrane-based separations, nanofluidic studies, molecular simulations and the current status of the CNM-based membranes.

Chapter 3: Sandwich-architected poly(lactic acid)-graphene composite barrier membranes. This chapter is a first attempt to explore the barrier properties of GO and rGO membranes and aims at understanding the permeability behaviors of these graphene-based barrier membranes. The GO and rGO membranes were sandwiched between poly(lactic acid) (PLA) membranes to demonstrate their good processability, membrane handling manageability and excellent barrier properties towards water vapor and oxygen gas molecules. The acquired results allow precise tuning of the diffusion rates of water through altering the thickness of the graphene-based membranes. Consequently, selective permeability is achievable which is demonstrated in the next chapter.

Chapter 4: Graphene oxide as effective selective barriers on a hollow fiber membrane for water treatment process. With conclusions from the previous chapter, the thickness of the GO barrier on a chemically cross-linked selective layer of a

hollow fiber substrate is engineered to observe selective permeability. In this chapter, GO sheets are demonstrated as effective selective barriers that reduce the pore size (and narrow its distribution) of the cross-linked hollow fiber substrate to achieve enhanced membrane selectivity. This allows a reduction in the duration of the cross-linking process which improves the mechanical properties of the hollow fiber substrate. Most importantly, the little hydrodynamic resistance contributed by the GO selective barrier helps to realize selective permeability as observed by the higher water permeability in the NF process.

Chapter 5: Fabrication of novel functionalized multi-walled CNT immobilized hollow fiber membranes for enhanced performances in FO process. Next, the focus is shifted to multi-walled carbon nanotubes (MWCNTs). Functionalized MWCNTs are immobilized via a vacuum-assisted filtration method and chemically cross-linked to form the selective layer on a hollow fiber substrate. By carefully tuning the thickness of the MWCNTs layer and ensuring the integrity of the selective layer, enhanced water permeability without compromising on membrane selectivity can be attained in both the NF and FO processes, thus demonstrating MWCNTs as effective water nanochannels to facilitate water transport in the selective layer.

Chapter 6: All-carbon nanoarchitectures as high-performance separation membranes with superior stability. Ultimately, an all-carbon nanoarchitecture is proposed through amalgamating rGO sheets and MWCNTs. By reducing GO into rGO, the constricted interlayer spacing between the rGO sheets offers excellent membrane selectivity while the intercalated MWCNTs serve as effective water

channel spacers, leading to improved water permeability and enhanced selectivity of the all-carbon nanoarchitected membranes. In addition, the strong interactions between the rGO sheets and the intercalated MWCNTs have instilled superior membrane stability which allows the all-carbon nanoarchitected membranes to manage cross-flow hydrodynamic conditions used in practical membrane processes.

Chapter 7: Conclusions. Major empirical findings of each chapter are being summarized here. Notably, future research strategies are recommended and an outlook on CNMs as diffusion barriers in membrane-based separations is provided to answer the question “the potential of carbon nanomaterials for advancing high-performance membranes?”.

2.1. Introduction

In the last decade, an emerging class of nanomaterials based exclusively on carbon has been intensively studied due to their extraordinary properties. The basic building material of these nanomaterials, graphene, is a two-dimensional (2-D) monoatomic structure made up of densely packed sp^2 hybridized carbon atoms in a honeycomb lattice. From this building block, 0-D fullerenes and 1-D CNTs are attainable via wrapping and rolling of a graphene sheet respectively. Stacking of the 2-D graphitic sheets, on the other hand, yield 3-D graphite as illustrated in Figure 2-1.

Figure 2-1. Schematic illustrating 2-D graphene as the basic building block of various carbon structures such as 0-D fullerene, 1-D CNTs and 3-D graphite via wrapping, rolling and stacking respectively. Adapted from [23].

Among these CNMs, graphene and CNTs possess the highest potential to be engineered as diffusion barriers to tackle the first two challenges of membrane-based separations as described in Chapter 1. The following sections of this chapter summarize the key structural and physicochemical properties of these CNMs generally believed to be valuable in promoting fast water diffusion, the theoretical background of the osmotically-driven membrane-based separations and review the current status of CNM-based membranes.

2.2. Structural and physicochemical properties of CNMs

2.2.1. Graphene-based materials

Graphene-based materials usually refer to pristine graphene, GO, rGO and chemically-converted graphene. The chemical differences between pristine graphene, graphene oxide and reduced graphene oxide are illustrated in Figure 2-2. GO is obtained by chemical oxidation of graphite before ultra-sonication to exfoliate into GO sheets [24, 25]. Thus, GO possesses large amount of oxygen-containing functional groups with carboxyl groups localized mainly at the edges while hydroxyl and epoxy groups are found at the basal planes. RGO, which is chemically reduced from GO, has most of the hydroxyl and epoxy groups removed from the basal planes, leaving only carboxyl groups at the edges and restoring back the π -network of the basal planes [26-28]. Despite the differences in their chemical structures, both the GO and rGO sheets retain the 2-D structure of graphene. Molecular dynamic simulation has also demonstrated the impermeability of the basal planes due to the high energy needed to overcome the large electron density around the aromatic carbon rings [29, 30]. As such, graphene, GO and rGO sheets are promising selective barriers when applied in membrane-based separations.

Figure 2-2. Chemical structures of (a) pristine graphene (b) graphene oxide and (c) reduced graphene oxide.

To demonstrate how these unique characteristics provide a competitive advantage in membrane-based separations and in promoting water diffusion, the individual GO sheets were stacked on top of each other to yield a lamellar microstructured freestanding GO membrane via vacuum filtration (Figure 2-3a and b). The freestanding GO membrane exhibited no permeability towards He gas but allowed unimpeded permeation of water through it [21]. Such a fast diffusion of water molecules was attributed to the frictionless flow of a monolayer of water molecules through the non-oxidized and hydrophobic 2-D nanocapillaries formed by the interlayer spacing between the GO sheets (Figure 2-3c-e) [19]. The hydrophilic regions on the GO basal planes served as spacers to open the interlayer spacing at ~ 1.0 nm for monolayer water transport. On the contrary, the freestanding rGO membrane failed to reproduce such fast diffusion because the interlayer spacing between the rGO sheets was smaller at ~ 0.4 nm which rendered the rGO membrane 100 times less permeable to water [21]. In addition, the interlayer spacing between the GO sheets further opened to ~ 1.3 nm when hydrated and exhibited a precise sieving ability with sharp cut-offs at $4.5 \text{ \AA}$ (Figure 2-3c and f) [20]. Thus, freestanding GO membrane with its tunable physicochemical properties and well-defined interlayer spacing has been demonstrated with extraordinary water transport behavior and molecular sieving ability.

Figure 2-3. (a) Photo of a submicrometer thick GO membrane. (b) SEM image of the cross-sectional morphology of the GO membrane. (c) Schematic illustration of water transport through stacked GO sheets. (d-e) Permeation rate of H₂O and other organic solvents through GO and rGO membrane. (f) Permeation rate of various ions and solutes through hydrated GO membrane. (a-b) and (d-e) adapted from [21], (c) adapted from [19] and (f) adapted from [20].

Alternatively, freestanding, single-layer graphene is considered the ultimate thin membrane with the promise of greatly increased water permeability [31, 32]. This is because water flux is inversely proportionate to membrane thickness and graphene, being monoatomic in thickness, is the thinnest membrane with the lowest possible hydrodynamic resistance. By creating subnanometer pores on the surface, the graphene can allow water to pass through with ease while rejecting larger salt ions effectively as depicted in Figure 2-2a. Molecular dynamic simulation suggests that a single layer graphene with hydrogenated subnanometer pores can provide up to $66 \text{ L cm}^{-2} \text{ day}^{-1} \text{ MPa}^{-1}$ water throughput at full salt rejection, which is 2-3 orders of magnitude higher than the current polymeric reverse osmosis (RO) membranes (Figure 2-2b and c) [31]. However, intrinsic defects and defects created during handling of the graphene membrane, controlled generation of the subnanometer pores

with a narrow pore size distribution and robustness of the ultrathin membrane to handle high pressure operating conditions are some critical issues impeding the practical application of such graphene membrane [32-35].

Figure 2-4. (a) Schematic illustrating monoatomic nanoporous graphene as a selective membrane. Adapted from [32]. (b) Simulated model of a hydrogenated pore small enough to reject NaCl salt. (c) Comparison table to show the high performance of single-layer nanoporous graphene membrane. Adapted from [31].

2.2.2. CNT-based materials

Carbon nanotube (CNT) is a nano-sized, needle-like cylinder made up of a rolled-up graphene sheet (Figure 2-1). A CNT, which consists of only one graphitic shell, is named single-walled carbon nanotube (SWCNT) while those with several graphitic shells is known as multi-walled carbon nanotube (MWCNT) as represented in Figure 2-5. The ends of CNTs are usually capped with hemispheres of fullerene-like structure and SWCNTs usually fluctuate from a few angstroms to ~5 nm in diameter while MWCNTs can go up to range of 100 nm in diameters and potentially stretch up to a few centimeters in lengths [36, 37].

Figure 2-5. (a,c) Schematic diagrams to illustrate SWCNT and MWCNT. (b) High resolution image of a SWCNT bundle. (d) High resolution images showing MWCNT with different number of graphitic walls. (a,c) adapted from [38]. (b) adapted from [39]. (d) adapted from [40].

Similar to the graphene-based materials, CNTs possess unique properties which make them attractive for transport applications. First, the high aspect ratio of CNTs allows them to extend over millimeters in length and yet maintain only a few nanometers in diameter [41]. Second, the atomically smooth, hydrophobic graphitic inner channels of CNTs provide high slip length and frictionless transport of water [18]. Third, the nanoscale and tunable diameters of the tips of CNTs act as efficient pores to enable sieving capabilities as illustrated in Figure 2-6a and b [42].

Figure 2-6. Schematic illustrations of (a,b) different sizes of CNTs for size exclusion membrane-based applications and different chemical functionalization of CNTs for high flux and anti-fouling separations. Adapted from [42]. (c) Hydrogen-bonded water wire occurring inside the (6,6) CNT. Adapted from [43].

These characteristics were demonstrated by molecular dynamic simulations. Hummer *et al.* discovered that water molecules fill up the empty cavity of a (6,6) CNT within a few tens of picoseconds and this filled state was able to sustain over the entire simulation time of 66 ns. The water molecules also formed a quasi-one-dimensional wire, which was approximately aligned to the tube axis and connected by hydrogen bonds, as a consequence of the nanoscale confinement [44]. Despite losing on average two out of four hydrogen bonds as water molecules move into the CNT, the binding energies of the water molecules were found to be more narrowed and this contributed to a lower excess chemical potential which resulted in transmission burst of water molecules into the rigid and hydrophobic CNT inner channels (Figure 2-6c) [43]. Kalra *et al.* also reported similar findings and described the movement of water molecules within the (6,6) CNT as appeared frictionless with a high observed flow rate of 5.8 water molecules per nanosecond per CNT. Such high flow was independent of the length of the CNT, which was in contrary to predicted macroscopic hydrodynamics, and was only primarily limited by the chemical potential barriers at the entry and exit points of the CNT pores [45]. Overall, these molecular dynamic simulation results provided detailed nanofluidic information on the flow properties through an individual CNT.

In addition to using the tips of CNTs of different diameters as pores to achieve sieving capability, the concept of chemical gatekeepers can be introduced by exploiting the carboxyl functional groups which exist at the tips of opened CNTs to improve membrane flux and selectivity. M. Majumder *et al.* grafted short-chained alkane, long-chained alkane, long polypeptide and highly negatively charged dye molecule on the tips of plasma-opened MWCNTs via a simple carboimide linking chemistry. Small and large dye molecules methyl viologen (MV^{2+}) and ruthenium bipyridine ($Ru[bipy]_3^{2+}$) were respectively permeated through the CNT-based membrane. Results from the polypeptide-grafted membrane

validated modest gatekeeper activity with a small/ large molecule selectivity of ~ 3.6 . In addition, grafting the negatively charged dye molecule as gatekeeper resulted in increased fluxes (~ 5 folds) of the cationic dye molecules owing to the electrostatic interactions [46]. Diazonium gatekeepers grafted on CNT-based membrane also provided the same conclusion as the increased negatively charged carboxyl groups due to diazonium grafting at the tips of the MWCNTs facilitated permeation of the positively charged solutes [47]. These findings suggest that advancement in membrane design can be achieved using CNT-based membrane with well-defined placement of chemical gatekeepers at the entrances of the CNT pores.

2.3. Relevance of CNMs in osmotically-driven membrane-based separations

2.3.1. Reverse osmosis

Reverse osmosis (RO) is currently the most widely used desalination technology globally. The working principle behind RO is the use of hydraulic pressure to overcome the osmotic pressure of an aqueous feed solution through a semi-permeable membrane. By applying a driving force, water transport through the membrane is achieved while the salt is being rejected. This process produces purified water from sea water. Over the years, due to scientific advances in the area of RO membranes fabrication and improvements made in module and process designs, the overall desalination efficiency have been improved by at least 7 folds. Nonetheless, as already discussed in Chapter 1, there exists many pressing issues yet to be resolved, which include reducing production costs of drinking water, increasing the membrane selectivity to obtain good water quality through a single pass and mitigating membrane fouling [1]. These issues can be, to a great extent, alleviated by

strategically focusing on advancing the membrane fabrication processes. Among the many methods studied, the nano-enabled approach to membrane fabrication has been deemed as a promising solution [5, 48].

At the core of the RO process is a thin-film composite (TFC) membrane. The TFC membrane is fabricated by interfacial polymerization (IP) where two monomers, usually m-phenylenediamine (MPD) and trimesoyl chloride (TMC), cross-linked at the interface of a polar and non-polar solvent to form a polyamide (PA) layer (~100 nm) at the membrane surface. This PA layer acts as the selective layer of a porous substrate membrane (Figure 2-7a and b) and, being extremely thin (~100 nm), the TFC membrane exhibits much higher intrinsic water permeability as compared to the first generation asymmetric RO cellulose acetate membranes synthesized in the early 1960s. In addition, the TFC membrane offers excellent membrane selectivity, robustness and has the ability to remain stable over a great pH range [1, 3, 12, 49, 50]. Despite these benefits, the flux of the TFC membrane is still considered relatively low and the membrane surface properties make them susceptible to fouling (Figure 2-7c). Fouling can further reduce the membrane performances. While dosing chlorine into the feed solutions could potentially mitigate this issue, the PA layer is vulnerable to chlorine attack [1, 51, 52]. Thus, there is an urgent need to create an all-rounded PA selective layer to handle the above-mentioned issues.

Figure 2-7. (a) Schematic illustration of the IP process at the membrane surface. (b) FE-SEM image and (c) the surface properties of the PA selective layer. Adapted from [3].

Water and salt transport through the PA selective layer is driven by a solution-diffusion mechanism where species are first adsorbed onto the PA layer before diffusing into and across a concentration gradient [3, 53, 54]. The incorporation of CNMs therefore provides opportunities to enhance the TFC membrane performances by selective diffusion of water through the PA selective layer given the unique water transport properties of the CNMs. To substantiate this, both Kim *et al.* and Choi *et al.* reported the use of GO sheets to modify the PA selective layer via a layer-by-layer (LBL) method. The studies observed a 10-20% moderate enhancement in the flux of the TFC membrane without compromising the membrane selectivity when an additional GO multilayer was deposited. This phenomenon was attributed to the hydrophilicity and the high water diffusion through the stacked GO sheets. Besides, the GO multilayers, which act as a protective coating, instilled higher chlorine resistance to the TFC membrane [51, 52]. In addition, Ratto *et al.* demonstrated a near double enhancement in water flux (44 as compared to 26 L m⁻² d⁻¹ bar⁻¹) of the TFC membrane with a slight increase in the salt rejection (97.69% as compared to 96.16%) when MWCNTs were embedded in the PA selective layer in a random alignment [55]. All these examples aim to demonstrate the possibility of capitalizing on the unique water transport properties of CNMs to tailor the diffusion properties of the PA selective layer.

2.3.2. Nanofiltration

NF is a relatively newer technique and has been considered as a 'low pressure RO process' due to the looser membrane structure with more free volume in the polymer [56]. As such, NF has been gaining popularity among membrane-based separations as it offers higher fluxes than RO and significantly better retention capability than ultrafiltration (UF) at a lower pressure operating condition [57]. There are two unique characteristics of a NF membrane.

First, a NF membrane has an intermediate molecular weight cut-off (MWCO) between the RO and UF membranes, which ranges around 200 to 2000 Da. Second, the separation of electrolyte is driven by the electrostatic interactions between the NF membrane surface and the charge of the ions [58, 59]. In the situation of an uncharged NF membrane, the size exclusion effect dominates. On the other hand, for a charged NF membrane, the charge (Donnan) exclusion effect becomes predominant. In this case, the co-ions (ions with the same charge as the membrane surface) are repelled and the counter-ions (ions with the opposite charge) are attracted into the membrane. When this occurs, a Donnan potential is established and an electrochemical equilibrium between the solutes and the membrane is maintained. Such a Donnan equilibrium is dependent on the electrolyte concentration, fixed charge concentration in the membrane, valency of the co-ions and the counter-ions [60]. With a rise in the valency of the co-ions, the exclusion of co-ions increases which draws away the counter-ions to maintain electroneutrality, leading to an increase in the electrolyte rejection rate. This explains why charged NF membrane rejects multivalent ions better than the monovalent ones [58, 61, 62].

Despite the many advantages offered by the NF process, the NF membrane faces several drawbacks which are largely similar to the TFC RO membrane. These include unsatisfactory separation performances with low water permeability at high membrane selectivity due to external concentration polarization, membrane fouling issues and poor separation factor to allow precise separation of desired solutes [56]. To tackle these issues, CNMs can provide potential solutions with their abilities to engineer selective water and ions diffusion through the selective layer, increase hydrophilicity of the membrane surfaces and improve antifouling and antibacterial properties of the NF membrane. For example, an earlier study by L. Qiu *et al.* reported the fabrication of NF membranes via vacuum filtration of

chemically converted graphene (CCG) sheets. The CCG sheets with different extent of corrugation were controlled by increasing the temperature of the hydrothermal treatment. Water flux was observed to increase up to 5 folds while the pore sizes of the membranes widened from < 3 to > 13 nm with an increase in the extent of corrugation of the CCG sheets [63]. The results suggested the potential of using controlled corrugation on graphene sheets to realize tunable NF membranes (Figure 2-8a). Similarly, Huang *et al.* employed $\text{Cu}(\text{OH})_2$ nanostrands as sacrificial templates to fabricate nanostrand-channeled (NSC) GO membrane with NF-like properties as depicted in Figure 2-8b. The network of nanochannels was well controlled at 3-5 nm, which allowed high rejection rate of negatively charged Evan Blues at 83%. When positively charged solutes were evaluated, rejection rates increased with half the permeances due to the trapping of the positively charged solutes at the entrance of the negatively charged nanochannels which resulted in effective narrowing of the pore size of the NSC GO membrane [64]. Nonetheless, the creation of nanochannels in GO membrane has resulted in permeance more than 100 times that of commercial membranes with similar rejections.

Figure 2-8. (a) Schematic illustration of water transport across corrugated CCG NF membrane. Adapted from [63]. (b) Fabrication process of NSC GO membrane showing the nanochannels left behind after removal of the nanostrands. Adapted from [64]. (c) Schematic illustration of the MWCNTs-intercalated GO membrane. Adapted from [65].

In a different study, Y. Han and co-workers fabricated a MWCNT-intercalated GO NF membrane with antifouling properties. The result showed that the MWCNT-intercalated GO membrane exhibited excellent antifouling properties towards sodium alginate and humic acid with flux recovery rates at 94.4% and 86.5% respectively. This was attributed to the synergistic effect brought by assembling MWCNTs within the refluxed GO sheets (Figure 2-8c) which increased the hydrophilicity of the membrane surface [65].

2.3.3. Forward osmosis

On the contrary to RO and NF, the forward osmosis (FO) process is a naturally occurring one where water transfer across a selectively permeable membrane from a region of high water chemical potential to a region of lower water chemical potential [66]. This process leverages on the osmotic pressure difference across the membrane as the chief driving force. As such, FO emerges with several advantages. The main advantages include low or no hydraulic operating pressure, high rejection of a wide variety of contaminants and lower membrane fouling tendency [67]. In addition, due to the lower operating pressure, the equipment employed and process designs are usually much simpler. The working principle of FO involves a selectively permeable membrane separating a concentrated draw solution from a feed solution. The draw solution which has a higher osmotic pressure than the feed solution creates an osmotic pressure which drives water across the membrane from the feed to the draw solution. Theoretically, the asymmetric TFC RO membrane is suitable for use in the FO process. However, several studies, which involve RO membranes applied to FO processes, have shown lower than expected flux [68-70].

The lower than expected flux is attributed to the presence of internal concentration polarization (ICP) in the FO membrane. When an asymmetric membrane is used for FO, two

phenomena can occur depending on whether the membrane is used in the active layer facing draw solution (AL-facing-DS) or active layer facing feed solution (AL-facing-FS) orientation. In the AL-facing-DS orientation, the solute which passes through the active layer of the membrane get built up at the active layer and porous support interface as designated by C_3 depicted in Figure 2-9a. This is known as concentrative ICP. In the AL-facing-FS orientation, permeating water which transfers through the active layer dilute the draw solution at the permeate-membrane interface as designated by C_3 depicted in Figure 2-9b. This is known as dilutive ICP. Both concentrative and dilutive ICP are responsible for decreasing the effective osmotic pressure driving force. From Figure 2-9, it can be observed that the effective osmotic pressure driving force ($\Delta\pi_{\text{eff}}$) is smaller than the real osmotic pressure difference across the membrane ($\Delta\pi_m$). This is due to an increase in the solute concentrations in the porous substrate as shown from C_2 to C_3 in Figure 2-9a and the decrease in the solute concentrations in the porous substrate as shown from C_4 to C_3 in Figure 2-9b. As a result, lower water fluxes are obtained for both orientations.

Figure 2-9. Schematic illustration of the concentration profile of (a) concentrative ICP in the AL-facing-DS orientation and (b) dilutive ICP in the AL-facing-FS orientation across an asymmetric FO membrane.

To address this issue, FO membrane is designed with a thin and low porosity support layer so as to suppress the ICP. Other desirable characteristics include high density of active layer to provide high solute rejection and high hydrophilicity for enhancing water flux and reducing membrane fouling propensity [66]. In this regard, CNMs can play an important role in mitigating ICP by creating well-defined nanochannels for highly efficient water transport and molecular sieving functionality and increasing the hydrophilicity of the membrane surfaces to enhance antifouling properties. To corroborate this claim, Y.-X. Jia *et al.* performed a molecular dynamic simulation and predicted that with the optimization in the vertical alignment, filling density and lengths of CNTs, FO membrane incorporated with (8,8) CNTs can achieve the highest water flux at 100% salt rejection [71]. The promising results also suggested the potential of using CNTs in the FO process to overcome the trade-off hurdle observed in membrane-based separations as discussed in Chapter 1.

2.4. Current status of CNM-based membranes

The recent developments on CNM-based membranes, in particular graphene-based and CNT-based membranes, are being overviewed in this section. As highlighted in Figure 2-10, there are several approaches which can be employed to fabricate CNM-based membranes. Some of these approaches require higher degree of technicality and thus lower feasibility in scaled-up commercialization. Coincidentally, the CNM-based membranes fabricated from these approaches usually exhibit extraordinary performances, making them the state-of-the-art membranes. Nevertheless, approaches involving lower degree of technicality, such as membrane surface modification with CNMs, can still yield advanced membranes that fully exploit the unique properties of the CNMs [72]. As such, the following discussions focus on the state-of-the-art and surface-modified CNM-based membranes.

Figure 2-10. Different approaches commonly employed to fabricate CNM-based membranes.

2.4.1. Single-layer graphene membranes

As discussed in section 2.2.1, single-layer graphene offers the lowest hydrodynamic resistance given its ultimately thin, monoatomic thickness [31, 32] and, by creating subnanometer pores on the graphene sheet, the single-layer graphene can function as a semi-permeable membrane. As a proof-of-concept, S. C. O'Hern *et al.* demonstrated a single-layer, nanoporous graphene membrane with selective ionic transport for the NF process and potentially for desalination [73]. Pores were generated on a chemical vapor deposition (CVD) synthesized single-layer graphene (CVD) by bombarding with gallium ions to create defects before etching with potassium permanganate. The pores were subnanometer and limited to within ~ 1 nm in size (Figure 2-11a and b). As validated in Figure 2-11c-e, transport through these pores suggested a selective nature where smaller KCl can permeate through the created pores but larger Allura Red (AR) molecules were observed to permeate only when the pores were etched sufficiently large enough for the molecules to diffuse through.

Figure 2-11. (a) Pore size distribution profile after etching with potassium permanganate at various duration. (b) STEM images of the subnanometer pores. Scale bars are 0.5 nm. (c) Experimentally obtained permeability closely correlates to theoretical permeability based on pore size distribution suggesting selective nature of the membrane. (d) Diffusive flux through the membrane normalized by flux at 120 min etching and membrane potential measurements. (e) Schematic illustration of selective permeability across various subnanometer pore size due to different etching time. (a-e) adapted from [73]. (f) Different stages of multiscale sealing. (g,h) Experimentally obtained water permeability and rejection results agreeing well with theoretical simulation results. (f-h) adapted from [74].

In another work by the same group, the grain boundaries and tears generated during transfer of graphene to membrane substrate were respectively sealed via atomic layer deposition (ALD) of hafnia (HfO_2) and interfacial polymerization before generation of pores on the graphene surface (Figure 2-11f) [74]. It was reported that the multiscale sealing process realized a centimeter-scale graphene membrane which exhibited rejections towards MgCl_2 salt and low molecular weight compounds (AR and 4.4 kDa Dextran) and a water permeability consistent with molecular dynamic simulations in the FO process (Figure 2-11g and h, Table 2-1).

S. P. Surwade *et al.* also demonstrated the potential of using nanoporous single-layer graphene as a desalination membrane. Nanometer pores at ~ 0.5 to 1 nm in size were generated by exposing a suspended CVD synthesized graphene to O_2 plasma etching (Figure 2-12a) for a time as short as 1.5 s. The results were nearly 100% KCl salt rejection and an extremely high water flux of $10^6 \text{ g m}^{-2} \text{ s}^{-1}$ at 40°C when pressure difference was employed as the driving force. When an osmotic gradient was applied as the driving force, a water flux of $\sim 250 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was observed instead (Table 2-1). The high salt rejection, as represented in Figure 2-12 b and c, was attributed to the use of suspended, mono-crystalline, single-layer graphene with an effective membrane surface area of only $5 \mu\text{m}$. This small membrane area avoided exposure of the domain boundaries of graphene and reduced any potential for defect production during the O_2 plasma etching process [75]. The high water flux (Figure 2-12b) was, on the other hand, attributed to the low-friction flow of water on the hydrophobic, non-oxidized regions on the atomic-thick single-layer graphene [19, 21]. Despite these outstanding performances, the authors highlighted the significant technical challenges which need to be resolved in order to scale-up the fabrication of such single-layer graphene membrane for commercial applications.

