REDUCED GRAPHENE OXIDE MEMBRANES: APPLICATIONS IN FOG COLLECTION AND WATER PURIFICATION

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ABSTRACT

Reduced graphene oxide membranes: fabrication and applications

Bo Tang

Reduced graphene oxide (rGO) has attracted considerable interest recently as the low cost and chemical stable derivative of pristine graphene with application in many applications such as energy storage, water purification and electronic devices. This dissertation thoroughly investigated stacked rGO membrane fabrication process by vacuum-driven filtration, discovered asymmetry of the two surfaces of the rGO membrane, explored application perspectives of the asymmetric rGO membrane in fog collection and microstructure patterning, and disclosed membrane compaction issue during water filtration and species rejection. In more details, this dissertation revealed that, with suitable pore size, the filtration membrane substrate would leave its physical imprint on the bottom surface of the rGO membrane in the form of surface microstructures, which result in asymmetric dynamic water wettability properties of the two surfaces of the rGO membrane. The asymmetric wettability of the rGO membrane would lead to contrasting fog harvesting behavior of its two surfaces. The physical imprint mechanism was further extended to engineering pre-designed patterns selectively on the bottom surface of the rGO membrane. This dissertation, for the first time, reported the water flux and rejection kinetics, which was related to the compaction of the rGO membrane under pressure in the process of water filtration.
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<th>Full Form</th>
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<tbody>
<tr>
<td>2D</td>
<td>2 dimensional</td>
</tr>
<tr>
<td>AAO</td>
<td>anodized aluminum oxide</td>
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<tr>
<td>ACA</td>
<td>advancing contact angle</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>BOE</td>
<td>buffered oxide etch</td>
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<tr>
<td>CA</td>
<td>contact angle</td>
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<td>CAH</td>
<td>contact angle hysteresis</td>
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<tr>
<td>CNT</td>
<td>carbon nanotube</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DFT</td>
<td>density function theory</td>
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<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<tr>
<td>DRIE</td>
<td>deep reactive-ion etch</td>
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<td>EB</td>
<td>Evans blue</td>
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<td>FE</td>
<td>field emission</td>
</tr>
<tr>
<td>FED</td>
<td>field emission display</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GO</td>
<td>graphene oxide</td>
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<tr>
<td>HFM</td>
<td>hollow fiber membrane</td>
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<td>KAUST</td>
<td>King Abdullah University of Science and Technology</td>
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<td>MB</td>
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<td>molecular dynamics</td>
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<td>polyethylene terephthalate</td>
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<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
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<td>PVDF-HFP</td>
<td>polyvinylidene fluoride-co-hexafluoropropylene</td>
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<tr>
<td>RCA</td>
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<td>reduced graphene oxide</td>
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<tr>
<td>RB</td>
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<td>RO</td>
<td>reverse osmosis</td>
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<tr>
<td>SCA</td>
<td>static contact angle</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SOI</td>
<td>silicon on insulator</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TFC</td>
<td>thin film composite</td>
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<tr>
<td>UF</td>
<td>ultrafiltration</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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CHAPTER 1. INTRODUCTION

1.1 History of water treatment

Water scarcity is a serious global challenge nowadays and it is predicted to be worsened in the years to come as societal demand for freshwater continues to rise due to increased industrialization, population growth along with steadily improved life quality\textsuperscript{1-8}. In addition, rapidly emerging is another global challenge of contamination of water sources. According to recent study, currently 1.2 billion people lack access to safe drinking water\textsuperscript{4}. Furthermore, the ever increasing awareness of public health has increased water safety standards which drives more efforts and resources to treat water that was previously considered safe and clean\textsuperscript{1, 4, 9-12}. Given the vast bulk of the water to be treated to meet these requirements, low-cost and energy efficient water treatment technologies have been being highly sought after to keep pace with the development of human civilization throughout of the human history, but are generally falling short of expectations\textsuperscript{1, 13-16}.

The first record of water treatment was dated back to 2000 BC in ancient Greek and Sanskrit region\textsuperscript{17-19}. Sand and gravel filtration, straining, and boiling were used to produce drinking water\textsuperscript{17-19}. At around 1500 BC, coagulation was invented by ancient Egyptians and Alum (KAl(SO\textsubscript{4})\textsubscript{2}·12H\textsubscript{2}O) was employed as coagulant to destabilize particulate matters in water\textsuperscript{20-21}. The first bag filter was invented by Hippocrates in 500 BC to trap sediment in water\textsuperscript{22-24}.
No significant progresses were achieved in the next one and half century or so after the fall of the Western Roman Empire (between 4th century and 17th century). The water filter made of wool, sponge and charcoal was first applied for domestic water treatment application in 17th century. The first slow sand filter based water treatment plant was designed by Robert Thom in Scotland in early 19th century. Chlorination based water disinfection technique was first adopted by British scientist John Snow in 1900s to control waterborne diseases such as, cholera and typhoid. Chlorination of drinking water has since had major impacts on the incidence of waterborne disease worldwide and it, along with filtration, has been credited for a large part of the 50% increase in life expectancy in developed countries during the twentieth century and thus are hailed as one of the most significant public health advances of the millennium. It was not until the 1940s when drinking water standards were applied to municipal drinking water.

1.2 Membrane based water treatment technology

1.2.1 The rise of membrane based separation

In the last century, with the booming of food, biotechnology and pharmaceutical industries, the conventional separation technologies, such as, distillation, sublimation, crystallization, adsorption, became either less efficient or impossible to meet some special needs from these industries. For example, these conventional methods fail to work where the components are miscible and generate an azeotropic system. The membrane based separation came into being first in early 1900s to aid the development in these industries.
Compared to the traditional separation technologies, membrane based one has its niche benefits. (1) Membrane separation is largely physical and both permeate and retentate can be collected and utilized, which has a special meaning nowadays in wastewater treatment as there is a growing interest in recovering valuable resources, including water, nutrient, energy, etc., from municipal and industrial wastewaters. As resource recovery will be an integral part of wastewater treatment in the coming decades, the importance of membrane in water treatment cannot be overstated. (2) By employing membranes with different pore sizes or separation mechanisms, membrane separation provides fit-for-purpose products, which offers flexibility and precise separation at the lowest energy cost and thus vastly boosts the separation energy efficiency. Nowadays, available membranes range from microfiltration to reverse osmosis and by choosing suitable membranes for the same separation, 5-10 times less energy consumption can be generally expected than its conventional counterparts1,3. (3) From the engineering point of view, membrane based separation system requires 50-70% less space than most of the conventional technologies for the same purpose of separation34. All these advantages make membranes essential tools to the future water treatment industry.