Figure 2-12. (a) Schematic illustration of the O₂ plasma etching treatment on the suspended, single-layer graphene. (b) Water and KCl permeability and (c) Water/ salt selectivity of the nanoporous, single-layer graphene with different pore sizes as represented by the I_D/I_G ratio. C1 and C2 are controls with large tears or completely broken graphene. Adapted from [75].

2.4.2. Graphene-based surface-modified membranes

Unlike nanoporous single-layer graphene membrane fabrication, membrane surface modification is a technically more feasible approach to realize scaled-up graphene-based separation membranes. Surface modifications are generally categorized into two main methods. First, graphene-based materials can be grafted onto the membrane surfaces during post-treatment selective layer formation. Second, graphene-based materials can be assembled onto the membrane surfaces as stacked laminates. In the latter, the graphene-based laminates can be reckoned as freestanding membranes with the substrate membranes deemed as mechanical supports.

Grafting of graphene-based materials onto the selective layers of membranes are usually performed during the IP process, via covalent functionalization or the LBL methods. For example, H.-R. Chae *et al.* and M. Safarpour *et al.* respectively embedded GO and rGO/TiO₂ into the selective layer of the TFC membrane. In both studies, the graphene-based materials were first dispersed in the aqueous MPD phase before cross-linking with the organic TMC phase to yield a PA layer incorporated with the graphene-based material. Improved performances were reported with enhancements observed in water permeability,

antifouling property and chlorine resistance of the graphene-based TFC membranes (Table 2-1). These enhancements were attributed to the increased hydrophilicity, more negative zeta-potential and reduced surface roughness of the graphene-based PA selective layer [76, 77]. In another study, F. Perrault and co-workers grafted GO onto the TFC membrane surface through functionalizing the carboxyl groups into amine-reactive esters and covalently bound the GO sheets and PA layer using ethylene diamine (EDA) as the cross-linker. A strong antimicrobial property was imparted onto the GO functionalized PA selective layer without affecting the intrinsic TFC membrane transport properties (Table 2-1). The strong antimicrobial property, which inactivated 65% of the *E.coli* cells after 1 h exposure, was a consequence of the direct contact between the *E. coli* cells and the GO sheets [72]. In addition, M. Hu and B. Mi enabled GO on a polydopamine-coated polysulfone substrate membrane by LBL covalent bonding of the GO sheets using TMC as a cross-linker. Water fluxes which were 4 to 10 times that of commercial NF membranes and a high rejection rate towards organic dye with molecular weight around 500 Da were reported for the ensuing GO membranes. Nonetheless, the GO membranes performed moderately when rejecting smaller organic dyes and salts (Table 2-1) [78]. M. Hu and B. Mi also capitalized on the electrostatic interactions between the negatively charged GO and the positively charged poly(allylamine hydrochloride) (PAH) to fabricate a GO membrane via a LBL assembly method. The water permeability was observed to be about an order of magnitude higher than commercial membranes with ~99% rejection rate towards sucrose when evaluated under the FO process. However, swelling of the GO-PAH bilayers due to high ionic strengths of the draw solutions resulted in moderate rejections of charged species (Table 2-1) [79].

Stacking graphene-based materials as laminates is another approach to fabricate graphene-based surface-modified membranes. The laminates are commonly stacked via

pressure-assisted, vacuum-assisted filtration or evaporation-assisted assembling technique. To demonstrate this, C.-H. Tsou *et al.* fabricated GO composite membranes by assembling GO laminates on modified poly(acrylonitrile) (PAN) substrate membranes via these three methods. The pressure-assisted filtration yielded the most orderly GO laminate while the evaporation-assisted assembling technique resulted in the most random GO laminate as shown in Figure 2-13. This was attributed to the difference in the pressure distribution across the evolving GO laminate when pressure-assisted and vacuum-assisted filtration was employed. In the case of evaporation-assisted assembling technique, the upward driving force associated with the vaporizing liquid resulted in the highly random microstructure of the GO laminate [80]. As such, many studies adopted either vacuum-assisted or pressure-assisted filtration to fabricate graphene-based laminated membranes.

Figure 2-13. (a) Schematic illustrations of the different assembling technique to stack GO laminates. (b) FE-SEM images providing the microstructural integrity of the resulting GO laminates. The inserts show the homogeneity of the GO laminates. Adapted from [80].

Table 2-1. Overview of the current status of graphene-based membranes in terms of the fabrication approaches and performances.

Graphene-based membrane	Membrane description	Process	Fabrication method	Membrane performances			Ref.
				Flux (L m ⁻² h ⁻¹ bar ⁻¹)	Rejection (%)	Enhancement	
Single-layer	Nanoporous (~1 nm)	FO	O ₂ plasma	~250	~100 (1M KCl)	N.A.	[75]
	Nanoporous (~0.5 nm)	FO	KMnO ₄ etched	1.41	~70 (16.6mM MgSO ₄) ~90 (1.3mM AR) ~83 (1mM Dextran) ^a	N.A.	[74]
Surface	GO/PA/PSF	RO	IP	~1.1	99.4 (2000ppm NaCl)	Antifouling;	[76]
	rGO/TiO ₂ /PA/PSF	RO	IP	3.4	99.45 (2000ppm NaCl)	Chlorine resistance	[77]
	GO/PA/PSF	RO	Covalent functionalization	~1.5	97.8 (50mM NaCl)	Antimicrobial	[72]
	GO/TMC/PSF	NF	Covalent functionalization	8 -27.6	93-95 (7.5ppm R-WT) 46-66 (7.5ppm MB) 26-46 (10mM Na ₂ SO ₄) 6-19 (20mM NaCl)	N.A.	[78]
Stacked-laminate	GO/PAH/PAN	FO	LBL	2.1-5.8	~99 (1M sucrose)	N.A.	[79]
	Based-refluxed rGO/PVDF	NF	Vacuum-assisted	21.8	99.2 (0.02mM MB) 78 (0.02mM RhB)	N.A.	[81]
	HI reduced rGO/MCE	FO	Vacuum-assisted	~0.7	~99 (2M NaCl)	N.A.	[82]
	CDs-GO/MCE	NF	Vacuum-assisted	408-434	99.5 (10ppm MB) 99.2 (10ppm MO) 99.7 (10ppm RhB)	N.A.	[83]
	MWCNTs-refluxed GO/PVDF	NF	Vacuum-assisted	11.33	96.1 (0.05g/L MO) 99.8 (0.02mM DY)	Antifouling	[65]
	PNIPAM/CCG/NME	UF	Pressure-assisted	152	70 (RhB)	Temperature-responsive	[84]

aGO: aminated GO; PA: polyamide; PSF: polysulfone; PAH: poly(allylamine hydrochloride); PAN: poly(acrylonitrile); PVDF: polyvinylidene fluoride; MCE: mixed cellulose ester; CDs: carbon dots; PNIPAM: poly(N-isopropylacrylamide); NME: nitrocellulose mixed ester; AR: allura Red; R-WT: rodamine-WT; MB: methylene blue; RhB: rhodamine B; MO: methyl orange; DY: direct yellow; N.A.: not applicable. ^aM.W. of dextran: 4.4kDa.

Y. Han and co-workers fabricated an ultrathin graphene NF membrane with based-refluxed rGO sheets using the vacuum-assisted filtration. High water fluxes, up to four orders of magnitude greater than the values predicted by Hagen-Poiseuille equation, with high rejection rates towards organic dyes (~99%) were reported (Table 2-1). The high flux was a consequence of the ultrafast water transport across the hydrophobic nanocapillaries formed by stacking the 2-D rGO sheets while the high rejection was due to the negative charges and the reduced interlayer spacing between the rGO sheets [81]. In another study, H. Liu and co-workers fabricated a freestanding ultrathin rGO membrane for the FO process. A vacuum-assisted filtration was first applied to obtain the GO membrane before subjecting the membrane to HI reduction to yield the freestanding ultrathin rGO membrane. The FO water flux, which peaked at $57.0 \text{ L m}^{-2} \text{ h}^{-1}$ with 2.0 mol L^{-1} NaCl draw solution, was four times higher while the reverse salt flux was reported to be nine times lower than that of the commercial cellulose triacetate membrane (Table 2-1). Such high salt rejection was accredited to the small interlayer spacing between the rGO sheets. Interestingly, the ultrathin rGO membrane exhibited a linearly proportionate FO water flux with respect to the draw solution concentration, which indicated that dilutive ICP was almost not present in the ultrathin rGO membrane [82]. This important finding suggested the potential application of freestanding, ultrathin rGO laminate as robust membrane to mitigate the pervasive problem of ICP faced by the current conventional FO membranes.

To improve the water permeability of graphene-based laminated membranes, several different spacers are intercalated within the interlayer spacing of the graphene-based sheets. These include carbon quantum dots [83], MWCNTs [65, 85], stimuli-responsive polymers [84] and monolayer titania nanosheets [86]. The spacers not only serve to expand the interlayer spacing between the graphene-based sheets but introduce multi-functionalities to

the graphene-based laminated membranes. The performances of these membranes are summarized in Table 2-1.

2.4.3. Vertically aligned CNT-based membranes

Similar to single-layer graphene membranes, the fabrication of vertically aligned CNT-based membranes require a multistep process, making their large-scale applications equally challenging to achieve. Typically, the fabrication (Figure 2-14) first involves the synthesis of a vertically aligned CNT forest using the CVD method before filling up the spaces between the CNTs with a suitable filler. This is then followed by an etching process to remove the excess filler from the membrane surface and to open the tips of the CNTs to yield a membrane with the inner channels of the CNTs as well-defined nanopores [87]. B. J. Hinds *et al.* utilized such a fabrication process to synthesize vertically aligned MWCNT membranes which was 5 to 10 μm in thickness with a pore distribution of 6 ± 2 nm. TEM analysis of the MWCNTs suggested that the pore distribution was consistent with the inner diameters of the MWCNTs, providing solid evidence of CNTs inner channels acting as nanopores for solute transport [88].

Figure 2-14. Vertically aligned CNT-based membranes fabrication typically involves a multistep process. Adapted from [87].

The same group extended their study by performing a pressure-driven flow through a vertically aligned MWCNT membrane with 7 nm inner diameter. It was reported that liquid flow rate through this membrane was 4 to 5 orders of magnitude faster (Table 2-2) than what would be predicted from conventional fluid flow through pores of 7 nm in diameter [17]. In addition, J. K. Holt *et al.* synthesized a vertically aligned double-walled CNT (DWCNT) forest with sub-2-nanometer inner diameter and encapsulated it within a silicon nitride (Si_3N_4) matrix to yield a vertically aligned DWCNT membrane that was capable of rejecting gold nanoparticle of 2 nm in size. The measured water flow rates (Table 2-2) exceeded values predicted from a continuum hydrodynamic flow model by more than three orders of magnitude and was found to be comparable with flow rates extrapolated from molecular dynamic simulations [89]. Both studies attributed the fast flow rates to the nearly frictionless interface of the hydrophobic CNT walls as evident from the long slip lengths calculated. Recently, B. Lee *et al.* explored water transport through the walls of the vertically aligned MWCNTs without any encapsulation. Fabrication of the membrane was carried out by first synthesizing a MWCNT forest before densifying via mechanical compression into a membrane as shown in Figure 2-15a and b. The tips of the MWCNTs were capped (sealed) and the pores of the membrane were made up by the spaces between the outer walls of the MWCNTs. Membrane pore size was tunable in the range of 7 to 38 nm by simply manipulating the mechanical densification (Figure 2-15c-f). Water permeability of these membranes was observed to increase from 2,300 to 5,800 $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ when the pore size decreased from 38 to 7 nm. Concurrently, rejection rates increased up to ~97% (12 kDa dextran) for the membrane with 7 nm pore diameter (Figure 2-15g and h). The counter-intuitive water permeability was explained by the occurrence of nanoscale confinement when the pore diameter decreased to 7 nm. As a result, molecular ordering of water molecules

facilitated faster water transport through the frictionless CNT wall surface as previously discussed in section 2.2.2. When the caps of the MWCNTs were opened via an O₂ plasma etching process, the inner channels of the MWCNTs (6 nm in diameter) served as supplementary entrances and pores for water transport. As a result, an unprecedented water permeability that approached 30,000 L m⁻² h⁻¹ bar⁻¹ was obtained without compromising the membrane selectivity. This is by far the highest water permeability reported for a UF membrane in the literature. In addition, the vertically aligned densified MWCNT membrane exhibited antibacterial properties by impeding bacterial adhesion and resisted biofilm formation [22]. Nevertheless, the commercial application of such membranes is still greatly hindered by the small-area production of the CVD synthesized MWCNTs forest.

Figure 2-15. (a) SEM image of the MWCNT forest with a thickness of 1.3 mm (scale bar, 500 μ m). (b) Photo demonstrating the scale of the mechanical densification. (c-f) FE-SEM images of the cross-sectional morphology of the MWCNT membrane densified to different extent (scale bar, 100 nm). (g) Water permeability trend and (h) various dextran rejection rates of the various capped MWCNT membranes. Adapted from [22].

2.4.4. Randomly aligned CNT-based membranes

Scaled-up production of CNT-based membranes can be more easily realized by embedding commercially available CNTs into the PA selective layer of the TFC membranes.

This is because the fabrication of TFC membranes is already well-established and highly developed. Coupled with the continuously dropping cost of mass producing CNTs, it is not only chemically feasible but economically viable to commercially fabricate CNT-based TFC membranes for RO, NF and FO applications [90]. Nonetheless, the lack of control of the alignment of CNTs in the PA selective layer is a serious drawback of this approach and chemical functionalization of the CNTs is essential to make the hydrophobic nanomaterial compatible with the cross-linking fabrication process.

While limited studies have been carried out on post-synthesis alignment of CNTs due to its technical difficulties [91-95], significant amount of work has been done in chemical functionalizing CNTs for incorporation into the PA layer of TFC membranes. For example, H. J. Kim *et al.* treated the pristine MWCNTs with a mixture of sulfuric and nitric acid (3 : 1 ratio) for 4 h at 65 °C to obtain functionalized MWCNTs with higher oxygen-containing functional groups. This allowed the functionalized MWCNTs to be well-dispersed in the MPD aqueous solution. As a result, the water flux was reported to increase by 17% without compromising the membrane selectivity (Table 2-2) [96]. In addition, M. Amini and co-workers functionalized MWCNTs with amine functional groups to increase the surface roughness and hydrophilicity of the TFC membrane. The membrane with amine-functionalized MWCNTs showed a 160% enhancement in water flux when evaluated under the FO process in the AL-facing-DS orientation (Table 2-2). The membrane selectivity was also improved with a lower reverse salt flux observed [97]. Both studies accredited the increased water flux to the additional nanochannels created by the inner channels of the MWCNTs and the nanogaps between the MWCNTs and the PA layer.

Furthermore, CNTs can be chemically functionalized at the tips with gatekeepers to step-up the performances of the TFC membranes. W.-F. Chan *et al.* performed chemical

functionalization by attaching zwitterions to the opened tips of SWCNTs. This was followed by vacuum-assisted filtration of the zwitterionic SWNCTs onto a polyethersulfone (PES) substrate membrane before the IP process to yield a semi-aligned zwitterionic SWNCT membrane. The water flux was enhanced by 4 folds with increased membrane selectivity (Table 2-2). This was attributed to the additional transport mechanism brought by the incorporation of the SWCNTs and the gated entrance hindered by the zwitterions at the tips of the SWCNTs [98]. T.-Y. Liu *et al.* also reported a similar concept by grafting poly(sulfobetaine) (PSB) brushes at the tip of MWCNT to give a poly(zwitterionic) MWCNT (ZCNT). The PSB brushes were ion-responsive and served as gatekeepers to modulate the membrane selectivity at different ionic strengths of the feed solutions. With the incorporation of the ZCNTs into the PA selective layer, the water permeability was enhanced by almost one fold when compared to the TFC membrane with pristine MWCNTs incorporated. Such an enhancement was observed across a Na_2SO_4 feed concentration of 0.7 to 70 mol m^{-3} . Interestingly, the ZCNTs incorporated TFC membrane exhibited increased membrane selectivity when the feed concentration was raised from 0.7 to 70 mol m^{-3} . This was in contrary to conventional NF membranes where membrane selectivity decreased with higher feed concentration. The authors attributed this to the “nanoconfined stretching state” of the PSB gatekeepers induced by a higher ionic environment. As a result of this ion-responsiveness, the ZCNTs incorporated TFC membrane also demonstrated an ultrahigh selectivity with a separation factor of 93 over monovalent to divalent anions ($\text{Cl}^-/\text{SO}_4^{2-}$) [99].

2.5. Conclusions

CNMs appear to possess the extraordinary water transport properties and molecular sieving capabilities which are highly sought in membrane-based separations. These unique

properties, when translated into membranes, are able to enhance membrane performances as discussed above. At present, state-of-the-art CNM-based membranes demonstrated remarkable membrane performances in terms of water permeability and retention capability. However, these membranes are plagued by the highly elaborated membrane fabrication process. Alternatively, mixed-matrix CNM-based membranes require a less technical fabrication process but the remarkable properties of CNMs are unable to be fully capitalized when the CNMs are encapsulated in the polymer matrix. As a result, this thesis is strategically dedicated to the study of surface-modified CNM-based membranes in order to present scalable membrane fabrication processes with full exploitation of the unique properties of the CNMs.

Table 2-2. Overview of the current status of CNT-based membranes in terms of the fabrication approaches and performances.

CNT-based membrane	CNTs description	Process	Fabrication method	Membrane performances			Ref.
				Flux (L m ⁻² h ⁻¹ bar ⁻¹)	Membrane selectivity	Enhancement	
Vertically aligned	CVD MWCNTs (~7nm) ^a	UF	Multistep encapsulation in PS	~350-600	N.A.	N.A.	[17]
	CVD DWCNTs (~1.3-2nm) ^a	UF	Multistep encapsulation in Si ₃ N ₄	71-284	~100% (2nm Au nanoparticle)	N.A.	[89]
	MWCNTs wall (pore ~6nm) ^{a,b}	UF	Densified, O ₂ plasma etching	29,600	98.3% (100ppm Dextran 12kDa)	Antibacterial, Antibiofouling	[22]
	S.L. DWCNTs (~10nm) ^a	UF	Multistep encapsulation in epoxy	2309	N.A.	Magnetic-responsive	[100]
	CVD MWCNTs (~4.8nm) ^a	UF	Multistep encapsulation in epoxy	1,100	78% (200ppm PEO 100kDa)	Antibiofouling	[101]
Randomly aligned	Octadecylamine-funct. SWCNTs	RO	IP	1.84	97.7 (2000ppm NaCl)	N.A.	[55]
	Acid-treated MWCNTs	RO	IP	2.86	95.7% (2000ppm NaCl)	N.A.	[96]
	Amine-funct. MWCNTs	FO	IP	~1.2 (in AL-facing-DS)	~4-5 g m ⁻² h ⁻¹ (NaCl reverse flux)	N.A.	[97]
	Zwitterionic SWCNTs	NF	IP	4.47	73% (20mM NaCl)	N.A.	[98]
		RO	Vacuum-assisted filtration, IP	1.33	98.6% (2000ppm NaCl)	N.A.	
	PSB grafted MWCNTs	NF	IP	~19	98.5-97.6% (17.0-0.3 mol m ⁻³ Na ₂ SO ₄)	Ion-responsive	[99]
	Acid-treated MWCNTs	RO	GO/CNT hybrid, IP	3.80	96.6% (2000ppm NaCl)	Chlorine resistance; Radical scavenging ability	[102]

CVD: chemical vapor deposition; S.L.: super long; funct.: functionalized. PSB: poly(sulfobetaine); PS: polystyrene; PEO: polyethylene oxide; N.A.: not applicable. ^aValues refer to diameters of the inner channel of CNTs. ^bMWCNTs inner channel is 6nm while space between MWCNTs is 7nm in diameter.

Sandwich-architected poly(lactic acid)-graphene composite barrier membranes¹

3.1. Introduction

A defect-free graphene sheet is chemically inert, mechanically strong and impermeable to most gases [21, 29, 103, 104], making this material an excellent choice for a barrier membrane. Moreover, graphene sheets possess a high aspect ratio, owing to its monoatomic thickness and two-dimensional structure as described in Chapter 2 [23, 105]. Recently, a study reported the use of rGO as an impermeable barrier film and protective coating. The rGO film exhibits exceptional barrier properties towards He, H₂, water vapor, NaCl salt and HF acid [106]. In addition, another study highlighted the use of a layer-by-layer (LBL) technique to assemble GO with polyethyleneimine (PEI) multilayers onto a PET film. The PET film deposited with 10 bilayers of PEI/GO exhibits an exceedingly low oxygen permeability when compared to GO/polymer bulk composites and has an outstanding H₂/CO₂ selectivity [107]. Fundamentally, these results suggest that GO and rGO sheets display similar barrier properties as defect-free graphene sheets and is suitable to be exploited for barrier membrane applications.

This chapter aims to study the barrier properties of graphene-based materials through the development of poly(lactic acid) (PLA)-graphene composite membrane comprising of GO or rGO film as a core barrier of the membrane. A freestanding GO film is fabricated via a

¹(This chapter is reproduced with permission from K. Goh, J. K. Heising, Y. Yuan, H. E. Karahan, L. Wei, S. Zhai, J.-X. Koh, N. M. Htin, F. Zhang, R. Wang, A. G. Fane, M. Dekker, F. Dehghani, Y. Chen, Sandwich-Architected Poly(lactic acid)-Graphene Composite Food Packaging Films, *ACS Appl. Mater. Interfaces*, 8 (2016) 9994-10004. Copyright 2016. American Chemical Society)

pressure-assisted filtration process before undergoing a hydroiodic (HI) acid reduction to yield a freestanding rGO film. In contrast to the graphene-based bulk nanocomposite and multilayer membrane design as adopted by many in the literature [108-112], a deliberate choice is made to embrace a sandwiched architecture for the PLA-graphene composite membranes where the freestanding GO or rGO film is inserted in between two PLA films to act as an effective barrier membrane. PLA is a biodegradable polymer which has been deemed as a potential alternative to petroleum-derived polymers [113]. With its good mechanical and physical properties [114], the PLA films serve as an environmental friendly outer encapsulation to protect the inner core barrier from any physical abrasions. Such a sandwiched architecture aims to address potential problems with the bulk nanocomposite and multilayer membrane design. First, although lab-scale multilayer membrane fabrication via the LBL method appears feasible and promising, scaling up into an industrial process is still considered a technical challenge [115]. On the other hand, bulk nanocomposite fabrication may appear more scalable but it lacks design freedom as GO and rGO sheets are susceptible to aggregation[116]. Second, exposure of GO or rGO sheets on the surface of the bulk nanocomposite and multilayer membranes is undesirable in many applications. Therefore, by adopting a sandwiched architecture, the GO and rGO core barriers stay encapsulated and prevent any leaching of these graphene-based materials. In addition, freestanding GO and rGO films are solution-based processed and their scaled-up fabrications are more attainable [117, 118]. Most importantly, PLA films are easily available from commercial sources and with their production costs reduced in recent years [119], it will be more economical to produce the PLA-graphene composite barrier membranes.

To demonstrate the merits of the sandwiched architecture, different sizes and shapes of the GO, rGO and PLA-graphene composite membranes are prepared and tailored to

evaluate their processability. In addition, both water vapor and oxygen barrier properties of the PLA-graphene composite membranes are studied together with their detailed physicochemical characterization to evaluate the potential of using these graphene-based materials as barrier membranes. Last but not least, a mechanistic understanding of the excellent barrier properties is also elucidated by making reference to the unique morphology and physicochemical characteristics of the GO and rGO core barriers.

3.2. Experimental

3.2.1. Materials

Graphene oxide solution (GO, 4 mg mL⁻¹) was purchased from Graphenea (Spain) while the hydroiodic (HI) acid (57 wt%) was from Sigma-Aldrich. The commercial poly(lactic acid) (PLA, 0.05 mm thickness) film and the polyvinyl pyrrolidone (PVP, $M_w \sim 8$ -10 kDa) was obtained from Goodfellow (Cambridge) and Sinopharm Chemical (Beijing) respectively. The polyvinylidene fluoride membrane (PVDF, 0.22 μ m pore size, 293 mm diameter), which was used as a substrate for the filtration of GO film, was purchased from Merck Millipore. All the above-mentioned reagents and materials were used as-received.

3.2.2. Preparation of large-area GO and rGO films

GO films were obtained via pressure-assisted filtration [120]. Briefly, 105 mL of the as-received GO solution was added to 541 mL of deionized water (DI H₂O) to give a diluted GO concentration of 0.65 mg mL⁻¹. The resulting GO solution was then subjected to pressure-assisted filtration at 1 bar pressure over a trimmed PVDF membrane (250 mm diameter) using N₂ gas in an in-house made dead-end filtration cell. Upon completion, a GO

film was formed and left to dry in air before peeling off the PVDF substrate to yield a freestanding GO film. To prepare the rGO films, a freestanding GO film was first trimmed into a dimension of 12×12 cm before exposing the film to HI fumes at $90\text{ }^{\circ}\text{C}$ for 15 min. The freestanding rGO film was then obtained after washing it with DI H_2O to remove any surface HI and heating it at $80\text{ }^{\circ}\text{C}$ for 72 h to clear out the remaining HI intercalated within the rGO sheets.

3.2.3. Preparation of PLA-graphene composite membranes

The as-received PLA film was first trimmed into a dimension of 15×15 cm before a thin layer of PVP solution (65 wt%) was applied on top of the film using a handheld adhesive spreader. The PVP solution was employed as a binder as the freestanding rGO film was observed to delaminate from the ensuing PLA-graphene composite membrane. To study the effect of PVP concentration on its adhesiveness towards the GO and rGO film, 30, 40, 55 and 70 wt% of the PVP solution was prepared and utilized. The fabrication process comprised of the assembling of a freestanding rGO film in between two pieces of PLA film with pre-applied PVP solution before heat pressing (Carver Inc, USA) them at a compression force of 2000 pounds and a temperature of $65\text{ }^{\circ}\text{C}$ for 30 min to yield the as-prepared film (Figure 3-1). The same process was repeated using a freestanding GO film. These PLA-graphene composite membranes were designated as PLA-rGO and PLA-GO respectively. A blank film (PLA-blank) was similarly fabricated to act as a control.

3.2.4. Water vapor and oxygen permeability

The water vapor transmission rates (WVTR) of PLA-blank, PLA-GO and PLA-rGO were measured using a Labthink TSY-W3 water vapor permeability tester (Jinan, China).

These measurements were carried out at a temperature of 38 °C and 90% RH with a water vapor partial pressure of 0.05826 atm. The oxygen transmission rates (OTR) of the respective films were measured using a Mocon Ox-Tran Model 2/20 apparatus (Minneapolis, USA). All measurements were carried out at a temperature of 23 °C and an O₂ partial pressure of 1 atm under a relative humidity (RH) of 0% and 50%. The effective surface area of the samples for the WVTR and OTR measurements was 1.13 and 5.0 cm² respectively. All the measured WVTR and OTR values were then normalized by the partial pressure and the membrane thickness to obtain the respective water vapor permeability (WVP) and oxygen permeability (OP) of the membranes. The reported WVP and OP values were average of at least three different measurements from three discrete membranes.

The diffusion length of the gas molecules can be estimated using the Nielsen's gas transport model for a platelet-filled layered film as shown in the following equations:

$$l' = l + \langle N \rangle \frac{L}{2} \quad (1)$$

$$\langle N \rangle = \frac{l}{d + W} \quad (2)$$

where l' is the diffusion length, l is the film thickness, L and W are the lateral dimension and thickness of the platelet and d is the effective distance between the platelets [30, 116, 121]. Applying to the situation of the rGO film, L and W are the lateral dimension and thickness of the individual rGO sheet while d is the interlayer distance between the rGO sheets in the freestanding film. The height of the rGO sheet can be approximated as ~1.0 nm based on studies as described in the literature [21, 106].

Figure 3-1. (a) Fabrication scheme of the PLA-graphene composite membrane; (b) Optical image demonstrating the sandwiched architecture of as-prepared PLA-rGO membrane.

3.2.5. Physicochemical characterization

An atomic force microscope, AFM (MFP-3D, Asylum Research) in the AC mode, was employed to evaluate the lateral dimensions of the GO sheets used in making the freestanding GO and rGO films. The film cross-sectional morphology of PLA-rGO, PLA-GO and PLA-blank was imaged using a field emission-scanning electron microscope, FE-SEM (JSM-6701F, JEOL), at 5 kV. The reduction process was substantiated by studying the changes in the surface functional groups of the freestanding GO and rGO films using an attenuated total reflection Fourier transformed-infrared spectrometer, ATR FT-IR (IR

Prestige-21, Shimadzu). In addition, Raman spectroscopy (Reinshaw) equipped with a 514 nm laser source was also utilized to investigate the microstructural integrity of the freestanding GO and rGO films while the X-ray diffraction (XRD) patterns of these films, obtained using a X-ray diffractometer (D2 Phaser, Bruker) equipped with a Cu K α radiation source, indicated the degree of restacking of the rGO sheets after reduction. The water contact angles of PLA-blank, PLA-GO, PLA-rGO and the freestanding GO and rGO films were measured using a goniometer (OCA, DataPhysics, GmbH). A rheometer (Physica MCR 101, Anton Paar) was used to measure the viscosity of the PVP solutions at a shear rate of 10 s⁻¹ and a temperature of 25 °C.

3.3. Results and discussion

3.3.1. Design and fabrication of PLA-graphene composite membranes

PLA-graphene composite membranes are designed uniquely to have a core barrier to improve the barrier property of the as-received PLA film. GO is selected as the material due to the ease of processing aqueous GO solution into a film and the relatively small interlayer spacing between the GO sheets in the film [19]. To capitalize on GO as a barrier, a large-area GO film was fabricated. As described in Chapter 2, a pressure-assisted filtration can yield a GO laminate with a tight and highly ordered microstructure as opposed to other preparative methods [80]. Hence, this method is employed for the film fabrication. The resulting GO film was then HI reduced to give a freestanding rGO film with an even constricted interlayer spacing between the rGO sheets. HI is preferred over other alternative chemicals such as hydrazine given that its gentle chemical reduction can help to prevent microstructural damage to the rGO film [106]. Besides, the resulting rGO film from HI reduction has been

reported to retain the high flexibility and integrity of the GO film, with improved ductility and strength [27]. Therefore, through deliberate considerations over the filtration process and the reducing agent, large freestanding rGO films which possess minimal microstructural defects and can act as effective barriers are fabricated.

As shown in Figure 3-1a, the freestanding rGO film was assembled in between two as-received PLA films with PVP solution acting as a binder to secure the PLA-graphene composite membrane. This sandwiched architecture is specifically designed to address several issues. First, the pressure-assisted filtration process is an easy to administer preparative method but the fabricated rGO core barrier, which has a thickness of less than 5 μm (Figure 3-1b), is not sufficiently robust to resist surface abrasion. Second, the PVP binder is generally non-toxic and poses no health risk [122]. However, unnecessary leaching of the aqueous binder during membrane operations should still be avoided. Therefore, the synergistic sandwiched architecture provides a total solution, by leveraging on the rGO film as the inner core barrier while the PLA films serve as the outer encapsulation, which aims to protect the barrier as well as to prevent undesirable contaminations.

The PVP binder plays a crucial role in the fabrication process. This is because the freestanding rGO film tends to delaminate from the PLA films after the heat press treatment (Figure 3-2a), probably due to a lack of oxygen-containing functional groups on the rGO film which renders electrostatic interaction and hydrogen bonding to the PLA films unfavourable [123-125]. A series of PVP binder was prepared to understand the effect of concentration on its adhesiveness. It is observed that when the concentration of the PVP binder is low (30 to 40 wt%), the adhesiveness of the binder is not strong enough to prevent delamination. As the concentration is increased (55 to 65 wt%), the PVP binder exhibits good adhesion and PLA-rGO is delamination free. On the other hand, when the concentration further increases till 70

wt%, the rGO film becomes easily torn during the heat press treatment. Such a phenomenon can be explained by investigating the changes in the viscosity of the PVP binder at these concentrations. As revealed in Figure 3-2b, the viscosity of the PVP binder remains extremely low ($\sim 0.02 - 0.05 \text{ Pa}\cdot\text{s}$) at 30 to 40 wt% but slowly increases to $1.38 - 4.46 \text{ Pa}\cdot\text{s}$ at 55 to 65 wt% before escalating to $19.00 \text{ Pa}\cdot\text{s}$ at 70 wt%. This suggests that the amount of PVP at 30 to 40 wt% is inadequate to exert a strong adhesion towards the rGO and PLA film. However, at 70 wt%, the viscosity is so high that the stress on the rGO film, which is created by the shearing of the PVP binder during the heat press treatment, far exceeds the mechanical strength of the film. This causes the rGO film to tear. As a result, the concentration of the PVP binder was optimized at 65 wt% to ensure the integrity of the rGO core barrier during the fabrication process.

Figure 3-2. (a) FE-SEM image illustrating the microscopic delamination in the PLA-graphene composite membrane; (b) the change in the viscosity of the PVP binder with respect to its concentration and the effects on the PLA-graphene composite membrane.

The processability of the freestanding GO films and the PLA-graphene composite membranes is exemplified in Figure 3-3a and b respectively. Depending on the size of the pressure-assisted filtration setup, the size of the GO film is tunable and has been

demonstrated to be in the range of 42 to 230 mm in diameter as illustrated in Figure 3-3a. Although different in diameters, these GO films have the same loading of 1.01 mg/cm^2 . The loading is optimized at this value because a higher loading of the GO sheets decreases the water permeability of the film and increases the filtration duration (Figure 3-3c). However, a lower loading results in a thinner GO film which makes handling less manageable during the post-treatment. Therefore, the chosen GO loading allows a balance to be struck between pragmatic filtration duration and the manageability of the freestanding GO film. As the GO film is subjected to HI fumes, the yellowish-brown film is reduced into a freestanding rGO film with a metallic-silver lustre. Even after heat pressed with the PLA films, PLA-GO and PLA-rGO continue to display good processability as highlighted by their capacities to be tailored from circular to square membranes of dimensions $12 \times 12 \text{ cm}$ (Figure 3-3b) and the robustness of PLA-GO and PLA-rGO towards bending tests (Figure 3-3d and e).

Figure 3-3. Photos illustrating (a) the different sizes of the freestanding GO films; (b) the fabricated PLA-blank, PLA-GO and PLA-rGO in square shapes. (c) Normalized water permeability coefficient of the freestanding GO films at different GO loadings. (d-e) Bending tests of PLA-GO and PLA-rGO demonstrating membrane robustness.

3.3.2. Physicochemical characterization of PLA-graphene composite films

The cross-sectional morphology of PLA-blank, PLA-GO and PLA-rGO was investigated via FE-SEM to quantify the membrane thickness as well as to elucidate the microstructure of the membranes. From Figure 3-4a-c, the respective thickness of PLA-blank, PLA-GO and PLA-rGO is estimated to be $\sim 107.9 \pm 1.3$, $\sim 111.6 \pm 0.8$ and $\sim 109.2 \pm 1.1$ μm . The thickness of the residual PVP binder in PLA-blank after heat press treatment is also estimated to be $\sim 8.0 \pm 0.4$ μm (Figure 3-4d). In addition, the thickness of the GO and rGO film in PLA-GO and PLA-rGO is approximated to be $\sim 4.2 \pm 0.2$ and $\sim 3.5 \pm 0.1$ μm respectively (Figure 3-4e and f). The GO film is marginally thicker than the rGO film as the HI reduction induces a partial restacking of the exfoliated rGO sheets which tends to cause the rGO film to shrink in thickness [21, 106, 120, 126]. Considering the residual PVP binder and the inclusion of the GO and rGO films, the increased thickness exhibited by PLA-GO and PLA-rGO is reasonable. The sandwiched architecture of the PLA-graphene composite membranes, comprising of the PLA, the PVP and the GO/rGO layers, are clearly illustrated in Figure 3-4e and f. Both the GO and rGO films show a highly ordered lamellar microstructure as described in the literature [21, 27, 127]. This suggests that the microstructural integrity of the freestanding rGO film is well preserved during the reduction process and after the heat press treatment.

Figure 3-4. FE-SEM images showing cross-sectional morphology of PLA-blank, PLA-GO and PLA-rGO at (a-c) low magnifications and (d-f) high magnifications.

To further elucidate on the microstructure of the membranes, Raman and ATR FT-IR spectroscopy have been employed to examine the chemical states of the GO and rGO sheets used. As shown in Figure 3-5a, the intensity ratio of the D and G band (I_D/I_G) increases from 0.8 in the GO film to 1.1 in the rGO film. This increase in the I_D/I_G ratio implies an effective restoration of the sp^3 hybridized carbon in the GO film to sp^2 hybridized carbon in the rGO film [27, 128, 129]. An analysis of the FT-IR results corroborates this conclusion. Figure 3-5b reveals the presence of C–O (1034 cm^{-1}), C–O–C (1221 cm^{-1}) and C–OH (1398 cm^{-1}) stretching vibrations while the peak at 1620 cm^{-1} is assigned as the resonance peak of C–C stretching and absorbed hydroxyl groups in the GO film [130]. These peaks are absent from the rGO film spectrum which confirm the removal of these oxygen-containing functional groups during HI reduction. The observed peaks from the rGO film spectrum are assigned as the C–C (1543 cm^{-1}) stretching vibration arising from the graphitic domains and the C=O (1720 cm^{-1}) stretching vibration arising from functional groups which cannot be chemically reduced by HI. Therefore, these results indicate a successful reduction of the freestanding GO film into rGO film.

Next, the XRD patterns of the GO and rGO films are being studied to understand the changes in the interlayer spacing of the films. The XRD pattern of the GO film exhibits a sharp (002) peak at 10.38° , which corresponds to a 0.85 nm interlayer spacing between the GO sheets (Figure 3-5c). Upon HI reduction, this peak disappears and a new broad peak at 24.43° is formed. Such a 2θ shift indicates that the interlayer spacing between the rGO sheets has been reduced to 0.36 nm. The reduction in the interlayer spacing is driven by the removal of the oxygen-containing functional groups on the GO sheets, which induces partial restacking of the exfoliated rGO sheets [19, 21]. This validates that the rGO film has a more compacted lamellar microstructure as previously discussed.

Figure 3-5. Physicochemical characterization as elucidated by (a) Raman spectrum using a 514 nm laser; (b) ATR FT-IR spectrum; (c) XRD patterns of the freestanding GO and rGO film and (d) water contact angles of PLA-blank, PLA-GO, PLA-rGO and the freestanding GO and rGO films.

The hydrophilicity of the freestanding GO and rGO films, together with PLA-blank, PLA-GO and PLA-rGO, is also being quantified as water contact angle to understand the physicochemical changes brought by the removal of the oxygen-containing functional groups on the GO sheets. As depicted in Figure 3-5d, the water contact angle of the freestanding GO film dramatically increases from $35.1 \pm 1.7^\circ$ to $83.8 \pm 0.5^\circ$ after the HI reduction. This suggests that the removal of the oxygen-containing functional groups on the GO sheets reduces the wettability and increases the hydrophobicity of the freestanding rGO film [82, 117]. Despite the increase in the hydrophobicity, there appears to be no direct correlation between the water contact angle of PLA-rGO and the sandwiched rGO film. In fact, the water contact angle of the PLA-graphene composite membrane is stipulated only by the outer PLA film as verified by the comparable water contact angle of PLA-blank ($82.1 \pm 2.3^\circ$), PLA-GO ($82.6 \pm 0.9^\circ$) and PLA-rGO ($82.7 \pm 1.5^\circ$). Regardless, HI reduction has rendered the rGO core barrier increased hydrophobicity and greater resistance towards moisture penetration.

3.3.3. Water vapor and oxygen barrier properties of PLA-graphene composite membranes.

In order to evaluate the effectiveness of the sandwiched rGO film as a core barrier, the water vapor barrier property of the PLA-graphene composite membranes was first investigated at 38 °C and 90% RH conditions. Figure 3-6a summarises the WVP results. As shown, PLA-blank exhibits a moderate WVP value of $72.0 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{day}\cdot\text{atm}$. This value is in good agreement with the as-received PLA film (normalized to the same thickness) and those reported in the literature [108-110, 114]. With the inclusion of the freestanding GO and rGO films as core barriers, the PLA-graphene composite membranes demonstrated a more pronounced water vapor barrier property with the WVP values of PLA-GO and PLA-rGO

reduced to 29.6 and 8.9 g·mm/ m²·day·atm respectively. The decrease in the WVP of PLA-GO is attributed to the lamellar microstructure of the GO core barrier where the small interlayer spacing and the large lateral dimension of the GO sheets used (Figure 3-6b) result in a high total potential energy barrier and thus large mass transfer resistance across the GO film [30]. Diffusion of water molecules across the GO barrier will hence be slowed down. In the case of PLA-rGO, two other factors contribute towards the declining WVP value. The first factor is the more compacted lamellar microstructure of the rGO core barrier as a result of a more constricted interlayer spacing between the rGO sheets. The second factor is the increased hydrophobicity of the freestanding rGO film which renders the core barrier less susceptible towards wetting [21, 106]. Essentially, these factors combined together increase the resistance of the rGO core barrier towards hydration and swelling. This further elevates the potential energy barrier and greatly resists water molecules permeating across the barrier, leading to a heightened 87.6% reduction in the WVP of PLA-rGO when compared to PLA-blank.

Following, the oxygen barrier property of the films was investigated at 23 °C under both dry (0% RH) and humid (50% RH) conditions. The OP results are summarized in Figure 3-6c. At 0% RH, PLA-blank shows an OP value of 22.00 cc·mm/ m²·day·atm. A remarkable 97.2% and 99.0% reduction in the OP values are correspondingly observed when the freestanding GO and rGO films are sandwiched as core barriers. The more pronounced oxygen barrier property of PLA-GO and PLA-rGO are attributed to the same reasons which reduced the WVP values of the PLA-graphene composite membranes. From the viewpoint of food packaging applications, a membrane is considered a promising barrier when its OP is < 1.00 cc·mm/ m²·day·atm [109, 131]. As such, PLA-GO and PLA-rGO with OP values at 0.62 and 0.23 cc·mm/ m²·day·atm (insert of Figure 3-6c) respectively can be reckoned to

possess adequate oxygen barrier property to be considered as very promising membrane barriers for food packaging applications. To further validate this claim, the oxygen permeance of the PLA-graphene composite membranes is evaluated at 50% RH. As presented in the insert of Figure 3-6c, the OP values of PLA-GO and PLA-rGO at 50% RH are 0.56 and 0.13 cc·mm/ m²·day·atm respectively. These values are very similar to those evaluated at 0% RH, which suggest that relative humidity has minimal impact on the oxygen barrier property of the PLA-graphene composite membrane. Such results are unsurprising as both the GO and rGO core barriers are not susceptible to water vapor permeation and thus they are able to sustain the high oxygen barrier property even under a humid condition.

Figure 3-6. (a) Water vapor permeability of the PLA-as-received, PLA-blank and the PLA-graphene composite membranes. (b) AFM image of the GO sheets, their height and lateral dimension profiles. (c) Oxygen permeability of the respective membranes. ^aThe results of PLA-as-received were normalized to the same thickness as PLA-blank for comparison.

In an effort to provide a comprehensive explanation for the observed barrier property and to elucidate the mechanism involved, a simple gas permeability model for a regularly arranged platelets system as proposed by Nielsen is applied to the GO and rGO core barrier. In this model, it is first assumed that the GO and rGO sheets are impermeable to gas molecules. This assumption is, in fact, not unreasonable as molecular simulation has demonstrated that the electron density of the aromatic carbon rings on a defect-free single-crystalline graphene sheet can repel atoms and molecules [30]. Another simulation carried out using defective graphene sheets, including Stone-Wales (SW) defects and divacancy to decavacancy of the carbon atoms in the sheets, has also shown energies barriers which are too high for an He atom to pass through [29]. Thus, gas molecules penetrating the GO and rGO barrier are believed to diffuse preferentially around the graphene sheets and move in a highly tortuous pathway through the barrier [132, 133]. Next, the GO and rGO sheets are presumed to be highly aligned and oriented perpendicular to the direction of the gas diffusion as illustrated in Figure 3-4e and f. On the basis of these assumptions and that the GO sheet has a mean lateral dimension of $\sim 2\text{-}4\ \mu\text{m}$ (Figure 3-6b), the diffusion pathway through the rGO barrier can be up to 1450 times the thickness of the barrier as calculated by the equations shown in section 3.2.4 [30, 116, 134]. In essence, as predicted by Nielsen's model, the water and oxygen molecules are made to travel a highly extensive diffusion pathway through the core barrier (Figure 3-7) and this lengthened diffusion pathway, together with the more compacted lamellar microstructure and the increased hydrophobicity, has resulted in a decrease in the water vapor and oxygen permeance of PLA-rGO.

Figure 3-7. Mechanistic understanding of the high barrier properties of the PLA-graphene composite membranes using the Nielsen's gas transport model.

Another advantage of using the rGO core barrier is the simultaneously enhancement of both the water vapor and oxygen barrier properties of the membranes. Most studies choose to focus on OP and very few of these have reported good oxygen barrier under humid conditions [110, 116]. In this regard, the PLA-graphene composite membranes are compared to several other barrier membranes found in the literature [108-110, 132, 135-138]. Indeed, most of these membranes exhibit either good water vapor or good oxygen barrier properties. Only a handful of them show good barrier properties against both water vapor and oxygen gas. This is because it is difficult to achieve high water vapor and oxygen barrier properties without using two or more materials to complement one another [109, 116, 135]. The rGO film appears to have this competitive edge as illustrated by the low WVP and OP values of PLA-rGO (Figure 3-8). Moreover, it demonstrates barrier properties which are superior to a standard PET film (12 μm thick) and membranes made from biodegradable polymers. Whilst

this list is far from being exhaustive, the comparison provides meaningful evidence to highlight the potential of PLA-rGO to be used as a high barrier membrane. Most importantly, with the high processability of the PLA-graphene composite membranes and the readily scalable fabrication process, it is believed that PLA-rGO is commercially promising as a packaging film.

Figure 3-8. Water vapor and oxygen permeability of the graphene-based PLA membranes as compared to representative results from the literature. ^a[109]: tested at 23 °C, 20% and 50% RH for oxygen permeability and at 38 °C, 98% RH for water vapor permeability. ^b[110]: tested at 23 °C, 50% RH for oxygen permeability and at 23 °C, 50% RH for water vapor permeability. ^c[108]: tested at 23 °C, 0% and 75% RH for oxygen permeability and at 23 °C, 75% RH for water vapor permeability. ^d[135]: tested at 23 °C, 50% RH for oxygen permeability and at 23 °C, 50% RH for water vapor permeability. ^{e,f}[136, 137]: tested at 23 °C, 50% RH for oxygen permeability and at 23 °C, 50% RH for water vapor permeability. ^g[138]: tested at 23 °C, 50% RH for oxygen permeability and at 23 °C, 50% RH for water vapor permeability. ^h[132]: tested at 25 °C, 50% RH for oxygen permeability and at 25 °C, 100% RH for water vapor permeability.

3.4. Conclusions

Sandwich-architected PLA-graphene composite membranes comprising of GO and rGO core barriers were demonstrated with excellent barrier properties towards water vapor and oxygen gas. The water vapor permeability significantly declined by 87.6% while a reduction in oxygen permeability by two orders of magnitude was observed with rGO as the core barrier. The low oxygen permeability was also found to be sustainable under both dry and humid conditions. These results are attributed to the highly compacted lamellar microstructure and the increased hydrophobicity of the sandwiched rGO film. Moreover, the large rGO lateral dimension and the small interlayer spacing between the rGO sheets have created an extensive and tortuous diffusion pathway which is up to 1450 times the thickness of the rGO barrier, thereby further impeding diffusivity and enhancing the barrier properties. The processability of the sandwiched architecture was also illustrated through the fabrication of large-area PLA-graphene composite membranes, which can be tailored into various shapes. In general, the sandwich-architected PLA-graphene composite membranes, with their low oxygen and water vapor permeability, have limited applications as high diffusive and selective membranes for water purification. Rather, they demonstrate the necessary processability and high barrier properties for applications as packaging for oxygen and moisture sensitive items such as food.

Graphene oxide as effective selective barriers on a hollow fiber membrane for water treatment process²

CHAPTER

4

4.1. Introduction

As demonstrated in Chapter 3, both freestanding GO and rGO films, with several micrometers in thickness, exhibit slow diffusivity towards oxygen and water vapor molecules. This renders them with limited applications as selective membranes for water purification. In this chapter, it is hypothesized that the surface pore size and its distribution profile can be effectively engineered by leveraging on the 2-D structure of the GO sheets. However, in contrary to Chapter 3, this is achieved by significantly reducing the thickness of the GO film on the membrane surface in an attempt to exemplify the exceptional water transport properties of the GO sheets. The objective is to demonstrate the thin GO deposited surface as an effective barrier of the substrate membrane to enable fast water diffusion and molecular sieving capabilities.

A hollow fiber membrane is employed for this study. As compared to a flat sheet membrane, a hollow fiber membrane holds several advantages which include a higher energy efficiency in achieving complete mixing in modules, a larger membrane surface area in terms of module unit volume [139] and a self-supporting structure which does not require the use of permeate and feed spacers [140]. Polyamide-imide (PAI) is used to fabricate the hollow fiber substrate. This polymer is selected to capitalize on its reactive polyimide functional groups, which can chemically cross-link with polyethyleneimine (PEI), to achieve a positively

²(This chapter is reproduced with permission from K. Goh, L. Setiawan, L. Wei, R. Si, A.G. Fane, R. Wang, Y. Chen, Graphene oxide as effective selective barriers on a hollow fiber membrane for water treatment process, J. Membr. Sci., 474 (2015) 244-253. Copyright 2015. Elsevier)

charged membrane surface. The positive membrane surface can then act as an anchor for the negative GO sheets to deposit electrostatically using an instant dip-coating method. A dip-coating method is chosen to provide both convenience and easy processability suitable for a hollow fiber membrane as opposed to other adopted methods such as surface covalent functionalization [72] and LBL method [51, 78].

Generally, the water permeability decreases while the salt rejection increases with longer PEI cross-linking time given a smaller pore size and greater positive charges on the membrane surface [60, 141]. The effect of GO as a selective barrier is therefore exemplified by careful tailoring the duration of the PEI cross-linking post-treatment. The GO deposited PEI_PA1 hollow fiber membranes are then evaluated in the NF process and together with the detailed physicochemical characterization, a mechanistic understanding of the effect of GO deposition on the NF performance is elucidated.

4.2. Experimental

4.2.1. Materials

Graphite powders (Bay Carbon, Michigan) were used to synthesize GO. Potassium peroxodisulfate ($K_2S_2O_8$, $\geq 99.0\%$, Sigma-Aldrich), phosphorous pentoxide (P_2O_5 , $\geq 98.0\%$, Sigma-Aldrich), potassium permanganate ($KMnO_4$, $\geq 99.0\%$, Sigma-Aldrich), sodium nitrate ($NaNO_3$, $\geq 99.0\%$, Alfa Aesar), hydrogen peroxide solution (H_2O_2 , 30 wt% in H_2O , Sigma-Aldrich) and concentrated sulfuric acid (H_2SO_4 , 98%, Sigma-Aldrich) were employed as oxidizers at different stages of this synthesis. Torlon® 4000T (copolymer of amide and imide) (PAI, Solvay Advanced Polymers, Alpharetta GA) was the polymer used to fabricate the hollow fiber membrane substrate where N-methyl-2-pyrrolidone (NMP, $> 99.5\%$, Merck)

and lithium chloride (LiCl, anhydrous, Merck) were utilized as the solvent and additive/ pore former for the dope solution. Polyethyleneimine (PEI, branched, M_w : 50-100 kDa, Polysciences) was chosen as a cross-linker to perform chemical post-treatment on the hollow fiber membrane surface. Dextrans (M_w : 6-500 kDa, Sigma-Aldrich) were used to characterize the molecular weight cut-off (MWCO) of the hollow fiber membrane substrate. Sucrose (M_w : 342.3 gmol^{-1} , Ultrapure, MB Grade, USB), raffinose (pentahydrate, M_w : 594.52 gmol^{-1} , Merck), dextran (M_w : 1 kDa, Varian) and polyethylene glycol (PEG, M_w : 2 kDa, Sigma-Aldrich) were prepared as aqueous solutions to establish the pore size distributions of the modified hollow fiber membranes. Potassium chloride (KCl, anhydrous, Merck) was used to prepare the electrolyte solution, while hydrochloric acid (HCl, 37%, Merck) and sodium hydroxide (NaOH, Merck) were dissolved as diluted solutions to adjust the pH of the electrolyte solution for the zeta-potential characterization. Magnesium chloride (MgCl_2 , hexahydrate, Merck), calcium chloride (CaCl_2 , Merck) and sodium chloride (NaCl, Merck) were used to prepare salt solutions for evaluation of filtration performances. Purified water from a Milli-Q system (18 $\text{M}\Omega\text{cm}$) was employed as a solvent for all aqueous solutions preparation. All the above-mentioned reagents were used as received.