Generically, according to the molecular size cutoff by membrane, membrane based separation is classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and forward osmosis (FO) and reverse osmosis (RO)32. MF is the process in which molecules over 100 nm are retained by membrane, UF is from 2 to 100nm for retentate,
NF is up to 2 nm, and RO and FO is a process where only solvent permeates\textsuperscript{32} (Figure 1.1).

![Filtration Spectrum](image.png)

Figure 1.1: The filtration spectrum from microfiltration to reverse osmosis and the size of the common objects\textsuperscript{32}.

1.2.2 Brief history of modern membrane technology

In 1962, Loeb-Sourirajan invented so called asymmetric membrane, which heralded practical membrane applications\textsuperscript{35-37}. The first commercialized MF and UF membranes were established in 1970s\textsuperscript{32}. The industry-popular polyamide thin film composite (TFC) RO membrane was invented in 1981 by Cadotte and it has since been widely used around the world\textsuperscript{38-39}. The term “nanofiltration” was firstly proposed in 1984 to solve the terminology problem for a selective reverse osmosis process that allows ionic solutes in a
feed water to permeate through a membrane (Figure 1.2)\textsuperscript{32, 40}. NF membranes started to be commercialized in the market from 1990 and the technology has since been widely used. RO and NF are among the most investigated membrane separation processes due to their significance in a variety sectors, including water, food, energy\textsuperscript{1, 3, 41}. The RO membranes possess high rejection of all ions, but have to be operated under high pressure to overcome osmotic pressure, leading to their low flux\textsuperscript{38-39, 42-43}. On the other hand, the key distinguishing characteristics of NF membranes are low rejection of monovalent ions, high rejection of divalent ions and higher flux compared to RO membranes. These properties have allowed NF to be used in niche applications in many areas including water and wastewater treatment, pharmaceutical and biotechnology, and food processing\textsuperscript{32, 40}. 

1.2.3 Current facts and challenges of NF and RO

Most of the NF and RO membranes are made of polymers such as cellulose, polyamide and polysulfone and so on. Currently there are two major forms of NF and RO membranes commercially available, TFC membrane and hollow fiber membrane (HFM). A typical TFC membrane is composed of three parts, a thin, dense and selective top layer, a thick and porous support layer, and a bottom layer usually made of porous fabric such as polyester for holding the whole structure (Figure 1.3a). In most of the commercial RO membranes, the selective top layer is a thin polyamide membrane with a thickness of around a few hundred nanometers; the top selective thin film sits closely on the support layer which is generally made of polysulfone and possesses microporous structure with pore size around hundreds of nanometers. The support
layer does not contribute to the species rejection and it is the top selective layer where the separation occurs. A typical HFM consists of separation layer, macroporous layer and skin layer (Figure 1.3b). The position of the separation layer and skin layer can either be outside or inside depending on the membrane design whether it is out-in or in-out mode\textsuperscript{44-47}.

![Figure 1.3: The schematic diagram of TFC membrane and HFM. (a) Sketch of a typical commercialized TFC membrane composed by selective layer, microporous support layers and nonwoven net reinforcing fabric bottom layer. \textsuperscript{51} (b) Sketch of a typical in-out mode HFM which is consisted of skin layer, macroporous support and the separation layer.](image)

The major concern with both NF and RO processes is their high energy consumption caused by high operation pressure, which is in turn enforced by the need for high water flux\textsuperscript{51}. As discussed earlier, polymeric membranes are currently dominating the global membrane market for RO and NF processes, but there exist limitations in permeability and selectivity of polymeric membranes which are so called as the upper bound and are related to their intrinsic membrane material properties. For the polymeric membranes in NF and RO, there is a strong trade-off between species permeability and membrane selectivity. Moreover, the trade-off between permeability and selectivity is exacerbated by our inability of producing polymeric RO and NF membranes thinner than what is
currently available (i.e., a few hundred nanometers). Also, the polymeric membranes are susceptible to damage upon exposure to organic solvent, oxidative environment, and high temperature.

1.2.4 Nanomaterial-assisted polymeric membranes for water treatment

While actively searching for new membrane materials, the researchers are also looking for ways of improving the available polymeric membranes by means of nanotechnology. Mass transport in membrane is inherently nanoscale where the transport of water and salts across the membrane primarily depends on the chemical properties as well as physical structures of the membrane at nano- to microscales, and thus the application of nanotechnology to selectively target either enhancing or decreasing these interactions between the membrane and the species would be well suited and beneficial. So far, the nano-assisted polymeric membrane based filtration has produced some solid progresses, which generally is based on incorporation of some conventional hydrophilic nanomaterials, such as silica and zeolites, into the matrix of the polymeric thin film top layer with an expectation to introduce new water channels without sacrificing the membrane selectivity at the same time. For example, Hoek et al. fabricated a zeolite blended polyamide active layer on top of a polysulfone support, which exhibited a water flux twice that of the non-modified membrane under an optimized zeolite particle loading without decreasing the salt rejection rate\textsuperscript{52}. Due to the hydrophilicity and thermal stability of silica, in 2008, Singh et al. blended silica nanoparticles (16 nm and 3 nm) into the polyamide active layer in a RO membrane and reported a water flux increase of 200% with the same level of salt rejection under an optimal nanoparticle loading (21.3 vs. 9.0 L
m$^{-2}$ h$^{-1}$ with and without the silica blending). Later, Deng et al. incorporated mesoporous silica MCM-41 into a polyamide active layer and recorded a water flux of 46.6 L m$^{-2}$ h$^{-1}$ in comparison to 28.5 L m$^{-2}$ h$^{-1}$ without MCM-41. They suggested that the internal pores of MCM-41 contributed significantly to the increase in water permeability$^{54}$.