4.2.2. Preparation of GO

GO sheets were synthesized via a modified Hummers and Offeman's method [24]. 2.0 g of graphite powders were added into 14.4 mL H_2SO_4 (98%) before 3.0 g of $\text{K}_2\text{S}_2\text{O}_8$ and 3.0 g of P_2O_5 powders were added into the mixture consecutively. The mixture was allowed to react at 80 °C for 4 h. The product was washed using a filtration method and obtained after overnight drying in the oven at 60 °C. Subsequently, 2.0 g of this dried product was added into 46 mL of H_2SO_4 (98%). The beaker containing the mixture was immersed into an ice-

bath before 1.0 g of NaNO_3 powder was added. Next, 6.0 g of KMnO_4 was slowly added and the mixture was allowed to stir for 5 min in the ice-bath. The ice-bath was then removed and the mixture was allowed to react at 35 °C for 2 h. Upon completion of reaction, 92 mL of deionized (DI) H_2O was added slowly into the mixture and the mixture was allowed to stir for 15 min. Another 80 mL of DI H_2O and 10 mL of H_2O_2 aqueous solution was then added consecutively. The mixture was stirred for another 15 min before centrifugation at 4000 rpm for 10 min. The sediments were re-dispersed and stirred in 300 mL of 1M HCl solution for overnight to remove any remaining manganese impurities, after which they were washed via centrifugation till the supernatant achieved a pH value of ~ 5.0 . The GO solution obtained was concentrated to a concentration of 5.0 mg/mL and stored for further use.

To prepare the GO solution used for dip coating of the hollow fiber membranes, 2 mL of the stock solution was dispersed in 98 mL of DI H_2O to yield a diluted GO solution of 0.1 mg/mL. The diluted GO solution was bath-sonicated (Elamsonic S60H at 37 kHz) and subsequently tip-sonicated at 80% amplitude (Sonics, VCX-130) in an ice-bath for 30 min respectively. This GO solution was then freshly diluted with 500 mL DI H_2O to a concentration of 0.0167 mg/mL before using it for the dip coating process of the hollow fiber membranes.

4.2.3. Fabrication of PAI ultrafiltration hollow fiber substrate and GO deposited PAI_PEI hollow fiber membranes

The PAI ultrafiltration (UF) hollow fiber substrate membrane was fabricated via a dry-jet wet spinning technique. The required polymer dope solution was prepared by adding 70 g of PAI, 19 g of LiCl and 411 g of NMP solvent into a jacket flask. The contents were mechanically stirred at 70 °C for 3 days until a homogeneous dope solution was obtained.

This dope solution was degassed under vacuum for overnight prior to spinning. Details of the spinning procedure were described in the literature [141-143]. Table 4-1 summarizes the spinning conditions and parameters.

Table 4-1. Spinning conditions and parameters for the PAI UF substrate.

Parameters	Value
Dope composition (PAI/LiCl/NMP) (wt%)	14/3.8/82.2
Dope flow rate (g/min)	4.2
Bore fluid (NMP/H ₂ O) (vol.%)	50/50
Bore fluid flow rate (mL/min)	4.0
Air gap (cm)	1.0
Take up speed	Free fall
External coagulant	Tap water
Spinning temperature (°C)	22.0
Spinneret diameter (mm)	1.50
ID of bore fluid needle (mm)	0.70

Chemical cross-linking post-treatment of the PAI UF hollow fiber membranes were performed by sealing up their ends and exposing the outer surfaces of the membranes to a 1 wt% PEI aqueous solution at 70 °C for a duration ranging from 15 to 120 min. The treated membranes were thoroughly washed twice with DI H₂O before storing for characterization and the subsequent GO deposition step.

Negatively charged GO sheets were electrostatically deposited onto the positively charged outer surfaces of the treated hollow fiber membranes by a dip-coating method. The hollow fiber membranes were first straightened and immersed into the diluted GO solution before removing them instantly to complete the coating process. These steps were then repeated for the other PAI UF substrate cross-linked at different durations. Figure 4-1 illustrates the chemical modification processes involved in the fabrication of the GO

deposited PAI-PEI hollow fiber membranes. The PEI cross-linked hollow fiber membrane is designated as PAI-PEI(x) where x (min) is the subjected cross-linking time. Upon GO deposition, it is re-designated as GO-PAI-PEI(x). All the modified membranes were stored for characterization and evaluation of separation properties.

Figure 4-1. Schematic diagrams illustrating (a) the nucleophilic substitution reaction during chemical cross-linking ($x = 15, 30, 60, 90, 120$); (b) the negatively charged GO deposition on the positively charged PEI via instant dip-coating to form the NF-like selective layer.

4.2.4. Evaluation of the separation performances of the membranes

To evaluate the separation properties of the PAI UF hollow fiber substrate and its modified membranes, four pieces of each respective hollow fibers were potted into a tube ($3/8'' \times 1/2''$) to yield a lab-scale module with an effective length of 20 cm. The pure water

permeability coefficient (PWP), i.e. A value, of each module was determined by first compacting the membranes at a hydraulic pressure of 1 bar and a cross-flow rate of 600 ml/min (equivalent to 14 cm/s and a Reynolds number: ~ 870) for 1 h using DI H₂O on the shell side. The volume of the permeate collected was then measured and the PWP of the membrane was calculated using:

$$\text{PWP} = \frac{V}{tAr\Delta P} \quad (1)$$

where V is the volume of the permeate collected, t is the permeation time, Ar is the outer surface area of the hollow fiber membrane and ΔP is the hydraulic pressure applied to the membrane. The percentage salt rejections of the PAI-PEI hollow fiber membranes with and without GO deposition were evaluated using 500 ppm MgCl₂, CaCl₂ and NaCl aqueous solutions at a cross-flow rate of 600 ml/min and hydraulic pressure of 1 bar applied on the shell side of the module. The conductivities of the feed and permeate solutions were measured by a conductivity meter (Mettler Toledo) and the percentage rejection of the membrane was calculated using:

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_p and C_f were the conductivity of the permeate and feed solution respectively. By utilizing the A value and the percentage salt rejection, the salt permeability coefficient, i.e. B value, of the corresponding membrane was calculated using:

$$B = A \times \left(\frac{1}{R} - 1\right) \times (\Delta P - \Delta \pi) \quad (3)$$

where A is the PWP value, R is the rejection of the membrane and ΔP and $\Delta\pi$ are the hydraulic pressure and the osmotic pressure difference across the membrane respectively. All reported data in this study were average values obtained from sampling at least 3 modules of each membrane.

4.2.5. Physicochemical characterization

The lateral dimensions of the GO sheets and their distribution profile were examined by atomic force microscopy (AFM) using a MFP3D microscope (Asylum Research, Santa Barbara, CA) and a cantilever (Arrow NC, Nanoworld) in the AC mode. 5 μL of the diluted GO solution was dropped on a sliced silica wafer (1 cm $\times$ 1 cm). The silica wafer was first bath-sonicated in piranha solution (H_2SO_4 and H_2O_2) at 100 $^\circ\text{C}$ for 30 min prior to the analysis. The scan rate was set to 1 Hz at various scan sizes, while all data resolutions were set to 512 pixels $\times$ 512 lines. A first-order flattening was applied to the AFM amplitude profile to eliminate the Z offset between scan lines. The lateral dimension distribution profile was then determined using Image J software (National Institutes of Health, U.S.) by analyzing at least 200 GO sheets on a 5 μm $\times$ 5 μm area.

The cross-sectional and outer surface morphologies of the PAI UF hollow fiber substrate and its modified membranes were elucidated via field emission scanning electron microscopy (FE-SEM) using JEOL FE-SEM (JSM-6701F) at 5 kV. The hollow fiber membranes were first cryogenically fractured under liquid N_2 to expose their cross-sections. The samples were then freeze-dried overnight and sputtered with a thin layer of platinum using JEOL JFC-1600 auto fine coater prior to the analysis. The tensile strength examination of the PAI UF substrate and its modified membranes were conducted using a 0.5 kN Universal Testing Machine (Zwick) with an elongation velocity of 50 mm/min. The

experiments were performed under room temperature. Raman spectroscopy was utilized to detect the presence of GO sheets on the surface of the GO deposited PAI_PEI hollow fiber membranes using a Raman spectrometer (Renishaw) equipped with a 514 nm laser. The analysis was performed using a 0.1% power of the nominal laser intensity and an integration time of 15 s. The hydrophilicity of the PAI_PEI hollow fiber membrane with and without GO deposition was measured as a dynamic water contact angle using a Tensiometer (DCAT11, Dataphysics, Germany). Each measurement was made to run three advancing and receding cycles. The advancing value from the second cycle was then taken as the water contact angle of the sampled membrane. A Fourier transformed-infrared (FT-IR) spectroscopy was carried out to characterize the surface functional groups of GO sheets, the PAI UF substrate and its modified membranes using a FT-IR spectrometer (Shimadzu IR Prestige-21) via a ZnSe crystal attenuated total reflection (ATR) method. A total of 60 scans at a resolution of 4 cm^{-1} were performed over the wavenumber range of 400 to 4000 cm^{-1} for each samples. Surface charges (zeta-potential) of the PAI_PEI hollow fiber membranes with and without GO deposition were determined using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). A 500 mL of 1 mM KCl electrolyte solution was made to circulate over the membrane surface in an adjustable gap cell. The streaming potential generated was used to determine the zeta-potential by applying the Helmholtz-Smolchowski equation [144]. To study the stability of the GO deposited PAI_PEI hollow fiber membranes, the zeta-potentials of the membranes were measured over a pH range of 4 to 11 by adjusting the electrolyte using either 0.1 M HCl or 0.1 M NaOH aqueous solution.

The MWCO of the PAI UF hollow fiber substrate was assessed to give information of the pore size distribution of the membrane. The experiment was performed using a 2000 ppm dextran aqueous solution which comprised of dextrans of various molecular weights ranging

from 6 to 500 kDa. The solutions were made to flow on the shell side of the hollow fiber modules at a pressure of 1 bar for 30 min. The permeate from each module was then collected for analysis using gel permeation chromatography (GPC, Polymer Laboratories-GPC 50 plus) equipped with a double PL aquagel-OH Mixed-M 8 μ m columns. The MWCO of the substrate corresponds to the molecular weight of the dextran which exhibit a rejection of 90%. Similarly, the pore size distributions of the modified hollow fiber membranes were established using four different aqueous solutions (200 ppm) of sucrose, raffinose, dextran (1 kDa) and PEG (2 kDa). The permeates and feeds were collected and analyzed using a Total Organic Carbon analyzer (TOC_VCSH, Shimadzu). The rejection characteristics of these solutes through the respective membranes were obtained and used for calculations of the mean pore diameters and pore size distributions of these membranes by using a Levenberg-Marquardt equation and a two-parameter log-normal distribution function as respectively shown below [145, 146]:

$$\left(\sum_{i=1}^N \{R(a_i)|_{\text{Exp.}} - R(a_i)|_{\text{Cal.}}\}^2 \right) |_{\text{MIN}} \rightarrow (D^*, \sigma) \quad (4)$$

$$f(d) = \frac{1}{\ln(\sigma)d\sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\ln(d/D^*)}{\ln(\sigma)} \right)^2 \right] \quad (5)$$

where D^* and σ are the geometric mean pore diameter and its standard deviation of the membrane respectively, $R(a_i)|_{\text{Exp.}}$ is the experimental retention of the respective solute and $R(a_i)|_{\text{Cal.}}$ is the calculated retention coefficient of a solute with a diameter a . The detailed calculation of $R(a_i)|_{\text{Cal.}}$ is described elsewhere in the literature [145, 146].

4.2.6. Quartz crystal microbalance with dissipation monitoring

The quartz crystal microbalance with dissipation (QCM-D) technique was utilized to understand the surface adsorption of the GO sheets onto the PEI polymer using a Q-sense E4 system (Q-sense, Sweden) equipped with a flow module. Several harmonics ($z = 3, 5, 7, 9, 11$ and 13) were measured at a temperature of $25\text{ }^{\circ}\text{C}$ but only the frequency and dissipation shifts recorded at the 7th overtone were presented. 1 wt% PEI solution was circulated under a constant flow of $50\text{ }\mu\text{L}/\text{min}$ over a quartz sensor with gold electrode before DI H_2O was introduced at the same flow rate to wash away loose binding PEI polymer. After the frequency and dissipation shifts were stabilized, a GO solution with the same concentration as that used for dip-coating was circulated at the same flow rate into the module. The obtained data were analyzed using Q-Tools software (Q-sense, Sweden) to provide an estimated thickness of the PEI polymer and the mass of the GO sheets adsorbed onto the surface. The Sauerbrey equation [147], which was applied to estimate the amount of GO mass adsorbed, was as shown:

$$\Delta m = \frac{C \times \Delta f}{n} \quad (6)$$

where $C = -17.7\text{ ng}/\text{cm}^2\text{Hz}$, Δf (Hz) is the frequency shift at the 7th overtone and n is the overtone number at 7. The thickness of the PEI polymer adsorbed onto the quartz sensor was estimated using the Voight/Kelvin model [148]. The modelling was employed in order to give a more accurate thickness estimation. These processed data were presented as average values based on 3 repeated experiments. Similar study using the QCM-D technique can be found elsewhere in the literature [149].

4.3. Results and discussion

4.3.1. Characteristics of the PAI hollow fiber substrate membrane

Figure 4-2 shows the FE-SEM images of the cross-sectional morphology of the PAI UF substrate while the intrinsic properties of the substrate are summarized in Table 4-2. Similar to the previous study and those described in the literature, the PAI substrate developed finger-like structures in the outer and inner surfaces during the phase inversion process without any formation of large macrovoids [141, 143]. The substrate also comprises of a dense thin skin layer on the outer surface and a sponge-like middle layer as depicted in Figure 4-2b. The thickness of the sponge-like middle layer is estimated to be only $15 \pm 3 \mu\text{m}$. Coupled with a large lumen diameter and thin fiber wall thickness as listed in Table 4-2, the substrate possesses a high PWP, A value, of $161.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The dense skin layer is also validated by a low outer skin MWCO of 9.3 kDa. In addition, the large outer diameter of the substrate increases the effective membrane surface area for GO sheets to deposit at the later stage of the membrane fabrication.

Table 4-2. Intrinsic properties of PAI UF hollow fiber substrate.

Property	Value ^a
Outer skin MWCO (kDa)	9.3 ± 1.9
PWP shell side ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	161.3 ± 0.6
OD (μm)	1370 ± 4.0
ID (μm)	1047 ± 5.2
Fiber wall thickness (μm)	162 ± 2.8

^a Average value of at least two replicates.

Figure 4-2. FE-SEM images of the cross-sectional morphology of the PAI UF substrate at (a) 65x and (b) 300x magnification.

4.3.2. Characteristics of the modified PAI hollow fiber membranes

The ATR FT-IR spectra, as presented in Figure 4-3, are used to understand the chemical reaction on the PAI UF hollow fiber membranes. Careful analysis of Figure 4-3b shows that the characteristic PAI imide symmetric and asymmetric C=O stretching peaks which appears at 1778 and 1718 cm^{-1} are replaced by the amide C=O and C–N peaks at 1651 and 1531 cm^{-1} respectively [141, 143, 150]. This suggests a positive PEI cross-linking reaction on the PAI membrane surface as illustrated in Figure 4-1a. However, the infrared peaks of GO in both Figure 4-3a and b appear in the same region as the peaks of PAI and PEI polymers. Thus, characteristics peaks of GO are indistinguishable from the GO_PAPEI(90) spectrum. In addition, the low loading of GO increases the difficulty of observing the infrared peaks with sufficient intensities. As such, the FE-SEM was employed to detect the presence of GO sheets on the membrane surface.

Figure 4-3. ATR FT-IR spectra of the PAI UF hollow fiber substrate membrane, its respective modified membranes and GO sheets from (a) 2500 to 4000 cm^{-1} and (b) 2500 to 650 cm^{-1} wavenumber.

Figure 4-4. FE-SEM images showing cross-sectional morphologies of (a) PAI UF substrate; (b) PAI_PEI(90); (c) GO_PAI_PEI(90); and outer surface morphologies of (d) PAI UF substrate; (e) PAI_PEI(90) and (f) GO_PAI_PEI(90).

From Figure 4-4a, the cross-sectional morphology of the PAI UF substrate shows a thin dense skin and a sponge-like layer above the finger-like structure. The skin becomes denser while the sponge-like layer becomes less noticeable after 90 min of PEI cross-linking as shown in Figure 4-4b. Upon GO deposition, Figure 4-4c clearly reveals the GO sheets on the membrane surfaces with some of them collapsing onto the cross-section during fracturing of the hollow fiber membrane. Figure 4-4d-f contrast the outer surface morphologies of the membrane at different stages of modification. A rougher outer surface is observed after PEI cross-linking while GO sheets are seen wrinkling on the membrane surface after GO deposition. All these observations suggest strong evidence of successful GO deposition.

Figure 4-5. (a) Pore size distribution of the PAI UF hollow fiber substrate membrane; (b) AFM image and height profile; (c) Lateral dimension distribution profile of the GO sheets after bath and tip-sonication for 30 min each; (d) Raman spectra of the PAI UF substrate, PAI_PEI(90) and GO_PAPEI(90) membranes using 514 nm laser excitation.

In fact, the negatively charged GO sheets are expected to electrostatically deposit solely on the positive outer surface of the membrane given that the most common lateral dimension of the GO sheets at $\sim 0.2 \mu\text{m}^2$ far exceeds the mean pore diameter of the substrate at $\sim 5 \text{ nm}$ (Figure 4-5a and b). The existence of GO sheets on the surface can be further supported by the presence of D and G bands at 1340 and 1590 cm^{-1} respectively as observed from the Raman spectrum in Figure 4-5c. These bands are characteristic of graphitic carbon materials since the D and G bands are related to the disorder band caused by the graphitic edge and the in-phase vibration of the graphite lattice respectively [151].

The dynamic water contact angle is used as a measure of the hydrophilicity of the membrane outer surface. As tabulated in Table 4-3, the dynamic water contact angle decreases from 77.6° to 66.7° after the 90 min PEI cross-linked hollow fiber membrane is deposited with GO sheets. Similar decrease in the water contact angle is also observed for PAI_PEI(30) and GO_PAPEI(30). This suggests that the hydrophilicity of the membrane is enhanced by the oxygen containing functional groups of the GO sheets deposited at the surface.

Table 4-3. Dynamic water contact angles (2nd cycle) of the modified hollow fiber membranes.

Membrane	Dynamic water contact angle ($^\circ$)
PAI_PEI(30)	73.7 ± 2.1
GO_PAPEI(30)	64.8 ± 2.1
PAI_PEI(90)	77.6 ± 2.0
GO_PAPEI(90)	66.7 ± 3.1

The stability of the deposited GO sheets on the membrane surface is a key issue for any practical applications of such GO deposited PAI_PEI hollow fiber membranes. As such, several tests have been conducted to evaluate their stability. The GO deposited PAI_PEI hollow fiber membranes were first subjected to a 600 mL/min cross-flow rate (equivalent to a velocity: 14 cm/s and a Reynolds number: ~ 870) for at least 3 h in a typical performance evaluation. These membranes were then soaked in deionized water for close to 2 months before their performances were re-evaluated. Both evaluations exhibit similar performances. In addition, a backwashing assessment was conducted. As shown in Figure 4-6a, the water flux of GO_PAI_PEI(90) remains constant for three cycles after two rounds of backwashing for a period of 5 min at a pressure of 1 bar. A zeta-potential investigation is also conducted to study the surface charges of the modified hollow fiber membranes. It can be seen from Figure 4-6b that the negatively charged GO sheets suppress the positive charges on the membrane surface of PAI_PEI(90) to a certain degree over a pH range of 4 to 9. Consequently, the isoelectric point is found to decrease from pH 9.9 to 8.8. All these observations suggest that strong electrostatic attractions between the GO sheets and the membrane surface can be sustained between pH 4 to 9. Thus, a stable GO deposition can be achieved via the dip-coating method. Moreover, the decrease in surface charges after GO deposition seems to imply that the Donnan exclusion effect is not the only mechanism responsible for salt rejection. As such, the GO sheets may be deemed to act as hydrophilic selective barriers which reject salt by enhancing the size effect of the NF-like selective layer.

Figure 4-6. (a) Three cycles of normalized water flux of a two round backwashing evaluation of GO_PA_I_PEI(90) membrane. The blue regions represent the backwashing periods at a pressure of 1 bar; (b) Zeta-potential of the outer surfaces of PAI_PEI(90) and GO_PA_I_PEI(90) membranes across various pH using 1 mM KCl electrolyte solution.

4.3.3. Characteristics of the GO deposition layer

To further understand the GO dip-coating process, the quartz crystal microbalance with dissipation monitoring technique was used to study how the GO sheets adsorb onto the PEI polymer. An estimation of the amount of GO mass was performed using the Sauerbrey equation [147] since the GO sheets form a thin rigid film over the PEI surface with a low dissipation shift as illustrated in stage II of Figure 4-7. On the other hand, stage I of Figure 4-7 shows that the PEI polymer forms a soft (viscoelastic) overlayer with a high dissipation shift. Thus, a Voight/Kelvin model [148] was applied instead to estimate the thickness of the PEI polymer adsorbed onto the quartz sensor as the soft PEI overlayer can dampen the sensor's oscillation resulting in a deviation from the Sauerbrey equation. The mass of the adsorbed GO sheets on a 10 ± 1 nm thick PEI overlayer was found to be 92 ± 5 ng/cm². This value is smaller than the theoretical mass of 101 ng/cm² for a monolayer GO [149]. It can be deduced that gaps exist between the GO sheets. This deduction is reasonable considering a more realistic setting where GO sheets stack over one another during adsorption and the

presence of hydration effect (due to hydrogen bonding between water and the oxygen containing functional groups on the GO sheets) which increases the mass of the adsorbed GO sheets. In addition, the surface zeta-potential of GO_PAI_PEI(90) (Figure 4-6b) which remains positively charged after negatively charged GO sheets are deposited provides further evidence to support the presence of gaps between the GO sheets.

Figure 4-7. QCM-D data showing the changes in the frequency shift, Δf (blue) and the dissipation shift, ΔD (red) during the sequential build up of polyethyleneimine and GO on a gold substrate. Polyethyleneimine and GO solutions were added at stage I and II respectively while (*) represents a liquid exchange to water to remove excess polyethylenimine which was weakly bonded to the gold substrate.

4.3.4. Separation properties of the modified hollow fiber membranes

The effect of GO deposition is obtained by analyzing the separation properties of the hollow fiber membranes. It can be seen from Figure 4-8a that the PWP, A value, of the GO deposited membranes are all lower than their corresponding membranes without GO. This implies that the GO sheets deposited on the surface act as an effective barrier which restricts the flow of water. This decrease in PWP is exceptionally pronounced ($\sim 11 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) at short cross-linking times such as 15 and 30 min. However, the decrease is relatively

insignificant ($\sim 1.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) at longer cross-linking times such as 90 and 120 min. The MgCl_2 salt rejections and permeability coefficients, B values, of these membranes, as shown in Figure 4-8b and c, are also in good correlation to the PWP results. With GO deposition, the additional barrier has resulted in an overall improvement in the rejections and thus a drop in the salt permeability coefficients. Similar to the trends observed for the PWP, the increase in rejection and decrease in salt permeability coefficient is more pronounced ($\sim 14\text{--}15\%$ and $\sim 7\text{--}11 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ respectively) at short cross-linking times but relatively insignificant ($\sim 2.5\%$ and $\sim 0.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ respectively) at a longer time of 120 min.

Figure 4-8. Results showing (a) pure water permeability coefficient; (b) MgCl_2 salt % rejection and (c) salt permeability coefficient of the respective hollow fiber membranes (with and without GO) at different cross-linking times. The inserts highlight similar results between PAI_PEI(90) and GO_PAI_PEI(30) membranes; (d) Normalized resistance of the PEI cross-linked selective layer of the modified PAI hollow fiber membrane and the relative resistance of the GO sheets as compared to the resistance of the PEI cross-linked selective layer at different PEI cross-linking times.

To explain for the trends observed for MgCl_2 salt rejection and permeability coefficient, the size and charge effects of the modified membranes are examined. As previously reported by L. Setiawan *et al.*, no significant change in the zeta-potentials of the PEI modified PAI hollow fiber membranes was observed when cross-linking times increased from 30 to 75 min [150]. This implies that the increase in salt rejections at longer cross-linking time is mainly due to a size effect (pore tightening) rather than a charge effect. Similarly, in this study, an improvement of $\sim 10\%$ in the MgCl_2 salt rejection after GO deposition is observed despite a slight decrease in the positive surface charge of GO_PA1_PEI(90) (Figure 4-6b and 4-8b). This indicates that the Donnan exclusion (charge) effect is not the only operating mechanism present in the modified membranes. There is strong evidence to suggest for the presence of size effect after GO deposition. A comprehensive discussion of this size effect is being made in section 4.3.5.

To explain for the trend observed for PWP, the hydrodynamic resistances of the modified membranes are, however, being evaluated. At short cross-linking times such as 15 and 30 min, the resistance of the PEI cross-linked selective layer is merely ~ 0.2 times that of the selective layer that has been cross-linked for 120 min (Figure 4-8d). The effect brought on by the GO sheets thus appears substantial given that the resistances of the GO sheets are ~ 0.5 to 0.8 times that of the PEI cross-linked selective layer (Figure 4-8d). However, at longer cross-linking times, especially at 90 and 120 min, the denser PEI cross-linked selective layer exerts a much larger resistance and asserts itself as the predominant barrier instead. The effect of the GO sheets in this case is relatively and interestingly not as significant with a relative resistance less than 0.3 times that of the PEI cross-linked selective layer (Figure 4-8d). Previous studies have reported this similar phenomenon, and attributed it to the increased surface hydrophilicity [51] and unique water transport properties through the

stacked GO sheets [51, 78], which nullify the loss in water permeability due to the additional barrier.

Excessive cross-linking can result in undesirable deterioration of the PAI UF substrate [141]. As shown in Figure 4-9a, the strain at break significantly drops from 32 to 22% while the tensile strength remains relatively constant at approximately 8–9 MPa when cross-linking time increases from 30 to 90 min. The reason for this drop in strain at break is due to the increase in the PEI cross-linker to PAI polymer chain ratio which results in a significant decrease in the chain-relaxation ability of the PAI polymeric network [152]. To circumvent this problem, GO sheets can be used to substitute part of the PEI cross-linked selective layer. Taking a closer look at the data in Figure 4-8b and c (see inserts), it is observed that GO_PAPEI(30) has a comparable MgCl_2 salt rejection ($\sim 81\%$) as that of PAI_PAPEI(90). Similarly, the MgCl_2 salt permeability coefficients of GO_PAPEI(30) and GO_PAPEI(60) are also equivalent ($\sim 1.4 \text{ L m}^{-2} \text{ h}^{-1}$) to that of PAI_PAPEI(90). The same trends are also observed for both NaCl and CaCl_2 salts but at lower and higher rejections respectively as presented in Figure 4-9b. Monovalent salt like NaCl generally exhibits poor rejection by positively charged NF membranes as Na^+ ions has a small co-ion (i.e., ions of the same charge as the membrane surface) valence which will increase the concentration of the co-ion in the membrane [60]. However, for divalent salts such as MgCl_2 and CaCl_2 , the larger co-ion valence results in a greater Donnan exclusion effect and hence better rejections. The higher rejection for CaCl_2 as compared to MgCl_2 salt can be attributed to the larger Ca^{2+} surface charge density [140]. This suggests that it is possible to reduce PEI cross-linking time from 90 to 30 min with an instant GO deposition to achieve similar performing hollow fiber membranes without deteriorating the mechanical properties of the PAI UF substrate. Furthermore, an increase in the PWP by 86% (Figure 4-8a) are observed when the A values

of GO_PA1_PEI(30) and PA1_PEI(90) are contrasted. It is inferred that the GO sheets exert a smaller hydrodynamic resistance [19, 64] as compared to the additional 60 min of PEI cross-linked selective layer and thus allowing water to pass through easily.