In 2001, Hummer et al. reported a molecular dynamics (MD) simulation result that showed water molecules were able to rapidly move through the interior of carbon nanotubes with a pulse-like transmission behavior$^{55}$ and, in 2003, their MD simulation result further showed that water molecules may flow through membranes of vertically placed and open-ended CNTs under an osmotic gradient in an almost friction-less manner and the resultant water flow rate was comparable to those measured for biological water channels such as aquaporin$^{56}$. These results were effort-provocative. In 2011, Zhang et al. synthesized a functionalized multi-walled carbon nanotubes (MWCNTs)-incorporated polyamide-based active layer in a RO membrane, which exhibited a significantly increased water flux, from 26 L m$^{-2}$ h$^{-1}$ with the original membrane to 71 L m$^{-2}$ h$^{-1}$ with the MWCNTs-blended membrane$^{57}$. The frictionless CNT channels with precisely controlled pore entries could simultaneously facilitate the fast transport of water molecules and offer exceptional salt ion rejection capability. Kim et al. demonstrated that thin film RO nanocomposite membranes containing well-dispersed functionalized CNTs possessed tremendously high water flux and salt rejection that was comparable to that of without CNTs, which can be attributed to the hydrophobic nanochannels of CNTs$^{58}$. However, the efforts in fabricating pure inorganic vertical CNT array based membrane are met with very limited success due to the technological difficulty in obtaining high
purity CNT with both ends open, in placing individual CNT uniformly vertical, and in sealing the intertubual space.

1.3 Rise of graphene and graphene based membranes

It is an endless effort in membrane field to find ways to break the upper bound of the current membranes. Given the impasse with the polymeric membranes, the research attention is being diverted to materials others than polymers. As it is well known, water flux of a membrane is negatively related to its thickness. A thinner inorganic material based membrane in RO and/or NF, if successfully fabricated, would offer a higher water flux than the current polymeric RO and/or NF membranes. According to simulations, the theoretical flux can as high as 300 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) in RO processes if the separation layer is only one atom thick\(^{42,59}\). Two dimensional (2D) inorganic materials seems a good candidate in this situation. Among all of the known 2D materials, graphene attracts the most of the research attentions right now\(^{42,59}\).

1.3.1 Introduction to graphene

Graphene is a form of carbon consisting of planar sheets which are one atom thick, with the atoms arranged in a honeycomb-shaped lattice with sp\(^2\) hybridization\(^{61}\) (Figure 1.4). The delocalized electron clouds of \(\pi\)-orbitals occupy the voids of aromatic rings in a graphene sheet. The monolayer of graphene was successfully isolated by Geim and Novoselov in 2004 via mechanical exfoliation using Scotch tap method.
Many remarkable properties of graphene have since been reported: a large theoretical specific surface area of 2630 m$^2$ g$^{-1}$, high intrinsic electron mobility $\sim$200 000 cm$^2$ V$^{-1}$ s$^{-1}$, high Young’s modulus $\sim$1.0 TPa, thermal conductivity $\sim$ 5000 Wm$^{-1}$K$^{-1}$, and its optical transmittance $\sim$97.7%$^{61-63}$. These attractive properties of graphene have led to its presence in a variety of fields: catalysis$^{64-67}$, supercapacitor$^{68-72}$, battery$^{73-78}$, field-effect-transistor$^{62, 79-84}$, memory devices$^{85-90}$, photovoltaic devices$^{91-96}$, molecular sensing$^{96-98}$, etc.

At first, graphene was attractive for molecular separation membrane because of its atomic thickness, high mechanical strength, and chemical inertness. By theory, the only one-atom thickness and nearly frictionless surface enables them to form membranes that minimize the transport resistance and maximize permeate flux$^{42, 99-100}$. Unfortunately, theoretical calculation indicates that there is no gap in the electron-density around the aromatic rings of the carbon atoms in graphene to allow any molecule to pass$^{99, 101}$. Thereby graphene is expected to effectively prevent the permeation of even the smallest molecule$^{102-103}$. Bunch et al. first experimentally tested the permeation of several gases through a micro-chamber capped with a graphene sheet mechanically exfoliated from...
Kish graphite and the monolayer graphene membrane was demonstrated to be impermeable to helium\textsuperscript{104}. Therefore, the impermeability of graphene at its pristine state for any molecule makes it ideal barrier layer many applications.

1.3.2 Porous single or multi-layer graphene based membranes

The complete impermeability of graphene at its pristine state does not prevent creative ideas from being developed to push graphene into molecular separation membrane. In 2009, by using first-principle density functional theory (DFT) calculation, Jiang et al. investigated the gas permeability and selectivity of nanoporous graphene membranes bearing designed sub-nanometer pores\textsuperscript{99}. The simulation results indicated that high selectivity on the order of $10^8$ and $10^{23}$ for H$_2$/CH$_4$ could be achieved with nitrogen and hydrogen functionalized pores on single layer graphene, respectively\textsuperscript{99}. This work provoked some experimentalists to explore ways of making precise and nanometer pores on single or few layer graphene sheets.

In the year of 2012, Koenig et al. utilized an ultraviolet-induced oxidative etching technique to create sub-nanometer-sized pores in micrometer-sized graphene sheets and found that the resulting nanoporous graphene membranes acted as excellent molecular sieves toward various gases\textsuperscript{105}. In the year of 2014, free-standing, physically perforated double-layer graphene membranes were successfully fabricated by Celebi et al. and the graphene membranes contained nanopores with narrowly distributed diameters ranging from $<10$ nm to 1 μm (Figure 1.5a) made via focused ion beam\textsuperscript{106}. The measured
transport rates through the porous double-layer graphene membranes were in agreement with the previous predictions from the transport theories (Figure 1.5b and c).