Figure 4-9. (a) Mechanical properties of the PAI UF substrate and its respective modified hollow fiber membranes at different cross-linking times; (b) NaCl and CaCl₂ salts % rejection of PAI_PEI(30), GO_PA1_PEI(30), PAI_PEI(90) and GO_PA1_PEI(90) membranes.

4.3.5. Mechanism of the GO deposited PA1_PEI hollow fiber membranes

Based on the above experimental results, a mechanism to explain the separation behaviors of the GO deposited PA1_PEI hollow fiber membrane is proposed. As illustrated in Figure 4-10a-c, the surfaces of the PAI substrates are cross-linked to a greater extent as PEI cross-linking time increases resulting in smaller surface pores and a relatively narrower pore size distribution for PA1_PEI(90) as compared to that of PA1_PEI(30). This is evident from Figure 4-10e where the mean pore diameter decreases from 3.6 to 2.7 nm. Hence, besides the presence of Donnan exclusion effect due to increased positive surface charge, the size effect brought on by the smaller pore size is also enhanced by the denser PEI cross-linked selective layer of PA1_PEI(90). Without sufficient cross-linking, the selective layer of PA1_PEI(30) is

unable to achieve the same effectiveness to reject salt due to a larger surface pore sizes. This is because the hydrated diameters of Mg^{2+} and Ca^{2+} co-ions at 0.86 and 0.82 nm respectively [153] are much smaller than the mean pore diameter of PAI_PEI(30).

Figure 4-10. Conceptual illustrations showing (a) the PAI UF substrate; (b) smaller extent (30 min); (c) larger extent (90 min) PEI cross-linking and (d) a narrower pore size distribution after GO surface deposition on PAI_PEI(30); (e) Pore size distributions of (■) PAI_PEI(30); (▲) GO_PAPEI(30); (●) PAI_PEI(90) and (◆) GO_PAPEI(90) hollow fiber membranes.

After GO deposition, the GO sheets can increase the size effect of the modified membranes. As demonstrated in Figure 4-10d, the large GO sheets block some of the surface pores while exposing the others through the gaps between the GO sheets. The outcome is a reduced mean pore diameter and a significantly tapered pore size distribution of GO_PAPEI(30) and GO_PAPEI(90) as shown in Figure 4-10e. The mean pore diameters of GO_PAPEI(30) and GO_PAPEI(90) are reduced to 3.2 and 2.3 nm respectively. Salt flux through the GO barrier is thus restricted allowing increased salt retention by the positively charged PEI cross-linked selective layer via the Donnan exclusion effect. This also explains why both PAI_PEI(90) and GO_PAPEI(30) exhibit similar MgCl_2 salt

permeability coefficient and rejection. While the additional GO sheets improve the rejection efficiency of the membrane, the real value-adding feature found in this study is their small impact on the hydrodynamic resistance as can be observed from the A values (13.4 compared to $7.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) of GO_PAIEI(30) and PAIEI(90). This is attributed to the relatively larger pore diameter and the hydrophilicity of the GO sheets which facilitates water access into the exposed pores and nanochannels of the stacked GO sheets [64]. In addition, water molecules in the nanochannels are deemed to permeate ultrafast across the hydrophobic GO surface [21]. This probably mitigates the excessive loss in water permeability brought by the deposition of GO sheets, allowing them to exert a smaller hydrodynamic resistance as compared to an additional 60 min cross-linked PEI selective layer.

4.4. Conclusions

A novel NF-like GO surface deposited PAIEI hollow fiber membrane is successfully fabricated via an instant dip-coating method. The GO sheets are found to act as effective selective barriers which improve the membrane selectivity when thinly deposited. This is in contrary to the conclusions obtained in Chapter 3. As such, GO sheets have been used to substitute part of the PEI cross-linked selective layer which is equivalent to 60 min of cross-linking. This results in several advantages: shortening of membrane modification time from 90 to 30 min and better mechanical properties of the hollow fiber substrate by avoiding excessive cross-linking. More importantly, a better performance with up to 86% higher pure water permeability is observed when compared with merely PEI cross-linked hollow fiber membrane of similar selectivity. It is understood that the deposited GO sheets are able to reduce the surface pore diameter and narrow the pore size distribution of the hollow fiber

membrane. The GO sheets are also able to withstand a cross-flow rate of 600 mL/min and a backwashing pressure of 1 bar which suggest a stable electrostatic deposition. Overall, a simple membrane fabrication process has been proposed with the results demonstrating a high potential of using such GO deposited hollow fiber membranes for large scale water softening applications.

Fabrication of novel functionalized MWCNT immobilized hollow fiber membranes for enhanced performances in FO process³

CHAPTER

5

5.1. Introduction

CNTs are 1-D in structure and possess discretely different properties as compared to graphene-based materials. The studies in Chapter 3 and 4 have explicated the intrinsic barrier properties of the 2-D graphene-based materials where micrometers-thick freestanding GO and rGO films act as high barriers while nanometers-thick GO deposition act as a selective barrier on a hollow fiber membrane. In contrast, rather than serving as a barrier, CNTs have greater merits as water nanochannels given their exceptional water transport properties as highlighted in Chapter 2. Therefore, the use of MWCNTs as water nanochannels in the selective layer of a hollow fiber membrane is explored in this chapter.

In order to achieve this, functionalization of the MWCNTs is crucial in preventing aggregation and ensuring good manageability in an aqueous environment. This is a common problem encountered in many studies on CNTs applications. Among the various proposed solutions, covalent functionalization of the CNTs offers an easy solution to increase the surface hydrophilicity and improve their dispersibility by introducing hydroxyl and carboxyl groups on the walls of the CNTs using oxidizing agents [154-156] or ozone treatment [157, 158]. Additionally, surface groups can also be subsequently grafted to customize the CNTs with desired functionalities [155, 156]. In this study, oxidation of the MWCNTs with concentrated nitric acid is adopted as a mean of functionalization due to the simplicity of the

³(This chapter is reproduced with permission from K. Goh, L. Setiawan, L. Wei, W. Jiang, R. Wang, Y. Chen, *Fabrication of novel functionalized multi-walled carbon nanotube immobilized hollow fiber membranes for enhanced performance in forward osmosis process*, *J. Membr. Sci.*, 446 (2013) 244-254. Copyright 2013. Elsevier)

treatment method. Furthermore, commercially purchased MWCNTs is used given their availability and cost-effectiveness [90].

Similar to Chapter 4, PAI was used to fabricate the hollow fiber substrate membrane while PEI acted as the positively charged cross-linker for reasons already discussed. The functionalized MWCNTs, which exhibited negative charges, were solution-based processed prior to immobilization onto the PAI substrate membrane via a vacuum-assisted filtration method. The MWCNT immobilized PAI membrane surface was then chemically cross-linked with PEI to form a positively charged NF-like selective layer. Such a fabrication scheme leverages on the electrostatic interactions between the negatively charged MWCNTs and the positively charged PEI cross-linker. As a result, the MWCNTs are found to integrate seamlessly into the PEI cross-linked selective layer of the hollow fiber membrane. The separation performances of the MWCNT immobilized hollow fiber membranes are evaluated in the NF and FO processes to assess the role of the MWCNTs as water nanochannels. The detailed physicochemical characterization and the mechanistic understanding of the separation performance results are also revealed in this study.

5.2. Experimental

5.2.1. Materials

MWCNTs were obtained from CNano Technology Ltd (Beijing, China). Concentrated hydrochloric acid (HCl, 37.0%, CAS#7647-01-0) and nitric acid (HNO₃, 65.0%, CAS#7697-37-2) from Merck Chemicals, Singapore, were used to purify and functionalize the MWCNTs respectively. Absolute ethanol (C₂H₅OH, CAS#64-17-5, Merck) and sodium hydroxide pellets (NaOH, CAS#7310-73-2, Merck), prepared as aqueous solution, were used to wash the functionalized MWCNTs. Torlon® 4000T (copolymer of

amide and imide) (PAI), purchased from Solvay Advanced Polymers (Alpharetta, GA) was used to fabricate the porous hollow fiber substrate. N-Methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck) and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, Merck) were used as solvent and additive/pore former respectively in the membrane fabrication process. Purified water from a Milli-Q system (18 MΩcm) was one of the materials for the internal coagulant, and was also used as a solvent for preparation of all aqueous solutions. Dextrans of different molecular weights (from 600 to 500,000 Da, CAS#9004-54-0, Sigma Aldrich) were used to characterize the molecular weight cut-off (MWCO) of hollow fiber membranes. PEI ethylenediamine end-capped (molecular weight, M_w , ~600, Sigma Aldrich) was used to perform the chemical post-treatment of MWCNT immobilized hollow fiber membranes. Potassium chloride (KCl, CAS#7447-40-7, Merck) was prepared as electrolyte solutions. The pH of electrolyte solutions was adjusted using diluted solutions of hydrochloric acid and sodium hydroxide pellets. Magnesium chloride ($MgCl_2 \cdot 6H_2O$, CAS#7786-30-3, Merck) was prepared as salt solutions for filtration and FO performance tests. All the reagents mentioned above were used as received.

5.2.2. Preparation of MWCNTs

MWCNTs were first purified and functionalized prior to immobilization. The detailed procedure of the MWCNT purification was described elsewhere [159, 160]. To functionalize MWCNTs, 1.0 g of the purified MWCNTs was added to 200 mL of HNO_3 and refluxed at 150 °C for 8 h. The resulting dispersion was filtered, and the MWCNT residue was first rinsed with 500 mL of deionized water, followed by 1 L of 0.5 M NaOH solution and twice with 500 mL of deionized water until a pH of ~6.0 was obtained. The final rinse was completed with 200 mL of ethanol. This series of rinsing aid in the removal of excess acid on

the MWCNTs, oxidation debris [161, 162] and small carbonaceous materials produced during functionalization [163]. The functionalized MWCNTs obtained were left to dry at 60 °C for overnight.

To immobilize MWCNTs, 40 mg of functionalized MWCNTs were dispersed and subsequently shortened in 240 mL of deionized water by tip-sonication (Sonics, VCX-130) at 80% amplitude for 1 h in an ice-water bath. The dispersion was then ultra-centrifuged (HITACHI, Himac, CP80WX) at 14,500 rpm for 1 h in a swing bucket to remove various impurities and large CNT bundles. 200 mL (83.3%) of the supernatant solution was withdrawn and split into 4 equal portions of 50 mL. The MWCNT concentration in the supernatant was determined via ultraviolet–visible (UV-Vis) spectroscopy using a Cary Varian 5000 UV-Vis spectrometer in the range from 300 to 1300 nm. The UV-vis absorbance of well-dispersed MWCNT solutions was found to obey the Beer-Lambert's law, $A = \epsilon cl$, where A is the absorbance, ϵ is the extinction coefficient, c is the concentration of the MWCNT and l is the path length of the light [164]. As a result, the concentration of the MWCNTs supernatant solution (diluted 4 folds) was estimated to be 9.98 mg/L. This implies that approximately 10% of the dispersed MWCNTs were left in the supernatant after ultra-centrifugation. To each portions of this supernatant, 6350, 3150, 1550 and 750 mL of deionized water were added to dilute the MWCNT solutions in the ratio of 1:128, 1:64, 1:32 and 1:16 of MWCNT solution: deionized water. This gave MWCNT concentrations of 0.31, 0.62, 1.25 and 2.49 mg/L respectively. These solutions were then stored for the immobilization step.

5.2.3. Fabrications of PAI hollow fiber substrate and MWCNT immobilized PEI-PAI hollow fiber membranes

The dry-jet wet spinning technique, similar to that described in Chapter 4, was employed to fabricate the PAI hollow fiber substrate. 56 g of PAI and 14 g of LiCl were added into 330 g of NMP solvent to produce the dope solution for the spinning process. Table 5-1 summarizes the spinning conditions and parameters to obtain the PAI hollow fiber substrate used in this study.

Table 5-1. Spinning conditions and parameters for the PAI UF substrate.

Parameters	Value
Dope composition (PAI/LiCl/NMP) (wt%)	14/3.5/82.5
Dope flow rate (g/min)	5.0
Bore fluid (NMP/H ₂ O) (vol.%)	50/50
Bore fluid flow rate (mL/min)	5.0
Air gap (cm)	1.0
Take up speed	Free fall
External coagulant	Tap water
Spinning temperature (°C)	23.0
Spinneret diameter (mm)	1.50
ID of bore fluid needle (mm)	0.70

MWCNTs were immobilized onto the PAI hollow fiber substrate by a vacuum-assisted filtration method [165, 166]. The ends of each fiber were glued by epoxy into a 3 cm polypropylene tube (1/2" × 3/8"). The glued fibers were next immersed into the MWCNT solution of concentration 0.31 mg/L and a vacuum of 45 mbar was applied through the tube for 3.5 min. 0.5 min was needed for the vacuum to stabilize while 3.0 min was the duration for the MWCNT film to form on the outer surface of the substrate. The MWCNT

immobilized PAI fibers were then removed and cleaned in a beaker of 2 L deionized water, stirred at 1,200 rpm, for 20 s. This helps to remove loose binding MWCNTs on the membrane surface. The procedures were repeated using MWCNT solutions at 0.62, 1.25 and 2.49 mg/L concentrations. In total, four sets of MWCNT immobilized PAI fibers of different CNT loadings were synthesized and were designated as C1-C4 as listed in Table 5-2.

Table 5-2. Conditions used for MWCNT immobilization and formation of NF-like skin.

Membrane Code	Concentration of MWCNT solution (mg/L)	Duration of PEI post-treatment (min)
PAI	-	-
PP1		80
PP2	-	90
PP3	-	100
PP4	-	110
C1	0.31	-
C2	0.62	-
C3	1.25	-
C4	2.49	-
PP2-C1	0.31	90
PP2-C2	0.62	90
PP2-C3	1.25	90
PP2-C4	2.49	90

Chemical post-treatment was applied to the MWCNT immobilized PAI fibers by immersing the fibers into a 500 mL PEI solution of 1 wt% concentration at a temperature of 70 °C for 90 min. After treatment, the fibers were rinsed with deionized water three times to remove excess PEI solution on the membrane surface and subsequently stored for characterization. These MWCNT immobilized PEI-PAI fibers were designated as PP2-C1 to

PP2-C4 where PP2 represented a post-treatment duration of 90 min. The designations of all other different membranes being studied in this work are summarized in Table 5-2.

5.2.4. Evaluation of the separation performances of the membranes

Similar to that in Chapter 4, five pieces of the hollow fibers membranes were potted into a tube ($3/8'' \times 1/2''$) to yield a lab-scale FO module. The effective length of each fiber in the module was 20 cm. Pure water permeability (PWP), i.e. A value, and salt rejection of the respective membranes were tested in the RO mode in a pressurized cross-flow filtration unit. A constant pressure of 1.5 bar and compaction time of 1.5 h were applied to the shell side of the membranes to determine the PWP in deionized water. Similarly, the salt rejection tests were conducted using a 500 ppm MgCl_2 solution at a constant pressure of 1 bar. The percentage salt rejections were calculated based on the conductivities of the feed and permeate solutions measured by a conductivity meter (Mettler Toledo). The reported data in this study were average values obtained from sampling 2 to 3 modules of each type of membrane.

5.2.5. Physicochemical characterization

The length of the MWCNTs was examined by field emission-scanning electron microscopy (FE-SEM) using JEOL FE-SEM (JSM-6710F) at 5kV. Diluted solutions of MWCNT were spin-coated onto sliced silica wafer prior to the analysis. The length distribution profile was then determined using Image J software (National Institutes of Health, U.S.) by analyzing at least 200 MWCNTs. The detailed structural morphology of the MWCNT was observed by high resolution-transmission electron microscopy (HR-TEM) using a Tecna F20, 200kV, microscope from Philips. The MWCNTs were first dispersed in

ethanol by tip-sonication for 1 h before dropping 0.1 mL of the suspension onto a copper mesh coated with amorphous holey carbon film. The ethanol was allowed to evaporate before the TEM analysis. Raman spectroscopy was employed to study the as-received and functionalized MWCNTs. The analysis was carried out using a Renishaw Raman spectrometer with a 514 nm laser performing under a 10% power of the nominal laser intensity and an integration time of 10s.

The structures and morphologies of the substrate and modified hollow fiber membranes were observed by FE-SEM (JSM-6701F) at 5kV. The membrane samples were frozen by liquid nitrogen before fracturing to expose their cross-sections. These samples were then freeze-dried overnight and sputtered with a thin layer of platinum using JEOL JFC-1600 auto fine coater prior to their analyses. Surface functional groups of the substrate and modified hollow fiber membranes were analyzed by a Fourier transformed-infrared spectrometer (FT-IR, Shimadzu IR Prestige-21) using the attenuated total reflection (ATR) equipped with ZnSe crystal method. A total of 45 scans at a resolution of 4 cm^{-1} were performed in the range from 400 to 4000 cm^{-1} . Membrane surface zeta-potential was measured using streaming potential in the pH range from 4 to 11 by a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). 500 mL of 1.0 mM KCl solution was circulated through an adjustable gap cell containing the membrane samples. The streaming potential which arose due to the charged membrane surface was used to characterize the membrane zeta-potential by applying the Helmholtz-Smolchowski equation in the calculations [144].

Molecular weight cut-off (MWCO) of the PAI hollow fiber substrate was determined using a 2000 ppm dextran aqueous solution. The solution was circulated through the shell side of the modules and the permeate solution for each module was collected for analysis by a gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system

using a double PL aquagel-OH Mixed-M 8 μ m column. The molecular weight of dextran that gave 90% rejection was deemed as the MWCO of the substrate. Detailed procedures were described elsewhere [145, 167].

5.2.6. Evaluation of FO performances

Detailed procedures of the FO experiment [141] and the lab-scale FO unit used [59] in this study had been described elsewhere. Briefly, the same modules used in section 5.2.4 to obtain PWP and salt rejections were used for FO performance evaluations. The draw solution and feed water used was 0.5 M MgCl₂ solution and deionized water respectively. The experiments were conducted in two configurations namely active layer facing draw solution (AL-facing-DS, PRO mode) and that facing feed water (AL-facing-FW, FO mode). This was achieved by circulating the draw solution and feed water in the shell and lumen side of the module respectively for AL-facing-DS and vice versa. The volumetric water flux, J_v , and salt flux, J_s , were calculated via weight and conductivity changes of the feed water obtained through a computer logging system.

5.3. Results and discussion

5.3.1. Characteristics of MWCNTs

Figure 5-1a shows an image of the functionalized MWCNTs being able to disperse homogeneously in deionized water without the use of surfactants. A surfactant free membrane fabrication protocol is advantageous as it eliminates the subsequent need for surfactants removal or potential interference of the surfactants with the chemical post-treatment which may change the intrinsic separation behaviors of the membranes [168]. The

key factor to this homogenous dispersion is the introduction of carboxyl groups on the surface of the MWCNTs. This helps to increase the hydrophilicity of the MWCNTs as the carboxyl groups can deprotonate to give negatively charged carboxylate which electrostatically attract water molecules as shown in Figure 5-1b. As a result, the hydrated MWCNTs can hydrogen bond with water molecules achieving a good dispersion which can remain stable up to a few weeks. An estimated calculation based on data reported for SWCNTs [169] suggests an average of 7.8×10^{19} carboxyl groups being attached for per gram of MWCNTs which have been functionalized for 8 h. This enormous amount of carboxyl groups induces a high negative zeta-potential on the surface of the functionalized MWCNTs as illustrated in Figure 5-1c. Since the stability of the colloidal dispersion is largely determined by the electrostatic repulsion due to the surface charge [170], it is expected that the highly negative charged surface of the functionalized MWCNTs inhibits agglomeration and improves the stability of the dispersion.

Raman spectroscopy is used to determine the integrity of the MWCNTs by analyzing the D and G bands observed at Raman shifts of around 1350 and 1580 cm^{-1} respectively. The D band is related to the A_{1g} breathing mode of sp^3 hybridized defective carbon atoms while the G band is related to the E_{2g} tangential mode of sp^2 hybridized graphitic carbon atoms. As shown in Figure 5-1d, the largely similar profiles of the D and G bands of the as-received and functionalized MWCNTs suggest that the graphitic structure of the MWCNTs is preserved after functionalization [171]. The A_G/A_D ratios of the as-received and functionalized MWCNTs were calculated as 0.63 and 0.49 respectively. This decrease in the A_G/A_D ratio implies a higher concentration of functionalized amorphous carbon generated which act as surfactant to further improve the solubility of the MWCNTs [154].

Figure 5-1. (a) Photo image of MWCNTs homogeneously dispersed in DI water; (b) Reaction scheme of MWCNT functionalization and dispersion in water; (c) Zeta-potential profile of the MWCNTs dispersed in DI water; (d) Raman spectrum of functionalized and as-received MWCNTs.

The as-received MWCNTs have an average length of 10 μm and diameter of 11 nm. Upon tip-sonication, the functionalized MWCNTs were shortened with some of the tips of the MWCNTs opened. Most of the MWCNTs are shortened to the range of 215 to 280 nm as observed from Figure 5-2a and b while the average length is calculated to be 213 ± 113 nm. The overall reduced size of the MWCNTs aids in dispersing the MWCNTs into a colloidal solution [172]. Besides, a smaller MWCNT size is crucial in ensuring a closer packing of the MWCNTs when they are immobilized in a network film on the membrane surface. The diameters of these MWCNTs, as measured using Figure 5-2a, c and d, were calculated to be similar to that of the as-received MWCNTs. The arrows denoted in the HR-TEM image in Figure 5-2c indicate the opened tips of the MWCNTs after tip-sonication.

Figure 5-2. Morphology of the functionalized MWCNTs after tip-sonication: (a) FE-SEM image enlarged at 60,000x; (b) Length distribution profile of the MWCNTs measured from FE-SEM images; (c) HR-TEM image with arrows indicating the opened MWCNTs tips; (d) HR-TEM image of a single MWCNT.

5.3.2. Characteristics of the PAI UF hollow fiber substrate membrane

Figure 5-3a-c shows the FE-SEM images of the cross-sectional morphologies of the PAI hollow fiber substrate. Similar to those described in Chapter 4 and in the literature [150], the cross-sections of the substrate exhibits finger-like structures in the outer and inner surfaces without any visible large microvoids formed. The substrate had a thin dense skin layer above the sponge-like structure as depicted in Figure 5-3c. The thickness of the middle thin sponge-like structure is estimated to be $13 \pm 2 \mu\text{m}$. These features coupled with the large fiber lumen diameter of $1010 \mu\text{m}$ and thin fiber wall thickness of $143 \mu\text{m}$, as described in Table 5-3, make it favorable to lower internal concentration polarization in a porous substrate during FO applications [141, 150, 173, 174]. In addition, the high pure water permeability A value of $150.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and low MWCO of 13.6 kDa can be attributed to these features.

Figure 5-3. FE-SEM images of cross-sectional morphologies of the PAI UF substrate enlarged at (a) 60x; (b) 300x; (c) 10,000x; (d) Outer surface morphology of PAI UF substrate enlarged at 30,000x.

Table 5-3. Intrinsic properties of the PAI UF hollow fiber substrate.

Property	Value ^a
MWCO shell (kDa)	13.6 (± 0.9)
PWP ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	150.3 (± 5.0)
OD (μm)	1295 (± 7.1)
ID (μm)	1010 (± 8.3)
Fiber wall thickness (μm)	143 (± 2.4)

^a Average value of at least two replicates.

5.3.3. Characteristics of modified PAI hollow fiber membranes

The ATR-FTIR spectra of all the membranes used in this study are presented in Figure 5-4. As observed from Figure 5-4a and b, it appears that there is no observable change in the IR spectra for C1 to C3 membranes. The reason is because of the low difference in the reflective index (ZnSe: 2.41 compared with graphite: 2.15 at 546 nm) [175] of the MWCNTs

and the ZnSe crystal which results in a baseline-like spectrum [176]. In addition, the low loadings of MWCNTs on the membrane surfaces make it difficult to elucidate MWCNT IR peaks with sufficient intensities. Nonetheless, the occurrence of chemical cross-linking by PEI on PAI substrate is still evident from the ATR-FTIR spectra as presented in Figure 5-4b and d. The imide peaks of the PAI substrate at 1778, 1717, 1379, 1109 and 725 cm^{-1} have disappeared after cross-linking. Instead, new peaks belonging to the amide functional group at 1641 and 1532 cm^{-1} become stronger. Detailed interpretations of the IR peaks can be found in the literature [141, 150]. These observations suggest that PEI is able to penetrate through the MWCNT film and cross-link with the PAI substrate underneath. In other words, the positively charged PEI is able to wrap around the negatively charged MWCNTs via strong electrostatic attractions and fill up voids present in the MWCNT film.

Figure 5-4. ATR-FTIR spectra of PAI and its respective modified hollow fiber membranes before post-treatment in the wavenumber region of (a) 2500-4000 cm^{-1} ; (b) 500-2500 cm^{-1} and after post-treatment in the wavenumber region of (c) 2500-4000 cm^{-1} ; (d) 500-2500 cm^{-1} .

The charge characteristics of the membrane surfaces are also investigated. From Figure 5-5, PAI substrate has a negative zeta-potential with an isoelectric point of 4.1. After MWCNT immobilization and chemical post-treatment, the membrane surfaces of PP2-C1 to PP2-C3 are largely positive charged. Their isoelectric points increase to 9.2, 9.4 and 9.7 for PP2-C2, PP2-C1 and PP2-C3 respectively. These data are in good agreement to those reported in the literature [141, 150]. The reason for this change can be attributed to the PEI which was cross-linked on the surface of the PAI substrate. The cross-linked PEI possesses secondary and tertiary amine groups which are able to protonate in water via their lone pairs of electrons to give positively charged amines [177]. This resulted in the positively charged surfaces of the MWCNT immobilized membranes. Similarly, PP2 possesses largely positive zeta-potential with an isoelectric point of 9.2. These similar results suggest that there is no compromise in the surface charge of the selective layer even when MWCNTs were immobilized. An unanticipated result occurs when testing the zeta-potentials of C1 to C3. Given the highly negative surface charge of the functionalized MWCNTs, it is expected that the surface zeta-potentials of C1 to C3 be negative. However, it turns out otherwise as shown in Figure 5-5. The isoelectric points of C3, C2 and C1 are 7.6, 7.9 and 8.2 respectively. A possible explanation could be that the highly negative MWCNTs were able to trap K^+ cations in the electrolyte solution to create an electrical double layer on the surface of the MWCNTs. Due to the small quantity of MWCNTs used, the positive charges contributed from both the stern and diffuse layers can be intense enough for the overall surface zeta-potential of the MWCNTs to be registered as positive instead of negative [178]. Nonetheless, these positive surface charges seem very unstable given the small zeta-potentials of less than 10 mV.

Figure 5-5. Plot of zeta-potential against pH of ■: PAI; ●: PP2; △: C1; ▽: C2; ◇: C3; ▲: PP2-C1; ▼: PP2-C2; ◆: PP2-C3 using 1mM KCl aqueous solution as the electrolyte solution.

5.3.4. Intrinsic separation properties of MWCNT immobilized PEI-PAI hollow fiber membranes

The effect of duration of chemical post-treatment is summarized in Table 5-4. It is obvious that the optimal chemical post-treatment duration is chosen to be at 90 min. This is because the salt rejection at 80 min is not optimized while further increase in the duration decreases the PWP significantly without any change in the salt rejection. This can be understood by considering the fact that the pore size of the PAI substrate exhibits a distribution. When duration of the post-treatment increases, the PEI cross-linked layer becomes thicker resulting in small pores being sealed up while big pores becomes narrower in sizes [179]. As such, water molecules can no longer penetrate through the sealed small pores while the salt continues to penetrate through the unsealed big pores. This reduces the PWP without incurring much change in the salt rejection.

The intrinsic separation properties of the MWCNT immobilized PEI-PAI hollow fiber membranes are summarized in Table 5-5. It can be seen that all MWCNT immobilized PEI-

PAI membranes used in this study exhibit higher PWP values as compared to PP1 and PP2 (without MWCNTs). It is observed that when MWCNTs are immobilized, an increase in PWP ranges from 48% to 219% with a decrease in the salt rejection in the range of 2.5% to 7.9%. In addition, to demonstrate the effectiveness of the immobilized MWCNTs as water nanochannels, a comparison of the PWP values was made between PP1 and PP2-C2 given their very similar salt permeability, i.e. B values as observed in Table 5-4 and 5-5. It is found that an enhancement of 44% in the A value is obtained when MWCNTs are immobilized. To rationalize these data, an analysis of the FE-SEM images of the selective layers of these membranes is conducted.

Table 5-4. Effect of post-treatment durations on separation properties of modified membranes.

Code	PWP, A ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Salt permeability, B ($\text{g m}^{-2} \text{h}^{-1}$)	MgCl_2 rejection (%) ^a	Duration of post-treatment (min)
PP1	3.11 ± 0.26	0.37 ± 0.12	84.9 ± 3.0	80
PP2	3.02 ± 0.09	0.21 ± 0.01	90.3 ± 0.7	90
PP3	1.21 ± 0.12	0.09 ± 0.01	89.6 ± 0.1	100
PP4	1.11 ± 0.15	0.08 ± 0.03	89.8 ± 2.4	110

^aRejection performed with 500 ppm MgCl_2 solution at 1 bar pressure.

Table 5-5. Separation properties of MWCNT immobilized PEI-PAI hollow fiber membranes.

Code	PWP, A ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Salt permeability, B ($\text{g m}^{-2} \text{h}^{-1}$)	MgCl_2 rejection (%) ^a
PP2-C1	8.39 ± 1.39	1.20 ± 0.31	82.7 ± 1.4
PP2-C2	4.48 ± 0.24	0.41 ± 0.09	87.8 ± 2.0
PP2-C3	9.63 ± 0.29	1.39 ± 0.18	82.4 ± 1.5
PP2-C4	11.11 ± 1.72	2.41 ± 0.14	76.2 ± 3.5

^aRejection performed with 500 ppm MgCl_2 solution at 1 bar pressure.

As shown in Figure 5-6, the cross-sectional morphologies of PP2 and PP2-C1 to PP2-C3 appear similar to the PAI substrate. In addition, the MWCNTs in the films are found to be closely packed together without many visible voids in between. Under closer observation, these MWCNTs are well-dispersed without any visible signs of agglomeration, which can be attributed to the short lengths and functionalization of the MWCNTs as discussed in section 5.3.1. From Figure 5-6b, it is observed that as the concentrations of the MWCNT used for immobilization increases from 0.31 to 1.25 mg/L, the thickness of the MWCNT film on the selective layer increases as anticipated. The estimated thickness of the MWCNT film is calculated as 154, 215 and 265 nm for C1, C2 and C3 respectively. Upon further analysis, it is found that when the concentrations of MWCNT used are either too low or high, the MWCNT film thickness is not uniformly formed. The standard deviations of these estimated thickness show large differences of ± 42 and 36 nm. At 0.62 mg/L (C2) of MWCNT concentration used, the film thickness appears to be the most uniform with the lowest standard deviation at ± 14 nm. These observations suggest that greater surface defects might be formed when using a MWCNT concentration other than 0.62 mg/L. After chemical cross-linking, the interface between the immobilized MWCNTs and the PAI substrate become less obvious as shown in Figure 5-6c. This is evident of the fact that PEI was able to penetrate through the MWCNT film to cross-link with the PAI substrate underneath and thus integrating the two layers to complete the asymmetric membrane structure.

Figure 5-7 is a series of illustrations to depict the amount of surface defects present. At 0.31 mg/L (C1) and 1.25 mg/L (C3) MWCNT concentrations, the immobilized MWCNTs form films with undulating surfaces as mentioned above. Thus, when undergoing chemical post-treatment, some of the higher up MWCNT bundles were unable to be completely integrated as the PEI penetrated through the MWCNT film and were left to expose on the

membrane surfaces as shown in Figure 5-7f and h. The exposed MWCNTs therefore create defects within the PEI cross-linked selective layer where the salt can capitalize on to penetrate through this layer. This reduces the salt rejection and increases the B values of PP2-C1, PP2-C3 and PP2-C4. In contrast, when the appropriate concentration of 0.62 mg/L (C2) was used, PEI was able to integrate most of the MWCNTs due to the uniformity of the film. Only very minimal MWCNTs and some of their tips were left exposed as represented in Figure 5-7g. Hence, much less defects existed on the selective layer. As a result, insignificant drop in the salt rejection is observed for PP2-C2 and its B value at $0.41 \text{ g m}^{-2} \text{ h}^{-1}$ is also the lowest among the rest of the MWCNTs immobilized membranes. This data is also a good piece of evidence to substantiate that the negatively charged MWCNTs are highly compatible with the positively charged PEI polymer.

To summarize, when the concentrations of MWCNT solutions used are not appropriate, surface defects are formed through the immobilized MWCNTs. Consequently, PP2-C1, PP2-C3 and PP2-C4 membranes exhibit a typical trade-off phenomenon where both A and B values shows an increasing trend. However, with the suitable use of 0.62 mg/L of MWCNT solution, PP2-C2 is found to be the better performing membrane in the NF process which possesses little surface defects, leading to the lowest B value obtained. Comparing with the PWP value of PP1, the immobilized MWCNTs are effective as water nanochannels in enhancing the A value by 44%.

Figure 5-6. FE-SEM images of cross-sectional morphologies of (a) PP2, PP2-C1, PP2-C2 and PP2-C3 enlarged at 10,000x; (b) PAI, C1, C2 and C3 (without post-treatment) enlarged at 40,000x; (c) PP2, PP2-C1, PP2-C2 and PP2-C3 (with post-treatment) enlarged at 40,000x.

Figure 5-7. Illustrations of selective layers of modified PAI hollow fibers membranes: (a) PP2; (b) PP2-C1; (c) PP2-C2; (d) PP2-C3; FE-SEM images of outer surface morphologies of (e) PP2; (f) PP2-C1; (g) PP2-C2; (h) PP2-C3 enlarged at 30,000x.

Based on the above discussion, a possible mechanism for the enhancement of water transport through the MWCNT immobilized PEI cross-linked selective layer is proposed. The most plausible route is along the nanocorridors between the MWCNTs and the PEI polymer matrix (Figure 5-8). These nanocorridors are low-resistant nanogaps [180] which serve to enhance water transport by allowing water molecules to penetrate faster along the gaps and through the selective layer. The existence of nanocorridors between functionalized MWCNTs and PEI polymer matrix was reported previously in the literature [181]. Thus, with MWCNTs being immobilized, additional low friction water nanochannels are made available as opposed to water molecules diffusing only through the PEI cross-linked selectively layer conventionally. This increases the water permeability. Another route, where water molecules diffuse via the inner channels of the MWCNTs, may also be possible given that some of the MWCNTs were observed to have their tips opened (Figure 5-8). However, there is little evidence in the literature to support this proposal and a more dedicated study will be required to demonstrate the presence of water in CNTs.

Figure 5-8. Conceptual illustration of water transport enhancement through the MWCNT immobilized PEI cross-linked selective layer via (a) Route 1: Inside the inner channel of the MWCNT; (b) Route 2: Along the nanocorridor around the MWCNT.

5.3.5. FO performance of the MWCNT immobilized PEI-PAI hollow fiber membranes

The FO performances of PP1, PP2 and MWCNT immobilized PEI-PAI hollow fiber membranes with salt rejections over 80% were evaluated using 0.5 M MgCl_2 salt solution as the draw solution and deionized water as the feed water. The results are listed in Table 5-6.

Table 5-6. Performance of MWCNT immobilized PEI-PAI hollow fiber membranes in the FO process.^a

Code	AL-facing-DS		AL-facing-FW	
	J_v ($\text{L m}^{-2} \text{h}^{-1}$)	J_s/J_v (g L^{-1})	J_v ($\text{L m}^{-2} \text{h}^{-1}$)	J_s/J_v (g L^{-1})
PP1	11.3 ± 0.1	2.58 ± 0.11	10.1 ± 0.3	0.52 ± 0.13
PP2	14.7 ± 0.1	1.63 ± 0.15	10.4 ± 0.2	0.29 ± 0.02
PP2-C1	5.5 ± 0.2	10.77 ± 0.86	13.4 ± 1.4	0.33 ± 0.01
PP2-C2	11.4 ± 1.8	2.66 ± 0.14	12.5 ± 0.8	0.34 ± 0.02
PP2-C3	3.9 ± 0.6	15.91 ± 1.00	13.3 ± 0.7	0.34 ± 0.09

^aDraw solution: 0.5 M MgCl_2 and feed water: deionized water.

For the AL-facing-DS orientation, it is observed that all water fluxes, J_v , of PP2-C1 to PP2-C3 are lower while the J_s/J_v ratios are higher than PP2. Similarly, the same trend is observed for PP2-C1 and PP2-C3 when compared with PP1. PP2-C2 exhibits similar water flux and J_s/J_v ratio as PP1 given their similar B values. For the AL-facing-FW orientation, all water fluxes of PP2-C1 to PP2-C3 are higher than PP2 with no significant impact observed for the J_s/J_v ratios. In addition, all water fluxes of PP2-C1 to PP2-C3 in the AL-facing-FW orientation are much higher than that in the AL-facing-DS orientation while their J_s/J_v ratios are significantly lower as highlighted in Table 5-6. Only PP1 and PP2 shows an otherwise trend for reasons which have already been addressed in the literature [141]. These results conclude that the MWCNT immobilized PEI-PAI membranes are more suited for FO

application in the AL-facing-FW orientation, which is in good agreement with the conclusions reported in previous studies [141, 150, 179].

To understand these FO data, the salt transportations in both the MWCNT immobilized PEI cross-linked active layer and the PAI porous support layer are being considered. The MWCNT immobilized PEI cross-linked active layer contains most of the positive charges while the PAI porous support layer contains relatively less positive charges after chemical cross-linking. This is because the ends of the hollow fiber membranes were sealed and this limits the possibility of chemical cross-linking by the PEI solution with the lumen sides of the membranes. As a result, the penetrating PEI solution was only allowed to chemically cross-link with the PAI porous support layer from the outside in.

In the AL-facing-DS orientation, the positively charged PEI cross-linked active layer is directly facing the draw solution. This results in compression of the electric double layer given the high ionic strength of the draw solution and thus leading to suppression of the Donnan repulsion effect of this active layer due to the shielding effect from the Cl^- counter ions of the draw solution. This suppression in turn exacerbates the adverse effect brought by the presence of surface defects due to MWCNT immobilization. Hence, salt can penetrate through the active layer and into the PAI porous support layer via these surface defects more easily. In the PAI porous support layer, the cations of the penetrated salt experience repulsions by the positive charges of this layer and this facilitates movement of the ions into the feed water which has lower mass transfer resistance [141]. Consequently, these two effects coupled to increase the reverse salt diffusion into the feed water and result in an increase in the J_s/J_v ratio. At a high J_s/J_v ratio, the FO water flux, J_v , will decrease correspondingly as the high salt concentration at the interface between the active and support layers will aggravate the concentrative ICP and decrease the effective osmotic driving force

across the membrane. This explains why PP2-C1 and PP2-C3 with larger amount of surface defects have much lower water fluxes as compared to PP1, PP2 and PP2-C2. On the other hand, PP2-C2 with less surface defects on the active layer is able to restrict reverse salt diffusion to a certain extent and thus exhibits only a slight increment in the J_s/J_v ratio. As a result, the decrease in water flux for PP2-C2 is observed to be marginal when compared to PP2.

However, in the AL-facing-FW orientation, the ionic strength of the solution at the interface between the positively charged PEI cross-linked active layer and the porous support layer is weaker due to the presence of dilutive ICP. As a result, Donnan repulsion effect remains effective and the positively charged active layer is able to repel the salt back to the draw solution. This Donnan repulsion effect is evident given the lower J_s/J_v ratio when duration of chemical post-treatment increases as observed in PP1 and PP2. The salt flux and salt repulsion being in opposite directions also help to retard the reverse salt diffusion leading to much lower J_s/J_v ratios as compared to that in the AL-facing-DS orientation [141, 150, 179]. At a low J_s/J_v ratio, it now appears that the A value of the membrane is a key factor in influencing the FO water flux, J_v of the membrane. Indeed, the A values of PP1, PP2 and PP2-C1 to PP2-C3 from Tables 4 and 5 show close correlations to the FO water fluxes obtained in the AL-facing-FW orientation. Both PP2-C1 and PP2-C3 with higher A values exhibit larger FO water fluxes of 13.4 and 13.3 L m⁻² h⁻¹ respectively. This is a water flux enhancement of 29% and 28% respectively when compared to that of PP2. On the other hand, PP2-C2 has an A value that is lower than that of PP2-C1 and PP2-C3. Thus, a lower enhancement of 20% in the FO water flux is observed for PP2-C2.

Altogether, the immobilized MWCNTs have facilitated water transport and improved the water permeability of the positively charged PEI cross-linked active layer. Concurrently,

they introduce varying degrees of surface defects. This trade-off gives rise to an increase in the J_s/J_v ratio and thus a decrease in the FO water flux in the AL-facing-DS orientation. Nevertheless, these surface defects appear less detrimental in the AL-facing-FW orientation given the consistently low J_s/J_v ratios. The better performing membranes in the FO process are thus identified to be PP2-C1 to PP2-C3 which exhibit enhanced water fluxes in the AL-facing-FW orientation due to their improved A values. This is in contrary to most trends reported in other FO studies of membranes with NF-like selective layers where FO water flux is higher in the AL-facing-DS than in the AL-facing-FW orientation.

Table 5-7 lists the FO performances (in the AL-facing-FW orientation) of the MWCNT immobilized PEI-PAI hollow fiber membranes developed in this current work and other NF and FO membranes reported in the literature. As compared to previous work on PAI hollow fiber membranes, it appears that PP1-C1 to PP1-C3 exhibits a substantial improvement in the FO water flux without any compromise in the J_s/J_v ratios under the same experimental conditions. In addition, the performances of PP1-C1 to PP1-C3 are fairly superior as compared with other NF and FO membranes despite using only 0.5 M MgCl_2 solution as the draw solution. A noteworthy point is that these MWCNT immobilized hollow fiber membranes show better performance with higher water flux and lower J_s/J_v ratio as compared to the HTI commercial CTA FO flat sheet membrane [182].

Table 5-7. NF and FO performances of the MWCNT immobilized PEI-PAI hollow fiber membranes as compared to others in the literature.

Membrane	ID/OD (mm/mm)	PWP (L m ⁻² h ⁻¹ bar ⁻¹)	Rejection MgCl ₂ (%)	FO performance in AL-facing-FW orientation		Testing conditions		Ref.
				J_v (L m ⁻² h ⁻¹)	J_s/J_v (g L ⁻¹)	Feed solution	Draw solution	
PP2-C1	1.01/1.30	8.39 ± 1.39	82.7 ± 1.4	13.4 ± 1.4	0.33 ± 0.01	DI water	0.5 M MgCl ₂	Current work
PP2-C2	1.01/1.30	4.48 ± 0.24	87.8 ± 2.0	12.5 ± 0.8	0.34 ± 0.02			
PP2-C3	1.01/1.30	9.63 ± 0.29	82.4 ± 1.5	13.3 ± 0.7	0.34 ± 0.09			
PEI cross-linked PAI FO hollow fiber	1.24/1.58	2.25	92.7	8.36	0.3	DI water	0.5 M MgCl ₂	[141]
PEI cross-linked PAI FO hollow fiber	1.24/1.54	2.19	91.1	9.74	0.3	DI water	0.5 M MgCl ₂	[141]
PAI-PEI-PSS FO hollow fiber	1.25/1.51	3.7 ± 0.4	81.0 ± 6.2	13.0	0.4	DI water	0.5 M Na ₂ SO ₄	[150]
Cellulose Acetate NF hollow fiber	0.35/0.55	0.47	97.0	1.80	-	DI water	0.5 M MgCl ₂	[183]
Single layer PBI FO hollow fiber	0.14/0.27	0.50	86.0	4.05	-	DI water	1.0 M MgCl ₂	[184]
2h cross-linked PBI FO hollow fiber ^a	0.21/0.29	1.53	86.0	7.60	-	DI water	1.0 M MgCl ₂	[185]
4h cross-linked PBI FO hollow fiber ^a	0.21/0.29	1.34	92.0	5.50	-	DI water	1.0 M MgCl ₂	[185]
Dual-layer PBI-PES hollow fiber	0.54/0.95	1.74	87.0	12.6	0.03	DI water	1.0 M MgCl ₂	[186]
Single dense layer flat sheet membrane (thickness 34μm)	-	0.13	97.0	9.8 ± 0.7	0.12	DI water	2.0 M MgCl ₂	[187]
Double dense layer flat sheet membrane (thickness 35μm)	-	0.17	99.0	10.3 ± 0.3	0.08	DI water	2.0 M MgCl ₂	[187]
HTI commercial CTA FO flat sheet membrane (thickness 40μm)	-	-	-	9.7	0.58	DI water	0.5 M MgCl ₂	[182]

^aPBI chemically modified by *p*-xylylene dichloride

5.4. Conclusions

A novel MWCNT immobilized PEI-PAI hollow fiber membrane was fabricated. Functionalized MWCNTs were first deposited on the PAI hollow fiber membrane via a vacuum-assisted filtration process, before a chemical post-treatment was applied to form the NF-like positively charged PEI cross-linked selective layer. Compared with PEI-PAI hollow fiber membrane without MWCNTs, the water permeability of the better performing MWCNT immobilized membranes, PP2-C2, increases 44% without incurring a substantial change in the salt permeability in the NF process. In the FO process, the water flux can be enhanced up to 29% using 0.5 M MgCl_2 solution as the draw solution and deionized water as the feed water without substantial change in the salt flux for PP2-C1 and PP2-C3 membranes in the AL-facing-FW orientation. It is suggested that the enhancement in the water permeability can be attributed mainly to the additional water nanochannels manifested as nanocorridors between the MWCNTs and the PEI polymer matrix. Furthermore, the water flux enhancement in the FO process is found to be closely related to the increase in the A values of the membranes which is a result of the immobilization of the MWCNTs into the PEI cross-linked active layer. These promising results are encouraging and confirm the high potential of using MWCNT immobilized membranes to enhance water flux in water softening and wastewater treatment containing heavy metals using the FO process.

All-carbon nanoarchitectures as high-performance separation membranes with superior stability⁴

CHAPTER

6

6.1. Introduction

Leveraging on graphene-based materials as selective barriers and CNTs as water nanochannels has enabled membrane-based separations with enhanced performances. Such concerted efforts are a result of the desire to fabricate novel membranes which can provide high throughput, high selectivity and good membrane stability [7, 105, 188]. As already demonstrated in Chapter 4 and 5, the unique water transport properties of these CNMs can indeed be exploited when they are incorporated into the selective layers of the membranes. However, there are other issues stifling the practical applications of these CNMs for membrane-based separations. For example, the GO membranes fabricated so far often suffer from poor stability under practical hydrodynamic flow conditions [189, 190] because the presence of hydrophilic oxygen-containing functional groups and negative charges on the GO sheets result in undesirable redispersion of the membranes when hydrated [191]. In this study, all-carbon nanoarchitectures are presented as high-performance separation membranes by amalgamating rGO sheets and functionalized MWCNTs. The rGO sheets act as a barrier to improve the membrane selectivity while the MWCNTs serve as the water nanochannels to enhance the water permeability. Most importantly, the aim of integrating these CNMs is to focus on the membrane stability issue.

⁴(This chapter is reproduced with permission from K. Goh, W. Jiang, H.E. Karahan, S. Zhai, L. Wei, D. Yu, A.G. Fane, R. Wang, Y. Chen, *All-Carbon Nanoarchitectures as High-Performance Separation Membranes with Superior Stability*, *Adv. Funct. Mater.*, 25 (2015) 7348-7359. Copyright 2015. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

This work is inspired by a recent study which utilized hydroiodic acid to chemically reduced GO to rGO membrane so as to strengthen the membrane robustness for the FO process. As a result of the removal of the oxygen-containing functional groups from the GO sheets, the rGO membrane has a more compacted lamellar structure and exhibits much better membrane stability in water [82]. Unfortunately, the water permeability of such membrane tend to decrease drastically due to the higher hydrodynamic resistance of the narrower interlayer spacing between the rGO sheets [106]. Another recent study has also shown that multivalent cationic metal contaminants (primarily Al^{3+} and Mn^{2+}), which are unintentionally introduced during GO membrane processing, can act as effectively cross-linkers to improve the stability of the GO membrane in water [192]. Nevertheless, new methods are urgently needed to fabricate novel CNM-based membranes with both high throughput and membrane stability for realizing their practical applications.

To develop the all-carbon nanoarchitecture, GO sheets were first amalgamated with surface functionalized MWCNTs in different amounts and the membranes were fabricated via a filtration process. The ensuing membranes were then chemically reduced to create different all-carbon nanoarchitectures. By doing so, the following synergistic effects are capitalized on. First, GO sheets are known to be a good surfactant to stabilize the dispersion of CNTs in water [193, 194]. Second, the intercalation of MWCNTs between adjacent rGO sheets can effectively inhibit the restacking (or aggregation) of the rGO sheets and thus create nanochannels for water transport. Third, the nanochannels created can be engineered using MWCNTs of different diameters so as to retain the molecular sieving capability of the ensuing membranes. Last but not least, MWCNTs can also act as anchors to interact and interconnect with the adjacent rGO sheets so as to reinforce the membrane stability. The effects of MWCNT intercalation on the water permeability and molecular sieving capability

of the membranes are then systematically studied together with the detailed physicochemical characterization of these membranes. Most importantly, the stability of these all-carbon nanoarchitected membranes is assessed for the first time by subjecting the membranes to varying cross-flow rates of different hydrodynamic flow conditions. This is in contrast to previous studies where membrane stability was typically evaluated by just submerging the membranes in stagnant water [81, 84, 85]. In addition, the mechanistic understanding of the membrane stability of these all-carbon nanoarchitected membranes is also elucidated.

6.2. Experimental

6.2.1. Materials

GO was synthesized from graphite powder (Bay Carbon, Michigan) via a modified Hummers and Offeman's method as described in Chapter 2 [24, 195]. The prepared GO solution was then diluted to a stock solution with concentration of 6.5 mg/mL for the membrane fabrication. As received MWCNTs (10 nm: Cnano Technology Ltd. and 50 nm: Cheap Tubes Inc.) and SWCNTs (AP-SWCNT: Carbon Solution Inc.) were first functionalized by refluxing in 69.0% HNO₃ (Sigma-Aldrich) for 4 h. The detailed functionalization procedure can be found in the literature [143].

6.2.2. All-carbon nanoarchitected membranes fabrication

To fabricate the all-carbon nanoarchitected membranes, a diluted GO solution (0.1 mg/mL) was first prepared from the stock and subjected to bath-sonication for 30 min to exfoliate the GO. 20 mg of each type of CNTs were dispersed in 100 mL deionized water (DI H₂O) via tip-sonication (Sonics-VCX130) at 5 °C for 1 h to give well-dispersed CNTs solutions (0.2 mg/mL). These GO and CNTs solutions were immediately used for membrane

fabrication after sonication. 0.222, 0.857, 2 and 4 mL of the MWCNTs (10 nm diameter) solutions were correspondingly added into 4 mL of GO solution and then subjected to pressure-assisted filtration at 1 bar pressure on polycarbonate (PC) membranes (0.2 μ m pore size, 47 mm diameter, Millipore) using an in-house made dead-end filtration device to yield membranes containing 10, 30, 50 and 80 wt% MWCNTs respectively. The same procedure was repeated using MWCNTs (50 nm diameter) to produce 10, 30, 50 and 80 wt% GO_MWCNTs membranes and SWCNTs to produce 80 wt% GO_SWCNTs membrane. To prepare ultrathin GO membrane as a control, 4 mL of the GO solution was likewise filtered without addition of CNTs. The GO loading on all these membranes were kept the same at 0.35 g/m² to ensure same hydrodynamic resistance from the sheets for comparative studies. The as-prepared membranes were then dried in a drying chamber with temperature and humidity controlled at 35 °C and 40% respectively for 24 h. For the preparation of pristine rGO membrane and the nanoarchitected membranes, the dried membranes were treated with 57 wt% HI (Sigma-Aldrich) vapor at 90 °C for 2 to 5 min depending on the thickness of the membranes which changed with different wt% of the CNTs added. The reduced membranes were stable to water and thus they were washed with running DI H₂O thrice after the reduction process to remove any excess HI. These cleaned membranes were air-dried and stored under room temperature for evaluation of separation performances.

6.2.3. Evaluation of the separation performances of the membranes

The pure water permeability and separation evaluations were performed using an in-house made dead-end filtration device with an applied pressure of 1 bar driven by nitrogen gas. As reported in the literature, the water permeability usually stabilizes after 0.5 to 1 h of compaction [81, 84]. Thus, all of the reported water permeability coefficients of the

membranes were obtained after 1 h of compaction in DI H₂O at a pressure of 1 bar. Three different aqueous dye solutions, methylene blue (MB), acid orange 7 (AO7) and rhodamine B (RhB), obtained from Sigma-Aldrich, were utilized to evaluate the membranes separation properties at a pressure of 1 bar. The mean pore diameter and pore size distributions of the membranes were determined using a Levenberg-Marquardt equation and a two-parameter log-normal distribution function [146, 195, 196]. The effective membrane area for all these evaluations was 11.34 cm². Detailed calculation methods are summarized in Chapter 4.