With regard to the application to water desalination, using MD simulation, Cohen-Tanugi and Grossman showed that the nanometer-sized pores in single layer graphene can effectively desalinate NaCl from water and the desalination performance depended critically on the pore size and chemical functional groups terminating the edge of the nanopores. The water permeability of the nanoporous graphene was several orders of magnitude higher than the state-of-the-art polymeric RO membranes which is as less as ~1 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). This simulation result is the first in indicating that nanoporous graphene is promising for future water desalination. Recently, an experimental breakthrough was made by Surwade et al. in nanoporous graphene membranes for water desalination. In this work, nanometer-sized pores were created (Figure 1.5d) on monolayer graphene sheets via oxygen plasma etching process and the resulting nanoporous graphene membranes exhibited a salt rejection of nearly 100% while allowing fast water transport (Figure 1.5e and f). O’Hern et al. showed that the nanopores can also be obtained on single layer graphene by using hot ion bombardment (Figure 1.6a) and the as-made nanoporous graphene would have a rather uniform pore size distribution around ~1 nm, which can successfully reject molecular dyes but allow potassium and chloride ions to pass through (Figure 1.6b and c). It is worth pointing out that, without any exception, the results from the above single or few layer graphene membrane based water filtration (1) were all based on special and in many cases forgiving and unrealistic experimental conditions; (2) required extreme care during
operations to avoid damage and leak pathways in the systems; (3) relied on the effective transport areas in the range of several square micrometers due to the size of pristine graphene sheet.

Figure 1.5: (a) The comparison of H\textsubscript{2}/CO\textsubscript{2} separation of nanoporous graphene with other separation membrane. The insert shows the 7.6-nm-wide apertures perforated by He focused ion beam. (b) Comparison between water permeance through nanoporous graphene with other membranes\textsuperscript{102}. (c) Comparison between water vapor permeance through nanoporous graphene with other membranes. (d) The schematic diagram of the nanopore fabrication process. The insert shows the single layer graphene is exposed to oxygen plasma for a certain amount of time and is mounted on top of a 5 µm diameter hole. (e) The relationship between water loss and ionic conductivity across the nanoporous graphene membranes as the function of I\textsubscript{D}/I\textsubscript{G}, C1 and C2 are the control experiment of graphene with large tears/fraction and completely broken. (f) The relationship between the H\textsubscript{2}O/KCl selectivity as the function of I\textsubscript{D}/I\textsubscript{G}.\textsuperscript{107}
Figure 1.6: (a). Schematic diagram of the process creating nanometer holes on graphene using hot ion bombardement. (b) The flux as the function of etch time through nanoporous graphene with the normalized flux at 120 min etch time and the corresponding membrane potential mesurements (0.5 M KCl/0.1667 M KCl).(c) The schematic diagram of selective transport through graphene membranes at various etch times. 

Although nanoporous single or few layer graphene membranes exhibit supreme performance in separation, they are hard or even impossible to be scaled up for industrial-scale applications. More specifically, synthesis of large sized graphene sheet with high density of controlled nanopores is still a great challenge. The yield of the well-developed chemical vapor deposition (CVD) technique in producing large area, high-quality and mechanical robust monolayer graphene sheets is far from being satisfying and so far a non-destructive post-transfer process is lacking which leads to constant introduction of undesired defects into the graphene sheets during the transfer. In addition, the available nanopore drilling techniques are all at their infant stages and need a lot of improvement in order to drill regularly shaped nanopores with well-controlled and narrowly-distributed sizes. The uniform pore size is beneficial for
minimizing the stress concentration effect and enhancing the mechanical strength of nanoporous graphene membranes.

1.3.3 Graphene oxide as a substitute of pristine graphene

In light of the challenges of producing pristine and defect free graphene, graphene oxide (GO) and reduced graphene oxide (rGO) have recently attracted a lot of research interest in various fields. GO is a compound of carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities (e.g., hydroxyl, epoxy, carbonyl, carboxyl groups, etc.) are introduced in the graphite structure which not only expand the layer separation, but also makes the material hydrophilic. This property enables the graphite oxide to be exfoliated in water using sonication, ultimately producing GO, single or few layer graphene with defects and a lot of oxygenated groups.

The synthesis of GO has a history dated back one and half century ago. The first investigation was in the year of 1859 when Brodie found the carbonic oxide by accidentally oxidizing graphite flakes using potassium chlorate and nitric acid. Afterwards, L. Staudenmaier improved Brodie’s KClO₃-fuming HNO₃ preparation by adding the chlorate in multiple aliquots over the course of the reaction. Then Hummers and Offeman developed a new approach using a stronger oxidant of potassium permanganate with concentrated sulfuric acid and achieved similar oxidation rate and this method has been well known as Hummers method. The improved Hummers method
recently reported by James et al. uses phosphoric acid as a replacement for nitric acid\textsuperscript{129}. It is found that the final yield of the GO by the improved Hummers method can be 3 times that of the regular Hummers method\textsuperscript{129}. Also given the less toxicity of phosphoric acid as reactant and NOx as product, the improved Hummers method is and will be widely adopted\textsuperscript{129}.

The most attractive advantages of GO is that (1) it can be prepared in a large scale and at a large quality in a solution based process, which is especially true with the improved Hummers method. This is partially the reason why GO is being wide used as a common and inexpensive substitute to graphene and the industrial scale production of GO has been available. (2) Due to the oxygen functionalities, GO has an easy dispersability in water (Figure 1.7a) and other organic solvents, as well as in different matrixes. This remains as a very important property when mixing the material with ceramic or polymer matrixes when trying to improve their electrical and mechanical properties. GO flakes can be readily dispersed in water by sonication and the GO flakes in water can be easily restacked into a macroscopic lamellar membrane via various methods such as drop-casting\textsuperscript{85}, spin-coating\textsuperscript{130}, and vacuum filtration\textsuperscript{110, 131-133}, which would be otherwise impossible with pristine graphene due to its intrinsic hydrophobicity. Figure 1.7b and c present a typical setup of vacuum-driven filtration of making GO membrane from a stable GO in water dispersion, along with a digital photo of a stacked GO laminate membrane made in our group at KAUST. The SEM image (Figure 1.7d) confirms that the membrane consists of stacked GO flakes, which is schematically presented in Figure 1.7e.
The resulting GO stacked laminate membranes possess excellent mechanical strength compared to single or few layer graphene sheet membranes. Consequently, the as-prepared GO membranes can be detached from the filtration substrates to form freestanding membranes, which opens some new applications of graphene based membranes48, 134-136.

1.3.4 Possible water transport mechanisms within stacked GO membrane

The groundbreaking discovery of the unique mass-transport properties of the stacked GO membranes was first reported by Nair et al. in 2012 and in this work the sub-micrometer thick stacked GO membranes were found completely impermeable to liquids, vapors, and
gases but allowed unimpeded permeation of water vapor\textsuperscript{130}. This pioneering work indicates that the stacked GO membranes involve unique mass transport mechanism that favors water permeation, which inspired a lot of research effort from a number groups to follow up.

1.3.4.1 Inter-layer channels for molecular transport

Nair et al., believe that the anomalous water transport through the helium-leak-tight graphene-based membranes was resulted from a capillary-like driving force and low friction flow confined between the 2D inter-layer channels of the graphene sheets (Figure 1.8a and b)\textsuperscript{130}. Inside the stacked GO membrane, the pristine graphene regions without functional groups possess frictionless carbon walls, which are responsible for the fast transport of water. More hydrophobic liquids, such as isopropanol, ethanol, hexane, cyclohexane, and toluene, lead to lower flux through the membrane than water due to their greater interaction with the graphene walls.
In 2014, it was further reported by Geim et al. that the micrometer thick stacked GO membranes (Figure 1.9a and b) blocked all solutes with hydrated radii larger than 4.5 Å (Figure 1.9c and d), while smaller ions permeated at rates thousands of times faster than what is expected for simple diffusion\textsuperscript{131}. The membrane was mounted between the two separated chambers with feed and permeate (Figure 1.9a and b). They claimed that the interlayer space between the GO sheets became expanded when the membranes were soaked in water. In the dry state, stacked GO membranes are vacuum-tight, with a typical inter-layer spacing of 9 ± 1 Å, while in water, the oxygenated groups can absorb a large number of water molecules and subsequently expand the interlayer space to more than 13 Å\textsuperscript{131} which allows the mono valent and some divalent hydrated ions to pass through (Figure 1.9c). The expanded interlayer space thus provides channels for transporting certain small molecules with suitable molecular sizes. To this end, by the authors, the
transport of water and other species within the micrometer thick stacked GO membranes involves only the interlayer space as the sole mass transport pathway and the contribution from intrinsic defect-type holes is not insignificant.

Figure 1.9: (a) Photograph of a GO membrane covered by 1-cm diameter opening in a copper foil. (b) Schematic of the experimental setup. A U-shaped tube of 2.5 cm in diameter is divided by the GO membrane into two compartments referred to as feed and permeate. Each is filled to a typical level of ~20 cm. Magnetic stirring is used so as to ensure no concentration gradients. (c) Permeation through a 5-μm-thick GO membrane from the feed compartment with a 0.2 M solution of MgCl₂. (Inset) Permeation rates as a function of concentration in the feed solution. The chloride rates were found the same for MgCl₂, KCl, and CuCl₂. Dotted lines are linear fits. (d) Sieving spectrum in atomic-scale. The shown permeation rates are normalized per 1 M feed solution and measured by using 5-μm-thick membranes. No permeation could be detected for the solutes shown within the gray area during measurements lasting for at least 10 days. The thick arrows indicate our detection limit, which depends on a solute. Several other large molecules—including benzoic acid, DMSO, and toluene—were also tested and exhibited no detectable permeation. The dashed curve is a guide to the eye, showing an exponentially sharp cutoff at 4.5 Å, with a width of ~0.1 Å⁻¹.
1.3.4.2 Defect-type pores for molecular transport

Besides the interlayer channels, intrinsic defects in the GO sheets have been proposed as possible mass transport channels by some researchers. Li et al. reported that in an experiment of ultrathin GO membranes for selective hydrogen separation, the major gas transport pathway was structural defects within GO sheets and the work downplayed the role of the inter-layer spacing in the mass transport. The results showed that, with narrowed interlayer spacing of the stacked GO membranes by reduction, water permeation decreased approximately three orders of magnitude, but no obvious gas permeation change was found. In the meantime, Kim et al. also reported that by heating up GO, the surface defects size increased, and as a consequence, gas permeate flux increased but without sacrificing separation factor. In 2016, Grossman et al. used MD and simulated the defects on GO as a transport mechanism (Figure 1.10).

Figure 1.10: The MD simulation indicates that some of atoms of GO, in the process of thermal annealing, are removed, resulting in nanopores formed in the planar of GO with a variety of sizes. From left to right, these three figures exhibit three temperature conditions from low to high respectively. All structures are represented as ball and stick with carbon, oxygen and hydrogen atoms in grey, red and white color, respectively.
1.3.4.3 Functional groups for facilitating molecular transport

Recently, functional groups on GO have been proposed as another possible transport mechanism. It is believed by some that oxygen-containing functional groups on the basal plane and edge of GO would interact with water molecules to form hydrogen bonds (Figure 1.11), prohibiting fast water transport through the GO membranes. The bright side of this can be that these hydrophilic groups are able to selectively adsorb water molecules from solvent-water mixtures and thus can enhance pervaporation performance of the stacked GO membranes for solvent dehydration. Other scientists believe that the presence of negatively charged groups on GO could afford electrostatic interaction with the charged molecules.

Figure 1.11: The oxygen containing functional group on the basal plane of GO structure.

As can be seen from the above discussions, our understanding of the transport mechanisms within the stacked GO membranes is very limited and all of the proposed theories are under debate. So far, there is no single one that is dominant, which openly invites research efforts to unravel the mystery.
1.4 Selection of reduced graphene oxide

Although the recent progresses in the stacked GO membrane based water filtration, there are still some pivotal challenges. (1) The interspacing in the stacked GO membranes has a low limit of near 10Å which allows hydrated ions such as sodium, potassium to pass through\textsuperscript{131}. (2) The high water dispersability of GO is two-bladed sword, which makes easy membrane fabrication by such methods as vacuum filtration of an GO in water dispersion, but inevitably leads to the instability of the as-prepared stacked GO membrane in water\textsuperscript{146}. It was found that GO membrane would gradually dissemble in water due to its hydrophilicity, leading to a short lifetime of the stacked GO membrane in practical applications\textsuperscript{146}. (3) GO is susceptible to reduction under ambient conditions. The sun light irradiation and hot water have been reported to cause the reduction of GO\textsuperscript{85, 114, 122, 147-148}.