6.2.4. Physicochemical characterization

A UV-Vis spectrometer (UV-1800, Shimadzu) was used to quantify the concentrations of the dyes in the retentate, permeate and feed solutions to obtain the separation performances of the membranes. The membranes surface and cross-sectional morphologies were imaged using a field emission-scanning electron microscope, FE-SEM (JSM-6701F, JEOL), at 5 kV while the morphology and structural integrity of the MWCNTs were characterized using a transmission electron microscope, TEM (JEM-1400, JEOL), at 80 kV. The surface morphology, roughness, height profile of the GO and pristine rGO membranes were also elucidated via atomic force microscopy, AFM (MFP-3D, Asylum Research) in the AC mode. An attenuated total reflection Fourier transformed-infrared, ATR FT-IR (IR Prestige-21, Shimadzu) spectrometer was employed to study the surface functional groups of the membranes and the MWCNTs before and after reduction. The microstructural integrity of the membranes were investigated using Raman spectroscopy (Reinshaw) equipped with a 785 nm laser source while the X-ray diffraction patterns of the membranes in wet and dry states were obtained using a X-ray diffractometer (D2 Phaser, Bruker) equipped

with a Cu K $_{\alpha}$ radiation source. A goniometer (OCA, DataPhysics, GmbH) was used to measure the water contact angles of the membranes before and after reduction.

6.2.5. Membrane stability evaluation

Membrane stability was studied under various cross-flow rates using an in-house made membrane cross-flow testing cell. A peristaltic pump (Masterflex L/S, Cole Parmer) was utilized to pump DI H₂O into the cell at a cross-flow rate ranging from 40 to 2000 mL/min. The pristine rGO and nanoarchitected membranes were initially subjected to 40 mL/min cross-flow rate before the rates were increased to 500, 1000 and 2000 mL/min for a duration of 10 min at every rate. For the GO membrane, the highest cross-flow rate evaluated was 500 mL/min. The effective membrane area for these stability evaluations was 4.5 cm². The cross-flow rates were also quantified into Reynolds number, R_e , to assess membrane stability under different flow conditions. The Reynolds number, R_e , can be calculated using:

$$R_e = \frac{QD_H}{\nu A} \quad (1)$$

where Q (m³/s) is the volumetric flow rate, ν (m²/s) is the kinematic viscosity of water which is defined as 0.893 x 10⁻⁶ m²/s at 25 °C [197] and A (m²) is the cross-sectional area of the testing cell [198]. D_H (m) is the hydraulic diameter of the rectangular duct which can be estimated using:

$$D_H = \frac{4A}{P} \quad (2)$$

where A (m^2) is the cross-sectional area and P (m) is the wetted perimeter of the testing cell [198]. By substituting the above-mentioned dimensions into equation (2), D_H of the testing cell is calculated to be 1.88×10^{-3} m. In general, laminar flow occurs when $Re < 2300$ while turbulent flow occurs when $Re > 4000$. When Re falls between these values, occurrence of both laminar and turbulent flows is possible and thus it is termed transition flow [198]. When the flow in the cross-flow testing cell is laminar, the shear stress on the membrane surface, τ (N/m^2), can be calculated using:

$$\tau = \mu\gamma \quad (3)$$

where μ (Pa s) is the dynamic viscosity of water which is defined as 8.90×10^{-4} Pa s at 25°C [197] and γ (s^{-1}) is the local shear velocity. Since water is a Newtonian fluid and assuming no-slip condition at the wall, the local shear velocity, γ (s^{-1}), can be taken at the centerline of the flow and be estimated using [82]:

$$\gamma = \frac{u}{(y/2)} \quad (4)$$

where u (m/s) is the cross-flow velocity of water and y (m) is the gap height of the testing cell. At a cross-flow rate of 500 mL/min, the local shear velocity is thus calculated as 1100 s^{-1} which gives a shear stress of 0.98 N/m^2 .

6.3. Results and discussion

6.3.1. Fabrication of all-carbon nanoarchitected membranes

The initial fabrication of an ultrathin GO membrane via pressure-assisted filtration and its subsequent reduction using 57 wt% HI acid to obtain a pristine rGO membrane are illustrated in Figure 6-1a. MWCNTs were then intercalated between the GO sheets before the reduction step (Figure 6-1b) to create nanoarchitected membranes in order to mitigate the drop in water permeability brought by the decreased in the interlayer spacing due to the HI reduction [21]. The intercalated MWCNTs can inhibit the restacking of the rGO sheets and create nanochannels to facilitate water transport through the ultrathin rGO membranes. Depending on the amount of MWCNTs intercalated, the morphology of these membranes can be easily tuned into two different types, namely graphene-rich and CNT-rich nanoarchitectures (Figure 6-1b). This all-carbon nanoarchitecture design arises from the following rationales. First, a pressure-assisted filtration process can be employed to yield a tight GO laminate with highly ordered microstructure as reported by C.-H. Tsou *et al.* [80]. Second, HI is chosen over other reducing agents such as hydrazine as it helps to maintain structural integrity of the GO laminate by providing a gentle chemical reduction which produces water instead of CO and CO₂ gases. The water is believed to travel along the capillaries between the GO sheets without inflicting damage to the microstructure [106]. An alternative approach to minimizing defects in the GO membrane is to increase its thickness. However, two major drawbacks to this approach is the exponential decrease in the water permeability (as highlighted in Chapter 3) and the lack of improved membrane stability as membrane thickness increased. As such, this ultrathin membrane design is adopted to reduce hydrodynamic resistance and made deliberate considerations over the filtration process and the reducing agent to enhance the stability of the ultrathin membrane. Third, MWCNTs are

chosen to create the nanochannels for water transport in virtue of their high aspect ratios, excellent strength and smooth hydrophobic graphitic walls [18, 199]. Overall, all these factors come together to ensure the formation of tight and stable all-carbon nanoarchitectures with high water permeability and minimal structural defects.

Figure 6-1. Schematic illustrations of the fabrication process leading to (a) ultrathin rGO membrane and (b) all-carbon nanoarchitectured membranes.

As shown in Figure 6-2a, the as-prepared ultrathin pristine rGO membrane exhibits a smooth surface with a mirror-like finishing. This suggests that a highly ordered laminate structure is formed and the structural integrity is well preserved during the reduction process. The rGO membrane is estimated to be $\sim 55 \pm 3$ nm in thickness (Figure 6-2b and c) while the outer surface of the rGO membrane appears smooth and reveals minimal wrinkles as depicted

by the FE-SEM and AFM images respectively (Figure 6-2d and e). In contrary, the as-prepared ultrathin GO membrane lack the mirror-like finishing despite exhibiting a smooth surface (Figure 6-2f). The GO membrane is also slightly thicker at $\sim 90 \pm 5$ nm (Figure 6-2g and h) and reveals more wrinkles (Figure 6-2i and j). Due to the presence of these wrinkles, the surface roughness of the GO membrane is higher at 8.29 ± 0.96 nm as compared to the rGO membrane at 5.62 ± 0.95 nm (Figure 6-2k). Such wrinkles in the GO membrane arise from the hydrogen bonding between the hydrophilic functional groups on the basal planes and edges of the GO sheets. This hydrogen bonding affects how the convoluted GO sheets are assembled and thus contributing to the wrinkles [200]. On the other hand, the removal of these hydrophilic groups during the reduction process allows the rGO sheets to smoothen out before restacking into a less wrinkled laminate structure.

Figure 6-2. (a) Photo showing metallic luster; (b,d) FE-SEM images of the cross-sectional and surface morphology; (c,e) AFM height profile and topography of the pristine rGO membrane. (f) Photo showing less reflective luster; (g,i) FE-SEM images of the cross-sectional surface morphology with more wrinkles as highlighted by the white arrows; (h,j) AFM height profile and topography of the ultrathin GO membrane; (k) surface roughness of the ultrathin GO and pristine rGO membranes.

Intercalation of MWCNTs into the membrane is then explored by fabricating a series of nanoarchitected membranes consisting of 10, 30, 50 and 80 wt% MWCNTs. To demonstrate that MWCNTs can create nanochannels of different sizes to facilitate water transport, MWCNTs of two diameters, 10 and 50 nm are utilized. The MWCNT intercalated membranes are designated as rGO_xMWCNT(y) where x represents the wt% of MWCNTs loaded and y represents the diameter of the MWCNT used. For example, rGO_30MWCNT(10) denotes a membrane with 30 wt% MWCNT loading using 10 nm diameter MWCNTs. As shown in Figure 6-3a-d, nanoarchitected membranes of different MWCNT loadings all appear uniform and smooth with their colors looking darker as the MWCNT loading increases. At low MWCNT loadings (≤ 50 wt%), the membranes reveal a metallic grey luster (Figure 6-3a-c), but this luster disappears for rGO_80MWCNT(10) (Figure 6-3d). These observations suggest that the intercalated MWCNTs integrate well with the rGO sheets, and the structural integrity stays intact after the intercalation. However, the roughness of these membranes increases as a result of the undulating outer surfaces caused by the intercalated MWCNTs (Figure 6-3e-l). The cross-sectional morphologies of these membranes are also investigated via FE-SEM to elucidate their microstructures. As illustrated in Figure 6-3m-t, the MWCNTs are uniformly intercalated regardless of the diameters of the MWCNTs used. Further analysis of the FE-SEM images of rGO_10MWCNT(10) to rGO_80MWCNT(10) shows an increase of the membrane thickness from $\sim 64 \pm 2$ to $\sim 1230 \pm 70$ nm (Figure 6-3m-p). Such a dramatic change in the thickness indicates that the interlayer spacing between the rGO sheets have been immensely disrupted by the intercalated MWCNTs. Interestingly, the change in thickness of the membrane is not as radical when 50 nm diameter MWCNTs are loaded. The thickness of rGO_10MWCNT(50) to rGO_50MWCNT(50) is largely similar to their 10 nm MWCNT

counterparts (Figure 6-3q-s) except for rGO_80MWCNT(50) which has a thickness of $\sim 570 \pm 18$ nm (Figure 6-3t). This is at least 2 times smaller than the membrane thickness of rGO_80MWCNT(10).

While this observation seems counter-intuitive initially, it can be rationalized by studying the mass difference between the 10 and 50 nm diameter MWCNTs. Transmission electron microscopic (TEM) analysis of the MWCNTs ($n > 100$) reveals that the inner diameter of the 50 nm diameter MWCNTs is similar to that of the 10 nm MWCNTs and thus the number of graphitic walls possessed by the 50 nm diameter MWCNTs is significantly more (Figure 6-4). By estimating the number of walls and calculating the mass of the respective MWCNTs as described in the literature [201], a 50 nm diameter MWCNT is found to be at least 15 times heavier than a 10 nm MWCNT. This means that, for the same mass of MWCNTs loaded, the number of 50 nm diameter MWCNTs intercalated into the rGO membrane is significantly lower than that of the 10 nm MWCNTs, resulting in a weaker disruption of the interlayer spacing between the rGO sheets. This, in turn, induces a tighter membrane packing density and hence a smaller membrane thickness of rGO_80MWCNT(50). Such a phenomenon is only observable when the MWCNT loading exceeds 50 wt%, which suggests that the architecture of the membrane changes beyond this loading. As such, these two architectures are termed as graphene-rich and CNT-rich when the MWCNT loadings are below and above 50 wt% respectively (Figure 6-3).

Figure 6-3. (a-d) Photos and morphological FE-SEM images showing (e-l) surface and (m-t) cross-sections of the all-carbon nanoarchitected membranes with 10 nm diameter MWCNTs and 50 nm diameter MWCNTs intercalated.

Figure 6-4. TEM images and the diameter distribution profiles of the (a,b) 10 nm diameter and (c,d) 50 nm diameter MWCNTs.

6.3.2. Separation performances of all-carbon nanoarchitected membranes

The water permeability ($\text{L m}^{-2} \text{h}^{-1}$) of the respective membranes are evaluated under 1 bar pressure and represented as water permeability coefficients ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$) while the separation performances of these membranes are assessed using three different organic dye solutions, namely methylene blue (MB), acid orange 7 (AO7) and rhodamine B (RhB). MB (319.85 gmol^{-1}) is a positively charged molecule with a dimension of $1.6 \times 0.8 \text{ nm}$ while AO7 (350.32 gmol^{-1}) has a similar dimension ($1.6 \times 1.0 \text{ nm}$) but negatively charged [202]. RhB (479.02 gmol^{-1}) is an electroneutral molecule with a larger dimension of $1.8 \times 1.4 \text{ nm}$ [64]. These solutes are deliberately chosen due to their different charges and various molecular weights so that a comprehensive understanding of the sieving mechanism can be made. The results are summarized in Figure 6-5.

Figure 6-5. Separation performances and properties showing (a) water permeability coefficients; (b) hydrodynamic resistance; (c) membrane density and the (d-f) rejection rates of MB, AO7 and RhB respectively for the all-carbon nanoarchitected membranes.

As shown in Figure 6-5a, the water permeability coefficients of the nanoarchitected membranes are found to increase with higher MWCNT loadings. Consequently, the hydrodynamic resistances of these membranes decrease as the MWCNT loading increases (Figure 6-5b), taking into account that the resistance brought by the rGO sheets is the same given the same amount of rGO used in every membrane. These results suggest that MWCNTs have successfully created the nanochannels among the rGO sheets for water transport. To further validate this finding, the water permeability coefficients of the nanoarchitected membranes intercalated with 50 nm diameter MWCNTs are compared against their 10 nm MWCNT counterparts. The water permeability coefficients of those membranes with 50 nm diameter MWCNTs are higher than their 10 nm MWCNT counterparts at every MWCNT loading except for the MWCNT loading at 80 wt% (Figure 6-5a). These results are in good agreement with those recently reported in the literature [65,

84]. At the MWCNT loading of 80 wt%, the nanoarchitecture changes from graphene-rich to CNT-rich and thus an opposite trend is observed with rGO_80MWCNT(50) having a water permeability coefficient lower than that of rGO_80MWCNT(10). To further explain for this difference, the membrane density of the nanoarchitected membranes was explored. The density of these membranes exhibits a linear decreasing trend up to 50 wt% MWCNT loading, with rGO_10MWCNT(50) to rGO_50MWCNT(50) having smaller densities as compared to their 10 nm MWCNT counterparts. However, at the 80 wt% MWCNT loading, the membrane density of rGO_80MWNCT(10) increases marginally while that of rGO_80MWCNT(50) increases significantly (Figure 6-5c), for the same reasons which have already been discussed in section 6.3.1. This observation suggests that the nanoarchitecture of the rGO membrane with 80 wt% MWCNT loading is evidently different from the other rGO membranes of lower MWCNT loadings. It also shows that, for each distinct type of nanoarchitecture, the membrane density is inversely proportionate to the water permeability coefficient where a higher membrane density results in a lower water permeability coefficient and vice versa. In this regard, it is thus noteworthy to mention that such a shift in the nanoarchitecture as MWCNT loading increases is not only evident from the membrane morphology but also clearly manifested in the water permeability of the membrane and its microstructural parameter such as membrane density. Overall, intercalation of MWCNTs into rGO sheets has resulted in an increment of water permeability with rGO_80MWCNT(10) having a permeability up to 4.8 times that of the pristine rGO membrane.

Next, the separation performances of these membranes were evaluated. As illustrated in Figure 6-5d-f, the rGO membrane shows significant improvement in the rejection rates as compared to the GO membrane. With just an ultrathin rGO membrane, the three dye solutes can generally reach rejection rates above 95%. When 10 nm diameter MWCNTs are

intercalated, the rejection rates further exceed that of the pristine rGO membrane, indicating that the 10 nm intercalated MWCNTs integrate well with the rGO sheets. For its 50 nm MWCNT counterparts, the rejection rates increase slightly at low MWCNT loadings (up to 30 wt%) before dipping at higher MWCNT loadings (Figure 6-5d-f). Such a trend is coherent with those reported in the literature which suggests the generation of more pathways for the dye solutes to permeate due to a greater amount of 50 nm diameter MWCNTs loaded [65]. To further demonstrate that the membrane selectivity arises from the synergism of the rGO sheets and the intercalated MWCNTs, the separation performance of a pure reduced MWCNTs membrane was evaluated. Unsurprisingly, the pure reduced MWCNTs membrane exhibits a poor selectivity with dye solute rejection rates between 5% to 20%, despite having a much higher water permeability coefficient of $2234 \pm 63 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (Table 6-1). On this account, as with 10 nm diameter MWCNTs, it is conclusive that the seamless assimilation of MWCNTs into the rGO sheets has successfully created nanochannels to enhance water permeability and yet provide effective molecular sieving for larger solutes.

Table 6-1. Separation performance of the pure reduced MWCNTs membrane.

Membrane	Water permeability coefficient ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	Rejection rate (%)		
		MB	AO7	RhB
Pure reduced MWCNTs	2234.4 ± 63.4	20.2 ± 4.2	5.3 ± 1.7	8.7 ± 1.7

6.3.3. Physicochemical characterization

In an effort to provide plausible explanations to the above membrane separation performance results, various characterizations were carried out on the membranes. The chemical states of the membranes are first examined using Raman and Fourier transformed-

infrared (FT-IR) spectroscopy. As shown in Figure 6-6a, the Raman intensity ratio of the D to G band (I_D/I_G) increases from 1.2 to 1.6 when GO is reduced to rGO membrane. This confirms a successful restoration of sp^3 carbons in the GO membrane to sp^2 carbons in the rGO membrane by the HI reduction [27, 128]. The increased I_D/I_G ratio of 1.7 observed in the spectra of both rGO_80MWCNT(10) and rGO_80MWCNT(50) and the presence of the 2D bands also indicate effective restoration to give more graphitic sp^2 carbons in both the rGO sheets and the intercalated MWCNTs [129]. These findings can be corroborated by the FT-IR results (Figure 6-6b). The oxygen-containing functional groups on the GO spectrum assigned as C=O (1720 cm^{-1}), C–OH (1404 cm^{-1}) and C–O (1062 cm^{-1}) stretching vibrations [130] are absent from the rGO spectrum, implying their removal during the reduction process. On the other hand, the extent of reduction is limited for the MWCNTs given the sharp OH stretching vibrations in the region of $3500\text{--}3800\text{ cm}^{-1}$ due to free hydroxyl groups [203] present in both oxidized and reduced MWCNTs. Coupled with the presence of the C–O (1062 cm^{-1}), asymmetric and symmetric CH_2 (2902 and 2980 cm^{-1}) stretching vibrations in the spectra of rGO_80MWCNT(10) and rGO_80MWCNT(50), the successful reduction of GO to rGO sheets is evidently inferred while the intercalated MWCNTs remain largely hydrophilic in these membranes. As a result, the water contact angles of the nanoarchitected membranes decrease with increasing MWCNT loadings as demonstrated in Figure 6-6c. The X-ray diffraction (XRD) patterns (Figure 6-6d) were also analyzed to understand changes in the interlayer spacing of these membranes. A 2θ shift in the (002) peak of the GO membrane from 10.8° to 9.1° (corresponding to an increase in interlayer spacing from 0.82 to 0.97 nm) suggests that the GO membrane is highly hydrophilic and is susceptible to swelling when wetted [204]. However, upon successful HI reduction, a broad peak that appears at 24.3° (corresponding to an interlayer spacing of 0.36 nm), as a result of the removal of oxygen-

containing functional groups [28] which induces partial restacking of the exfoliated rGO sheets [126], does not produce the same shift when wetted. This is attributed to the hydrophobicity of the rGO sheets (Figure 6-6c) and the reduced interlayer spacing which restricts water intercalation. When 80 wt% MWCNTs are loaded, the broad peak disappears and instead MWCNTs peaks appear at 26.2° and 40.7° which correspond to the (002) and (100) planes of the hexagonal graphitic structures of MWCNTs respectively [205]. This implies that the MWCNTs have been effectively intercalated and inhibited the restacking of the rGO sheets during the reduction process [126].

Figure 6-6. Physicochemical characterization as elucidated by (a) Raman spectrum using a 785 nm laser, (b) ATR FT-IR spectrum, (c) water contact angles of the membranes at different MWCNT loadings and (d) XRD patterns of the membranes at wet and dry states.

From all these characterization results, it is deduced that the intercalated MWCNTs stay hydrophilic and continue to create effective nanochannels after the HI reduction process by allowing favorable water access through their hydrophilic sites [64] and faster water permeation through the enlarged interlayer spacing between the rGO sheets [21]. As a result, the water permeability coefficients increase with increasing MWCNT loadings (Figure 6-5a). When 50 nm diameter MWCNTs are intercalated, this interlayer spacing between the rGO sheets is widened to a larger extent and thus permitting greater water permeation through the graphene-rich nanoarchitected membranes [65].

On the other hand, the removal of oxygen-containing functional groups during the reduction process which induces restacking of the rGO sheets has rendered the pristine rGO membrane less negative electrostatic charges [117, 206] and a narrower interlayer spacing [21, 106]. Based on these conclusions and considering negligible dye adsorption rates by the respective membranes (Table 6-2), size exclusion is proposed as the dominant sieving mechanism for the retention of the dye solutes in the pristine rGO membrane [19, 20]. As verified by Figure 6-5d and e, the similar MB and AO7 rejection rates (~95%) of the rGO membrane suggests that Donnan (charge) exclusion is not the predominant mechanism given that different charges on solutes of similar molecular weights do not seem to have an effect on their rejection rates. In fact, the slightly higher rejection rate (97.3%) of the electroneutral RhB solutes of higher molecular weight (Figure 6-5f) validated this deduction. These results thus demonstrate that the pristine rGO membrane has a molecular weight cut-offs (MWCO) between the range of 200 to 2000 Da which classifies it as a NF membrane [62, 81]. Microstructural defects created during the restacking of the rGO sheets dismiss the possibility of absolute exclusion of the dye solutes which theoretically should be anticipated

given a relatively smaller interlayer spacing of 0.36 nm between the rGO sheets as compared to the larger dimensions of the solutes [207].

Table 6-2. Dye adsorption rates of the PC, GO, ultrathin pristine rGO and all-carbon nanoarchitected membranes.

Membranes	Adsorption rate (%)		
	MB	AO7	RhB
PC	5.6 ± 2.8	0.7 ± 0.1	5.2 ± 1.0
GO	50.7 ± 7.1	0	24.0 ± 3.9
Ultrathin pristine rGO	5.3 ± 0.2	1.5 ± 0.2	4.6 ± 0.2
rGO_80MWCNT(10)	3.8 ± 2.9	4.3 ± 0.7	6.7 ± 0.4
rGO_80MWCNT(50)	6.0 ± 2.6	4.0 ± 1.7	6.4 ± 0.4

The exact same trends in the rejection rates are also observed when MWCNTs are intercalated. Rejection rates of MB, AO7 and RhB respectively increase to 99.8%, 99.4% and 100% for rGO_80MWCNT(10) and 96.3%, 97.7% and 99.2% for rGO_30MWCNT(50) as depicted in Figure 6-5d-f. The increase in the rejection rates of the higher molecular weight RhB solutes again brought us to the same conclusion that size as opposed to Donnan exclusion is the predominant sieving mechanism. More evidence to support this conclusion is also demonstrated through the pore size distributions of these membranes (Figure 6-7). Assuming that the interlayer spacing between the rGO sheets is equivalent to a cylindrical pore with a circular cross-section, the mean pore diameters of rGO_10MWCNT(10) to rGO_80MWCNT(10) are found to be around 0.96 nm while their 50 nm MWCNT counterparts show an increasing mean diameter from 1.10 to 1.29 nm with increasing MWCNT loadings (Figure 6-7b and c). This means that the all-carbon nanoarchitected

membranes can effectively block out the evaluated dye solutes which are larger in dimensions. In addition, the highly tapered pore size distribution of rGO_80MWCNT(10), in contrast to the broader distributions of the other nanoarchitected membranes, accounts for the higher membrane selectivity of rGO_80MWCNT(10). As a result of these two factors, rGO_80MWCNT(10) can achieve almost 100% rejection rates which is unattainable at the same wt% loading when 50 nm diameter MWCNTs are loaded instead.

Figure 6-7. Comparison of the pore size distribution of (a) the pristine rGO membrane; (b) all-carbon nanoarchitected membrane (b) with 10 nm diameter MWCNTs intercalated and (c) with 50 nm diameter MWCNTs intercalated. The colored regions marked out the range of pore diameter where the mean pore diameters of the membranes are.

Essentially, the characterization and separation performance results have shown that the water permeability of the membrane is dependent on its membrane density while the membrane selectivity is closely related to the diameter of the MWCNTs loaded. With this understanding, synergism can then be fostered through assimilating a high loading of MWCNTs into the rGO sheets to immensely disrupt the interlayer spacing and create nanochannels to facilitate water permeation while the employment of small diameter MWCNTs to constrict these nanochannels effectively leads to smaller membrane pore size that can enhance size exclusion effect and hence the membrane selectivity.

6.3.4. Stability of membranes and the mechanism

Membrane stability was systematically studied under various cross-flow conditions using the ultrathin pristine rGO membrane and a representative from each type of the nanoarchitecture, namely rGO_80MWCNT(10) and rGO_50MWCNT(10). The membranes are first potted into an in-house made cross-flow testing cell before subjected to cross-flow rates of 500, 1000 and 2000 mL/min to evaluate their stability. These cross-flow rates are equivalent to cross-flow velocities of 0.55, 1.11 and 2.22 m/s and Reynolds numbers (Re) of 1167, 2333 and 4667 respectively. The rates are chosen to create varying flow conditions ranging from laminar, transition to turbulent flow. Ultrathin GO membrane with the same GO loading as the pristine rGO membrane is also subjected to cross-flow rates up to 500 mL/min as a control.

The pristine rGO membranes, rGO_80MWCNT(10) and rGO_50MWCNT(10) exhibit excellent stability when subjected to different flow conditions. These membranes were initially evaluated under a moderate 500 mL/min cross-flow rate which created a laminar flow that exerted a shear stress of 0.98 N/m^2 on the surfaces of the membranes

(section 6.2.5). The membranes managed the flow and stress well without incurring any visible damage as they were compressed. Next, the membranes were subjected to higher cross-flow rates of 1000 and 2000 mL/min. Similarly, the membranes handled the change in the fluid dynamics with ease as the flow transited from laminar to transitional and finally to turbulent. Stronger shear stress due to the increased cross-flow rates further compressed the membranes. As the turbulent flow and shear stress were alleviated by returning the cross-flow rate back to 40 mL/min, all the membranes loosened up without a glitch as shown in Figure 6-8a-f. To further validate such membrane stability, a long term stability evaluation is performed on rGO_80MWCNT(10). The membrane displayed excellent durability when subjected to a cross-flow rate of 500 mL/min over a duration of 24 h. No compromise on the integrity of the membrane was visible after the evaluation (Figure 6-8g-h), which again demonstrated the excellent membrane stability.

Figure 6-8. Photos showing the membrane integrity of the (a,b) pristine rGO, (c,d) rGO_80MWCNT(10) (e,f) rGO_50MWCNT(10) before and after cross-flow evaluations at different R_e ; Photos showing the membrane integrity of rGO_80MWCNT(10) (g) at the start and (h) after 24 h of membrane stability evaluation at cross-flow rate of 500 mL/min.