The drawbacks associated with GO leads our attention to a more water stable graphene substitute: rGO. As a matter of fact, GO can be readily reduced to rGO. The chemistry of reducing GO to rGO has been intensively studied. The common reducing agents include hydrazine\textsuperscript{148}, ethylenediamine, ascorbic acid\textsuperscript{147}, hydroiodic acid\textsuperscript{85, 134, 149}, and hydrogen gas\textsuperscript{85}. Apart from chemical agents, GO can also be reduced to rGO via physical process, such as ultraviolet laser impulse treatment and via electrochemical reduction as well\textsuperscript{114, 122}.

The reduction leads to the partial removal of the oxygen functional groups of the GO and thus greatly improved hydrophobicity and water stability of rGO. As a matter of fact, a
prefabricated stacked GO membrane can be readily reduced to rGO membrane by chemical reduction without degrading its structural integrity. In addition, the higher water stability of rGO membrane makes a possibility of stable and untrathin (less than 20 nm) rGO membranes.

So far, there are limited literature reports available on rGO membrane based water filtration. Ultrathin rGO NF membranes was first reported by Han et al. using vacuum-assisted filtration of base-refluxed rGO dispersion on porous substrates (Figure 1.12a). The water filtration performance of the stacked rGO membranes was evaluated on a dead end filtration device using pressure driven separation. The results showed that the as-prepared stacked rGO membranes possessed high water flux, high rejection rate over 99% for organic dyes (Figure 1.12b) and moderate rejection from 20% to 60% for salt ions (Figure 1.12c). In 2014, Geim et al. reported that a 1 micrometer thick stacked rGO membrane was impermeable to water, which, according to the authors, was due to the interspacing being reduced to 0.4 nm after reduction from GO. A 0.4 nm interspacing literally eliminates water channel through the interlayer space (Figure 1.12d and e). Although some argue that since the interlayer spacing can be further reduce down to ~6Å for rGO membrane, smaller than the size of sodium ion, rGO membrane holds hope for seawater desalination. Unfortunately there hasn’t been any convincing experiment results so far to support this argument.
Figure 1.12: (a) The top figure represents base refluxed GO membrane fabricated on AAO (left) and PVDF (right) substrate, to the bottom is the scheme of the chemical composition of rGO (b) The absorbance shows the rejection performance of the methylene blue (MB). The insert is the comparison between the feed and permeate. (c). The rejection test using different salt. (d) The weight loss of water that is sealed by the different membrane. The water vapor evaporates through the GO laminates and HI rGO is completely impermeable to water vapor. (e) The permeability of water through each membrane.

In 2015, Liu et al. demonstrated that rGO membranes reduced with HI exhibited high rejection toward both organic and inorganic species, but allowed rapid transport of water in a forward osmosis filtration process, which is contradictory to the results from Geim et al., who reported impermeability of rGO membranes for water.

1.5 Aims and scope of the dissertation

Through the review of the recent studies, we come to the belief that rGO has a great potential for water filtration. However, the rGO membrane for water filtration is at a very
early stage and the results in the field can be in many cases contradictory and there remain many questions to be answered. This dissertation is aimed at addressing the following topic: the origin of asymmetric wettability of rGO membrane, the microstructure patterning of rGO membrane, the asymmetric fog collection, and filtration kinetics of rGO membrane.

Despite vacuum-filtration being used to make stacked GO and thus rGO membranes, one aspect of the vacuum-filtrated membranes is generally overlooked. A vacuum filtrated GO and thus rGO membrane has two surfaces, which are formed at different interfaces. Taking GO as an example, at the filter membrane and GO sheet interface, one bottom surface is generated immediately upon direct contact between the GO sheets and the filter membrane substrate. A top surface is formed at a later stage upon the completion of vacuum filtration and is at relatively free GO sheets and air interface. Would the top and the bottom surfaces of the resulted GO and thus rGO membranes have same or different chemical and physical properties? In other words, are the resulted GO and rGO membranes symmetric or asymmetric? This question remains to be answered. Chapter 2 of this dissertation aims at providing answer to this question. For the first time, it reports the asymmetry of the vacuum-filtrated rGO membranes and discloses the filter membranes’ physical imprint on the bottom surface of the rGO membranes, which takes place when the filter membrane surface pores have similar dimension to GO sheets. The physical imprint of the filter membranes on the bottom surface of the rGO membranes leads to drastically different dynamic water wettability behaviors on the two surfaces of
the same rGO membrane. The mechanism behind the physical imprint and differed water
dynamic wettability has been thoroughly investigated in Chapter 2.

Chapter 3 takes the differed water wettability on the two surfaces of the rGO and the
revealed physical imprint mechanism to application level. The fact that the two surfaces
of the rGO membranes have the same chemical composition means that their differed
dynamic water wetting behaviors are solely from surface roughness (i.e., surface
microstructures). Therefore, the two surfaces of the rGO membranes offer a unique
opportunity to examine the sole effect of roughness-induced hysteresis on water related
phenomena. In the first half of Chapter 3, the two surfaces of rGO membranes with
different dynamic water wetting behaviors are employed for fog harvesting. By
thoroughly investigating the effect of water hysteresis on the efficiency of fog harvesting,
significantly differences are observed on the two surfaces for water condensation, droplet
growth, etc. In the second half of Chapter 3, the mechanism of physical imprint is taken
to rationally print pre-designed pattern selectively onto the bottom surface of the rGO
membrane by simple vacuum filtration of GO aqueous solution. This idea necessitates
fabricating a filter substrate with pre-designed pattern consisting of holes with similar
size to the flake size of GO to be filtered. To demonstrate, a silicon wafer with pre-
designed pore size and pore arrangement pattern (letters of ‘KAUST’) is fabricated and
then utilized to fabricate the predesigned microstructure pattern of rGO selectively only
on the bottom surface of rGO membrane via vacuum filtration. The bottom surface of the
synthesized rGO membrane possessed pre-designed and vertically aligned rGO
microstructures.
Given the fact there are only a few literature studies existing on stacked rGO membranes for water filtration often with contradictory results. Chapter 4 is dedicated to rGO membrane based water filtration. It was revealed for the first time that rGO membrane, during pressure-driven water filtration, possessed significant water flux kinetics. The water flux dropped quickly within an initial stage and obtained a stable value under sufficiently high applied pressure, which was resulted from less compact rGO stacking during its vacuum-filtration based fabrication. The membrane got more compact during the pressure-driven water filtration and both water flux and species rejection were highly dependent on the compactness of the membranes. Our results can be of help in explaining the discrepancy in the literature on the inconsistent water flux and special rejection by stacked rGO membranes. It is also believed that the results of Chapter 4 has a potential to inspire more creative research efforts to engineer rGO membrane for better water flux and species rejection.

Chapter 5 summarizes the major conclusions of this dissertation and presents some future perspectives.
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CHAPTER 2: ASYMMETRY OF THE TWO SURFACES OF VACUUM-FILTRATED RGO MEMBRANES

2.1 Introduction

As discussed in the introduction chapter, an added benefit of using graphene oxide (GO) as graphene substitute is that GO, due to its charges, can be well dispersed in aqueous media, which facilitates many methods of solution based graphene processing.\textsuperscript{1-4} Vacuum filtration, a conventional and simple laboratory technique of separating solids from fluids, has recently found its way into the emerging graphene field and established itself as an excellent method of fabricating free-standing GO and reduced graphene oxide (rGO) membranes.\textsuperscript{5-14} In vacuum filtration, the GO solution is filtered through a membrane substrate under vacuum, and GO sheets, due to their big lateral size compared with the size of the membrane pores, are retained and thus stack up on the membrane surface, forming a GO membrane. After a suitable chemical reduction, the GO membrane can then be converted into rGO membrane.\textsuperscript{13, 15-16} Due to its simplicity, low-cost, and ease of scale up, the vacuum filtration based graphene membrane fabrication has seen many applications in recent years, such as water purification,\textsuperscript{7, 10-11, 14, 17} energy storage,\textsuperscript{9, 12, 18} and oil–water separation.\textsuperscript{17, 19-22}

In a vacuum filtration system, commercial membrane filters are generally used as the filtration medium.\textsuperscript{23-28} Would the filter membranes leave their imprints on the thus-prepared GO and subsequent rGO membranes? This question remained unanswered until very recently when Huang and coworkers discovered that some ionic species in the membrane filters could make their way into the overlying GO membranes and significantly change the stability of the GO membranes in aqueous media.\textsuperscript{29} It was found
that the ionic species coming from the filter membranes would bind with partially
negatively charged GO sheets, which significantly increases the stability of the GO
membrane. This work helps explain inconsistency in the prior literature reports
regarding the GO membrane stability in aqueous solution and shows that the membrane
filters in vacuum filtration may chemically affect the thus-prepared GO membranes.

It is believed that the above-mentioned chemical imprint would be insignificant when the
GO membranes are reduced to rGO membranes as the charges on the GO sheets would
be minimized after reduction. However, there is another aspect of the filtration-based
membrane preparation that has potential to impact the produced rGO membrane
properties, but unfortunately has been overlooked in the past. A vacuum filtrated GO or
rGO membrane has two surfaces, which are formed at different interfaces. Taking GO as
an example, at the filter membrane and GO sheet interface, one GO surface, referred to as
the bottom surface hereinafter, is generated immediately upon direct contact between the
GO sheets and the filter membrane substrate. The other surface, referred to as the top
surface hereinafter, is formed at a later stage upon the completion of vacuum filtration
and is at relatively free GO sheets and air interface. Would the top and the bottom
surfaces of the resulted GO or rGO membranes have same or different chemical and
physical properties or in other words are the resulted GO or rGO membranes symmetric
or asymmetric? More specifically, would the membrane filter substrate leave its physical
imprint on the bottom surface of the rGO membranes? To the best of our knowledge, the
answers to these questions remain unexplored.
The aims of this chapter are (1) to disclose that vacuum filtrated rGO membranes indeed possess asymmetry and the filtration membranes do leave their physical imprint on the bottom surface of the resulted rGO membranes; (2) to reveal that it is the filter membrane's physical imprint on the bottom surface of the rGO membranes that gives rise to the asymmetric properties of the rGO membranes; and (3) to discover that it is the actual surface pore size of the filter membrane that controls its imprinting during the filtration, with the filter membrane imprinting taking place only when the filter surface pores have similar dimension to GO sheets.

2.2 Materials and methods

2.2.1 Materials

Graphite powder, sodium nitrate, potassium permanganate, hydrochloric acid (HCl), and hydriodic acid (HI) were purchased from Sigma Aldrich™ (St. Louis, MI, USA). De-ionized water produced by using a Milli Q™ filtration system was used in all experiments. The hydrophilic PVDF membrane filter with a stated pore size of 0.22 μm and the hydrophilic nylon membrane filter with a stated pore size of 0.45 μm were purchased from Millipore™. The AAO membrane filter with a pore size 0.20 μm and the filter paper were purchased from Whatman™. The 0.2 μm pore size PC membrane was purchased from Millipore™ and the 1 μm and 3 μm PC membranes were purchased from Whatman™.
2.2.2 Preparation of GO and rGO membranes

GO nanosheets were prepared from graphite by the Hummers’ method.\textsuperscript{32-33} In brief, graphite powder of 10 g and sodium nitrate of 5 g are added into 230 mL of concentrated sulfuric acid with caution. The mixture was then cooled using ice/water bath to 0 °C. Potassium permanganate of 30 g was slowly added into the above mixture slowly while the temperature of the mixture was always kept below 20 °C. Then, the ice bath was removed and the mixture was transferred to a 35-40 °C water bath and maintain the vigorous agitation for 0.5 h. Afterwards, a volume of 467 mL of DI water was added and the mixture was stirred for another 30 minutes. Then, additional 500 mL of DI water was added to the mixture followed by the slowly addition of 60 mL concentrated hydrogen peroxide (30%). The mixture was then centrifuged at 4000 rpm to remove any aggregates and then washed with 10% aqueous HCl solution four times to remove the metal ion residues. Afterwards, it was washed with DI water for at least 10 times in order to remove the acid until the final pH reached ~5-6. Then the aqueous suspension was sonicated for 1 h to form GO suspension followed by the centrifugation at 4000 rpm to remove any large and unexfoliated aggregates. The concentration of the final GO solution was determined by drying the suspension at 80 °C under vacuum for over 24 hour and then weighing the dried GO powder. Figure 2.1 showed a schematic representation of GO and then rGO membrane preparation procedure. In order to fabricate GO membranes with different thicknesses, a series of GO suspensions (~50 mL) with different GO masses ranging from 1 mg up to 10 mg were prepared by diluting the GO suspension prepared previously, then the diluted GO suspension was filtrated under vacuum by the membrane filters (e.g., PVDF, nylon, PC, AAO). Upon completion of the filtration, the intact
GO/membrane filter complex was dried under room temperature overnight before reduction. The reduction of GO to rGO was conducted in a sealed container where a glass bottle containing 2 mL of HI solution was placed uncapped to allow the HI vapor to evaporate. The container was sealed and placed in an oven at 90 °C for 2 h. A freestanding rGO membrane was ultimately obtained by peeling the reduced GO from the membrane filter.