To highlight the disparity in the membrane stability, an ultrathin GO membrane is put to the test. The GO membrane started to peel off from the polycarbonate (PC) substrate at a relatively low cross-flow rate of 100 mL/min. This rate is equivalent to a cross-flow velocity of 0.11 m/s and a Re of 233. At a higher cross-flow rate of 500 mL/min, fragmented GO platelets were also found to be carried away by the cross-flow. The observations suggest that the ultrathin GO membrane is highly unstable and is incapable of withstanding a shear stress as low as 0.2 N/m^2 . This is attributed to its hydrophilicity which allows the oxygen-containing functional groups on the GO sheets to form strong hydrogen bonding with the water shearing on the membrane surface [191, 192]. As a result, the shear stress is able to rupture the GO membrane as shown in Figure 6-9.

On the basis of these experimental results, a mechanism is then proposed to explain for the good membrane stability of the pristine rGO and the nanoarchitected membranes. As already discussed, oxygen-containing functional groups on the GO membrane induces hydrophilic interactions with water and makes the membrane susceptible to water intercalation. Therefore, the strategy revolves around the removal of these oxygen-containing functional groups in the pristine rGO membrane, which not only makes its surface hydrophobic but increases the van der Waals attractions and π - π stacking interactions between the rGO sheets [199, 208]. As a result, the interlayer spacing between the rGO sheets decreases, preventing water intercalation and thus swelling and redispersion of the pristine rGO membrane. Explanations as such have been widely accepted as the reasons for rGO stability in water [82, 191, 192].

Figure 6-9. Photos showing the membrane integrity of the (a,b) GO membranes before and after cross-flow evaluations at different Re . The black arrows indicate the regions where the integrity of the GO membrane is being compromised.

This same mechanism can be extended for the nanoarchitected membranes. Before that, it is essential to recall an important protocol during the processing of the MWCNTs. The MWCNTs have undergone surface functionalization using nitric acid oxidation for 4 h and tip-sonication at 60% amplitude for 1 h prior to membrane fabrication. The strong sonication process not only shortened the lengths of the MWCNTs [143] but at the same time thinned the MWCNTs through exfoliating the oxidized but defective outer walls [154]. Judging from the chemical states of the oxidized MWCNTs (Figure 6-6b) and the analysis of the TEM images (Figure 6-10a and b), the observed fragments anchored on the surfaces of the oxidized MWCNTs after tip-sonication are in fact nanoscale GO foliates. Similar observations have also been reported in previous reports [208-211]. As such, it is proposed that these nanoscale GO foliates on the MWCNTs get reduced into rGO foliates by HI reduction and induce strong van der Waals attractions and π - π stacking interactions [208] between the assimilated rGO sheets and the inner graphitic walls of the MWCNTs (Figure 6-10c). The excellent stability observed in the nanoarchitected membranes is a result of such strong interactions.

Figure 6-10. TEM images of the (a) 10 and (b) 50 nm diameter MWCNTs after tip-sonication. The white circles highlight the presence of rGO foliates. (c) Pictorial illustration of the van der Waals attractions and π - π stacking interactions between the assimilated rGO sheets and the inner graphitic wall of the MWCNTs via the rGO foliates.

As an attestation to the above reasoning, 80 wt% single-walled carbon nanotubes (SWCNTs) intercalated rGO membrane was fabricated to study its membrane stability. The same processing protocols were applied on the SWCNTs to ensure an unbiased comparative study. Unsurprisingly, the rGO_80SWCNT membrane did not exhibit the outstanding membrane stability as its rGO_80MWCNT(10) counterpart. The rGO_80SWCNT membrane appears highly porous with water intercalating rapidly into the membrane when exposed to water. Consequently, this causes the membrane to rupture in less than a minute of exposure (Figure 6-11). Such an observation provides an important implication concerning the mechanistic understanding of the nanoarchitected membranes. The intercalated MWCNTs

emerge to anchor themselves onto the assimilated rGO sheets through the rGO foliates via strong van der Waals attractions and π - π stacking interactions which is similar to the CNT vein supports as proposed by X. Lin *et al.* [210] and the “rebar graphene” as proposed by Z. Yan *et al.* [208]. Without the support from the inner graphitic walls of the MWCNTs, the nanoarchitecture quickly collapses in water just like in rGO_80SWCNT. In essence, by leveraging on the inner graphitic walls of the MWCNTs as spacers and using the nanoscale rGO foliates to extend towards assimilated rGO sheets via strong interactions, membrane stability can be instilled from within the nanoarchitected membranes. Such membrane stability is considered superior when compared to those reported in the literature (Table 6-3).

Comparing with representative results across the recent literature, rGO_80MWCNT(10) has exhibited comparable water permeability and excellent dye rejection capability. In fact, the water permeability of rGO_80MWCNT(10) is at least twice that of previously reported rGO membranes with similar rejection capabilities (Table 6-4) and 5-10 times higher than most commercial NF membranes [64, 78]. The superior stability furnished by the pristine rGO and rGO_80MWCNT(10) membranes also offer a greater competitive advantage over other graphene-based membranes with higher water permeability when it comes to commercial separation applications which utilize cross-flow filtration to mitigate concentration polarization [66]. The membrane stability of such graphene-based membranes is often not reported or generally evaluated in unrepresentative hydrodynamic conditions such as submerging in stagnant water. In comparison, this study has demonstrated the feasibility of employing nanoarchitected membranes in cross-flow filtration by engineering the membrane stability through MWCNT intercalation. Considering that the costs of mass producing GO and MWCNTs will continue to drop with the development of

better and cheaper scale-up methods [90], it is confident that the all-carbon nanoarchitected membranes will be able to find their places in niche separation applications.

Figure 6-11. Photo showing the ruptured rGO_80SWCNT membranes after exposing to water for less than a minute.

Table 6-3. Comparison of the extent of membrane stability and its origin of the rGO_80MWCNT(10) membrane with representative results from recently published works.

Graphene-based membrane	Fabrication method	Extent of membrane stability	Origin of stability enhancement	Ref.
Freestanding GO	Vacuum filtration on AAO	Great membrane stiffness and highly stable in aqueous medium	Multivalent cationic cross-linking via Al^{3+} and Mn^{2+}	[192]
Freestanding ultrathin rGO	Vacuum filtration on MCE	Stable under a hydraulic pressure up to 0.25 bar and a shear stress of 0.005 N/m^2	HI reduction to give rGO film with a compacted lamellar structure	[82]
rGO_80 MWCNT(10)	Pressure-assisted filtration on PC	Stable under a shear stress greater than 0.98 N/m^2 and cross-flow of $4667 R_e$. Able to withstand cross-flow of $1167 R_e$ for at least 24 h	Strong VDWs attraction and π - π stacking between assimilated rGO and rGO foliates on MWCNT anchors	This work

AAO: anodic aluminum oxide; MCE: mixed cellulose ester; PC: polycarbonate

Table 6-4. Performance and membrane stability of ultrathin pristine rGO and all-carbon nanoarchitected membranes together with several representative results from recently published works.

Graphene-based membrane	Fabrication method	Feed system	Water permeability coefficient ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Rejection (%)	Membrane stability	Ref.
Corrugated CCG	Vacuum filtration	0.01 mM DY	45	67	N.A	[63]
PNIPAM/CCG (3:1)/NME	Pressure-assisted filtration	RhB	152	70	stable in water for a month without leakage of PNIPAM	[84]
GO/PC	Vacuum filtration	15 μM EB	71	85	N.A	[64]
Nanostrand channelled GO/PC	Vacuum filtration	15 μM EB	695	83.5	N.A	
CDs-GO/MCE	Vacuum filtration	10 ppm MB 10 ppm MO 10 ppm RhB	408-434	99.5 99.2 99.7	N.A	[83]
MWCNTs-refluxed GO/PVDF	Vacuum filtration	0.05 g/L MO 0.02 mM DY	11.33	96.1 99.8	stable under 450 rpm stirring during performance evaluation	[65]
Base-refluxed rGO/PVDF	Vacuum filtration	0.02 mM MB 0.02 mM RhB	21.8 5	99.2 78	stable in water for at least 0.5 year without visible change	[81]
Ultrathin pristine rGO/PC	Pressure-assisted filtration	0.01 g/L MB 0.03 mM AO7 0.02 mM RhB	11	95.2 95.5 97.3	stable under 4667 R_e cross-flow evaluation	this work
rGO_80MWCNT (10)/PC	Pressure-assisted filtration	0.01 g/L MB 0.03 mM AO7 0.02 mM RhB	52.7	99.8 99.4 100	stable under 4667 R_e cross-flow evaluation and withstand 1167 R_e cross-flow for at least 24 h	

CCG: chemically converted graphene; PNIPAM: poly(N-isopropylacrylamide); NME: nitrocellulose mixed ester; PC: polycarbonate; CDs: carbon quantum dots (1-3.5 kDa); MCE: mixed cellulose ester; PVDF: polyvinylidene fluoride; DY: direct yellow; EB: evans blue; MO: methyl orange; N.A: not applicable.

6.4. Conclusions

All-carbon nanoarchitected membranes were demonstrated with high water permeability, excellent organic dye rejection rates and superior membrane stability. By loading small diameter MWCNTs (10 nm diameter) in the rGO membranes, the microstructures of the nanoarchitectures can be easily tuned from a graphene-rich type to a CNT-rich type. As a result of this intercalation of MWCNTs, the rGO membrane with 80 wt% MWCNT loading exhibited a water permeability which is 4.8 times higher than that of the pristine rGO membrane. In addition, this membrane provided a better size exclusion effect, with almost 100% rejection rates for three types of organic dyes of different charges. Furthermore, the unprecedented study on the membrane stability has revealed exceptional stability of the all-carbon nanoarchitected membranes when subjected to a turbulent cross-flow hydrodynamic condition of 2000 mL/min and Reynolds number of 4667. Mechanistic understanding suggests that the van der Waals attractions and π - π stacking interactions between the assimilated rGO sheets and the nanoscale rGO foliates on the intercalated MWCNT anchors have successfully engineered such membrane stability. These results have demonstrated the effectiveness of the strategy to use MWCNTs as spacers to create nanochannels which selectively facilitate water transport and anchors to instill the membrane with superior stability for water purification. In general, this nanoarchitecture design is highly versatile in creating both graphene-rich and carbon nanotube-rich all-carbon membranes with engineered nanochannels and superior membrane stability for realizing practical separation applications of graphene-based membranes.

7.1. Overview

Carbon nanomaterials (CNMs), with their unique structures and physicochemical properties, have generated immense interests worldwide. The fast growing number of publications, diverse applications and new commercial products introduced into the consumers market are strong evidence of the current value and the future promise held by these CNMs [212]. As such, the aim is to capitalize on the unique water transport properties of the CNMs to fabricate novel, efficient and advanced separation membranes for water purification in an effort to mitigate the pervasive challenges faced by membrane-based separations (Chapter 1). In particular, CNMs such as graphene oxide (GO), reduced graphene oxide (rGO) and multi-walled carbon nanotubes (MWCNTs) are exploited as the selective layer of the separation membranes to achieve fast diffusion of water molecules through the layer while offering excellent membrane selectivity by retaining bigger solutes.

This thesis presents the functionalization and engineering of CNMs to realize the design and fabrication of novel CNM-based membranes as diffusion barriers. In Chapter 3, micrometers-thick freestanding GO and rGO films were fabricated via a facile pressure-assisted filtration method before heat pressing with poly(lactic acid) (PLA) films to yield sandwich-architected PLA-graphene composite membranes. It was found that the composite membranes exert high barrier properties towards oxygen and water vapor molecules. Although they are unsuitable as selective membranes for water purification, these composite membranes are promising as packaging films for items like food. In this regard,

the idea of using GO sheets as a selective barrier is explored in Chapter 4. This was achieved by electrostatic dip-coating the negatively charged GO deposition on the surface of a polyamide-(imide) (PAI) hollow fiber membrane cross-linked with positively charged polyethyleneimine (PEI). By reducing the GO deposition to nanometers in thickness, the hydrodynamic resistance exerted was surprisingly lower than that of the PEI cross-linked selective layer. In addition, the GO deposition was able to effectively reduce the pore size of the membrane given the 2-D structure of the GO sheets. As a result, GO sheets are reckoned to be effective selective barriers for nanofiltration (NF) membranes. Next, Chapter 5 presented the immobilization of functionalized MWCNTs on the surface of the PAI hollow fiber membrane via a vacuum filtration method. The MWCNT immobilized membrane was then cross-linked with PEI to create the selective layer with MWCNTs seamlessly integrated. NF and FO performance evaluations corroborated the idea of MWCNTs as effective nanochannels to facilitate water transport in the selective layer. Last but not least, the amalgamation of rGO sheets and MWCNTs as all-carbon nanoarchitecture was presented in Chapter 6 to respectively leverage on their selective barrier and water nanochannels properties.

Generally, the membrane fabrication methods employed in the above-mentioned studies were specially selected with the notion of feasibility, scalability and ease of implementation as the core motivation. Detailed physicochemical characterization on all the CNMs and their modified membranes were also rigorously performed so as to substantiate all the findings and conclusions made. In conclusion, surface-modified CNM-based membranes are simple to fabricate with the unique water transport properties of the CNMs fully exploitable for enhancing membrane performances.

7.2. Empirical findings

The major findings and conclusions are thus summarized as follows:

- 1) Sandwich-architected PLA-graphene composite membranes demonstrated high barrier properties towards oxygen and water molecules. In particular, PLA-rGO showed a significant 87.6% decline in water vapor permeability with a reduction in oxygen permeability by two orders of magnitude. Mechanistic analysis attributed this to the extensive and tortuous diffusion pathway which can be up to 1450 times the thickness of the rGO barrier.
- 2) The freestanding rGO barrier, with thickness of several micrometers, exerts such a slow diffusion that it is rendered more suitable as a packaging film rather than a selective membrane for water purification. Furthermore, the resulting PLA-graphene composite membranes are scalable, easily processable and possess the robustness needed of packaging films for moisture and oxygen sensitive items such as food.
- 3) When the thickness shrinks to only several nanometers, the GO deposition serves as an effective selective barrier and can achieve 86% higher water permeability without sacrificing on membrane selectivity when used to substitute a part of the PEI cross-linked NF-like selective layer. The relatively lower hydrodynamic resistance of the GO sheets and their abilities to effectively fine-tune the pore size distribution of the NF membrane are the main value-adding factors.
- 4) Despite being only immobilized by electrostatic interactions, the GO deposition can withstand a backwashing pressure of 1 bar and a cross-flow rate of 600 mL/min (14 cm/s and R_e of ~ 870). In addition, by substituting a part of the PEI cross-linked

selective layer, the membrane post-treatment duration can be shortened from 90 to 30 min and the mechanical properties of the membranes can be enhanced by avoiding excessive cross-linking.

- 5) Unlike graphene-based materials, functionalized MWCNTs serve as effective water nanochannels instead. The water permeability of the membrane can be enhanced up to 44% in the NF process with inconsequential impact on the membrane selectivity when MWCNTs are integrated into the PEI cross-linked selective layer. As a result of this enhancement, the FO water flux can also be increased up to 29% in the active layer-facing-feed water orientation without compromising on the reverse salt flux when using 0.5 M MgCl_2 as the draw solution.
- 6) The functionalized MWCNTs create water nanochannels through two discrete routes. First, the nanogaps between the PEI polymer matrix and the outer walls of the MWCNTs can generate nanocorridors. Second, the inner channels of the MWCNTs can function as low friction water passageways. Both routes provide additional water transport through the PEI cross-linked selective layer. While the latter is more controversial, the former is believed to be more representative of the water nanochannels which enhanced the water permeability in the NF and FO process.
- 7) The all-carbon nanoarchitecture is a highly versatile design. As demonstrated by the changes in the water permeability and the microstructural parameters, the nanoarchitecture can be engineered from a graphene-rich to a CNT-rich type by intercalating more than 50 wt% of MWCNTs into the rGO sheets.

- 8) Different diameters MWCNTs give distinct separation performances when intercalated. With 80 wt% of 10 nm diameter MWCNTs intercalated, the water permeability can reach $52.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with almost 100% rejection rates towards methylene blue, acid orange 7 and rhodamine B solutes. This is 4.8 times that of the pristine rGO membrane and 5 to 10 times higher than most commercial NF membranes. On the other hand, its 50 nm counterpart exhibited much lower rejection rates as a result of the wider pore size distribution given the larger MWCNTs diameter.
- 9) The all-carbon nanoarchitectures demonstrate superior membrane stability to realize application of graphene-based membranes under practical hydrodynamic conditions. Notably, the nanoarchitecture with 80 wt% of 10 nm diameter MWCNTs endures turbulent hydrodynamic flow conditions up to 2000 mL/min cross-flow rate. This is equivalent to 2.22 m/s flow velocity and a R_e of 4667. Moreover, the membrane withstands a cross-flow rate of 500 mL/min (0.55 m/s and R_e of 1167) for at least 24 h, suggesting its good durability.
- 10) Physicochemical characterization reveals that the inner graphitic walls of the MWCNTs can serve as anchors for the nanoscale rGO foliates on the outer walls of the MWCNTs to interconnect with the assimilated rGO sheets via van der Waals attractions and π - π stacking interactions to instill this superior membrane stability. Without the inner walls as anchors, the nanoarchitecture quickly collapses in water like in the case when SWCNTs are used.

7.3. Recommendations and outlook

In the quest to achieve the ideal membrane for seawater desalination and water purification, the fabrication of efficient ultra-permeable membranes to realize high water transport and good selectivity has always been the main driving force. Similarly, the thesis is also driven by this same purpose. As already demonstrated in the previous chapters, CNMs have shown promising results in increasing the intrinsic water permeability of the membranes with good selectivity. However, does high water permeability equate to high apparent water flux? Is there really a potential of using CNMs for advancing high-performance membranes? These questions need to be appropriately addressed in order not to provide a distorted assessment of the real potential of these CNMs in membrane-based separations. Hence, the following sections are aimed at providing greater insights and recommending future research strategies to address these questions.

7.3.1. Concentration polarization

High water permeability does not necessarily mean high water flux operation. This is because solutes transported towards the membrane surface during retention tend to accumulate there, leading to a higher solute concentration near the membrane surface as compared to the bulk concentration. Consequently, there is an increase in the osmotic pressure at the upstream face of the membrane and this reduces the effective transmembrane pressure (TMP) driving force [213]. Such a phenomenon is known as concentration polarization (CP). Using a classical boundary layer film model and assuming absolute intrinsic rejection, the CP can be defined as [214]:

$$CP = \frac{C_m}{C_b} = \exp(J_w/K) \quad (1)$$

where C_m and C_b is the concentration of the solute at the membrane surface and bulk concentration respectively, J_w is the water flux, K is the mass transfer coefficient and $\exp(J_w/K)$ is defined as the CP modulus.

In addition, according to the solution-diffusion model, water flux through a RO membrane can be defined as [214]:

$$J_w = A(\Delta P - \exp(J_w/K) \cdot \Delta \pi) \quad (2)$$

where J_w is the water flux, A is the water permeability coefficient, ΔP is the TMP, K is the mass transfer coefficient and $\Delta \pi$ is the osmotic pressure difference between the membrane surface and the permeate water.

From equation (1), the CP modulus increases at a higher water flux and a reduced mass transfer coefficient. This in turn causes a reduction in the effective TMP which exerts a detrimental impact on the water flux as shown in equation (2). Furthermore, a simulation performed on the basis of absolute rejection and no fouling indicates that a membrane with a high A value only exhibits high water flux in the absence of CP (Figure 7-1). In the presence of severe CP (low K value), however, the apparent water flux can be seriously impeded despite the membrane possessing a high A value. Putting this into perspective, the state-of-the-art CNMs membranes, such as the vertically aligned CNT and single layer graphene membranes with high A values, may not demonstrate a high operational water flux if there is no way of mitigating and controlling CP.

Figure 7-1. Correlation of the apparent water flux with respect to the water permeability coefficient, A of the membrane.

7.3.2. Fouling

Similar to CP, fouling can severely negate the benefits of high water permeability. Fouling is typically classified into scaling, colloidal, organic and biofouling [214]. When fouling occurs on the membrane surface, an additional hydraulic resistance, known as fouling resistance (R_f), is incurred which results in a lower water flux. If constant flux operation is to be maintained, the TMP need to be increased. As such, the rise in TMP is also a mean to measure the extent of fouling. According to the classical osmotic pressure filtration model, the TMP is estimated as follows [215]:

$$\Delta P = J_w \mu (R_m + R_f) + CP \cdot \Delta \pi \quad (3)$$

where ΔP is the TMP, J_w is the water flux, μ is the viscosity of the solvent, R_m and R_f is the intrinsic membrane resistance and fouling resistance respectively, CP is concentration polarization and $\Delta \pi$ is the osmotic pressure difference between the membrane surface and the permeate water.

By replacing R_f in terms of J_w and substituting equation (1) into (3), the TMP can be represented as shown below:

$$\Delta P = J_w \mu [R_m + (J_w - J_{critical}) \cdot \alpha_f \cdot C_b \cdot t] + \exp(J_w/K) \cdot \Delta \pi \quad (4)$$

where $J_{critical}$ is the critical volumetric flux caused by the convective diffusion through the CP boundary layer, α_f is the volume fraction of the foulant layer, C_b is the bulk solute concentration, t is the filtration time and K is the mass transfer coefficient [216]. Equation (4) suggests that fouling is also flux-driven. This means that the higher the water flux, the greater the extent of fouling given a faster rise in the TMP (Figure 7-2).

Figure 7-2. Rate of the TMP rise of the RO system at different water fluxes. Adapted from [217].

Translating this into actual membrane-based operation using CNM-based membranes, the initial high water flux, which is driven by the intrinsically high water permeability, will not stay constant but decline with a greater extent of fouling taking place. Even state-of-the-

art CNM-based membranes, such as the vertically aligned CNT and single layer graphene membrane, have no means of escaping from these undesirable effects brought by fouling. Nevertheless, CNMs possess anti-fouling and anti-bacterial properties as described in Chapter 2. Table 2-1 and 2-2 also summarized a number of examples which demonstrated anti-fouling and anti-microbial effects when evaluated under bench-scale conditions. In spite of this, more evaluations on the anti-fouling and anti-microbial effects of these CNM-based membranes need to be scrutinized at a larger scale basis.

7.3.3. Recommendations

To control CP and mitigate membrane surface fouling, the use of hydrodynamic methods to create shearing at the membrane surface is a potential solution. By doing so, the CP boundary-layer thickness can be reduced which induce an increased mass transfer coefficient, K [218]. As illustrated in Figure 7-1, the higher the K value, the lower the extent of CP and the closer the water flux is to the intrinsic water permeability of the membrane. Similarly, the extent of fouling can be reduced since the thinner the CP boundary layer, the higher is the critical flux, $J_{critical}$, and the smaller will be the rise in the TMP as shown in equation (4) [215].

The utilization of cross-flow as a mean to introduce the feed solution is currently the most widely used method by the membrane community to introduce hydrodynamic shearing (Figure 7-3a). Besides that, other methods, such as unsteady-state shearing (Figure 7-3b and c), have also shown great promise in controlling CP and mitigating fouling. However, these methods would require the surfaces of the CNM-based membranes to handle a certain amount of shear stress. As demonstrated in Chapter 6, nanoarchitected membranes consisting of rGO and MWCNTs have provided preliminary results to suggest superior

membrane stability to deal with the shear stress brought by turbulent hydrodynamic cross-flows. Further studies like this should therefore be performed using CNM-based membranes to evaluate their stability under hydrodynamic shearing. In addition, molecular dynamic simulations can be employed to obtain optimized parameters for such studies. This will be especially useful for less robust membranes such as those state-of-the-art vertically aligned CNT and single layer graphene membranes. Another area of study could focus on the use of novel spacers to improve the mass transfer coefficient, K , in an effort to mitigate both CP and fouling [219]. In general, it is only through a greater understanding of how CP and fouling can be alleviated using hydrodynamic methods can more meaningful research efforts be directed on realizing high flux CNM-based membranes.

Figure 7-3. (a) Typical methods to reduce CP and membrane fouling; (b) Enhancement factor as a function of the average shear rate γ_{ave} and (c) the specific power consumption for different unsteady-shear methods, demonstrating the potential of using unsteady-shear methods as an effective and lower power consumption methods to mitigate CP and fouling. Adapted from [218].

In Chapter 2, it is highlighted that surface-modified and mixed-matrix CNM-based membranes are easier to scale-up but possess less than optimal separation performances. On the contrary, elegant and state-of-the-art CNM-based membranes have demonstrated performances several orders of magnitude higher than theoretical hydrodynamic models but their scale-up fabrications have always been a persistent problem. Therefore, there is an urgent need to research on ways to produce these membranes in large-scale. These include large-area synthesis of vertically aligned CNT forests, uniform and large-area post-synthesis alignment of CNTs, defect-free synthesis of large-area single layer graphene, large-area transfer of single layer graphene onto different substrates and controllable techniques to produce tunable and evenly distributed pores with a narrow pore size distribution on single-layer graphene. If these are achievable, novel modules to house and evaluate these large-area, state-of-the art membranes need to be designed and optimized as opposed to the current small area testing devices.

Last but not least, the cost-effectiveness of the CNMs needs to be taken into consideration. Graphene-based materials generally are more competitive in terms of prices as compared to CNTs given that the precursor of GO sheets comes from inexpensive graphite flakes. Nevertheless, with more efficient scale-up production of CNTs [90], the prices of CNTs, especially MWCNTs, will continue to drop and stay affordable for applications into devices [212]. Nevertheless, the prices of CNM-based membranes will not be as competitive as the well-established polymeric membranes in the near future. To make up for this, multifunctionalities can be easily and precisely incorporated into CNM-based membranes by respectively intercalating and grafting functional spacers and gate-keepers as highlighted in Chapter 2. The ease and precise incorporation of desired functionalities into customized membranes will allow the CNM-based membranes to find their places in niche separation

applications and hopefully get a fair share of the potential market. Therefore, greater research efforts can be strategized on creating and tailoring multi-functional CNM-based membranes to realize a built-to-order concept for separation membranes.

7.3.4. Outlook

Overall, the development of CNM-based membranes has been deemed as revolutionary in terms of potential performance enhancement but has little commercial viability given the many technical difficulties in their scale-up fabrication (Figure 7-4a) [48].

Figure 7-4. (a) Comparison of the potential performance and commercial viability of nano-enabled membranes. Adapted from [48]. (b) Evolution of the RO water permeability over time, showing the potential and practical standing of the ultra-permeable membranes. Adapted from [15].

If these technical difficulties can be overcome by technological advances, the ultimate performances of CNM-based membranes will still be well below the potential which they can offer given the limits defined by the hydrodynamic constraints. As demonstrated by the RO water permeability in Figure 7-4b, the practical upper limit of CNM-based membranes, as

proposed by A. G. Fane and co-workers, can never reach their maximum potential due to limitations in mass transfer. Despite this, the authors proposed a 5 folds enhancement in the water permeability, on top of the other competitive advantages offered by CNM-based membranes, as a feasible target for the RO process [15]. Indeed, CNMs, with their unique water transport properties, have shown interesting potential to be applied for membrane-based separations. By carefully addressing each and every challenge, CNM-based diffusion barriers as realistic high-performance membranes will be able to provide fast water permeation and good selectivity to help advance one of the world's most pervasive issues.

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