2.2.3 Membrane characterization

All contact angle data were measured on a dynamic contact analyzer OCA35 from DataPhysics. The droplet volume applied for static CA is 4 μL. For all advancing CA and receding CA, the volume of the droplet at the starting point is 4 μL and the dispensing and withdrawing speed is 0.5 μL s⁻¹. The surface morphology of the substrate was examined using scanning electron microscopy (SEM) (FEI Quanta 600). Surface roughness analysis was carried out by atomic force microscopy (AFM) (Agilent 5400 SPM). X-ray photoelectron spectroscopy (XPS) studies were carried out on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV) operating at 150 W, a multi-channel plate and a delay line detector under a vacuum of ~10⁻⁹ mbar.
2.3 Results and discussion

2.3.1 Preparation and characterization of vacuum-filtrated rGO membrane

Figure 2.2 presents SEM and AFM images of the GO flakes synthesized in this work and clearly the flake size of the GO is no uniform, with a size range from 1 to 5 µm. The synthesized GO is in the form of single to a few layer GO sheets (Figure 2.2b and c).

![Figure 2.2: (a) SEM images of GO flakes synthesized in this work; (b) AFM images and (c) height profiler of monolayer GO.](image)

Digital photos of the vacuum filtration setup along with HI reduction chamber for fabricating rGO membranes are presented in Figure 2.3. In more details, a commercial
hydrophilic polyvinylidene fluoride (PVDF) filter membrane with a stated pore size of 0.22 μm, a commonly used filter, was employed as the filtration medium in the vacuum filtration of GO suspension with a known GO mass (e.g., 10 mg) under a pressure difference of 730 mmHg. The GO suspension was undisturbed during the filtration. Upon the completion of filtration, a dark brown GO membrane was formed (Figure 2.4, left side). The GO membrane along with the supporting PVDF filter membrane was air dried before being transferred to a sealed chamber where GO was reduced to a rGO membrane by a hydroiodic acid (HI) vapor for 2 hours (Figure 2.3b). Upon reduction, the coloration of the membrane changed from dark brown before the reduction (Figure 2.4, left side) to a metallic grey of the resulted rGO membrane (Figure 2.4, right side). A free-standing rGO membrane was readily obtained by peeling it off from the filter membrane.

Figure 2.3: (a) Digital photo of the vacuum filtration system and (b) photo of HI reduction chamber used in this work.
Figure 2.4: Digit photos of the GO and rGO membrane before and after reduction. The insets show a side view of the static water contact angels on the top membrane surfaces.

The thickness of the resulted rGO membrane was determined by the cross-sectional SEM images of the membranes (Figure 2.5). As plotted in Figure 2.6, the thickness of the rGO membranes increased linearly with the mass of the GO in the starting suspensions. The successful reduction of the GO to rGO was confirmed by the Fourier transform infrared (FTIR) and Raman spectroscopy measurements (Figure 2.7). After the HI treatment, the FTIR spectrum in Figure 2.7a shows the significantly weakened or disappearance of oxygen containing functional group peaks, such as a hydroxyl group at 3421 cm\(^{-1}\), an epoxy group at 1259 cm\(^{-1}\), an alkoxy group at 1065 cm\(^{-1}\), a carboxyl group at 1624 cm\(^{-1}\) and a carbonyl group at 1725 cm\(^{-1}\).\(^{33-34}\) In the Raman spectrum, the GO membrane showed two prominent peaks at 1589 and 1365 cm\(^{-1}\) (Figure 2.7b), corresponding to the well-documented G and D bands. After the HI treatment, the G and D bands were still present, but the intensity ratio of the D and G bands, I\(_D\)/I\(_G\), increased dramatically, which was attributable to the increased number of isolated sp\(^2\) domain after reduction.
Figure 2.5: SEM images of rGO membrane with (a) 3 mg GO loading and (b) 8 mg GO loading during the vacuum filtration.

Figure 2.6: rGO membrane thickness as a function of GO loading during the vacuum filtration.

Figure 2.7: (a) FTIR and (b) Raman spectra of the GO (black) and rGO (red) membrane.

Moreover, consistent with the prior literature reports, the two surfaces (top and bottom) of the same GO or rGO membranes exhibited almost the same static water contact angles, with the two surfaces of the GO membranes having static water contact angles at $\sim 34 \pm$
2° while those of the rGO ones at ∼76 ± 5° (insets in Figure 2.4).7,35 These results further confirm the successful reduction of the GO to rGO as the chemical reduction reduces the polar functional groups of GO and it also seem to suggest that two surfaces (i.e., top and bottom surfaces) of the GO and rGO are symmetric.

2.3.2 Asymmetry of the vacuum-filtrated rGO membranes

However, some seemingly contradictory but interesting results were later observed. In one experiment, one of our rGO membranes was soaked in water and as soon as the membrane was pulled out of the water vertically, a drastic difference in water behaviors on the two surfaces was immediately spotted of the same rGO membrane (Figure 2.8a): on the top surface, a dry surface with no water residue at all was obtained, while, in a sharp contrast, on the bottom surface of the same rGO membrane, there was a thin layer of water film, which adhered to the entire surface firmly. As a matter of fact, these seemingly contradictory wettability results are not against each other as they belong to two different domains: the static wettability versus dynamic wettability. The observed different wetting behaviors on the rGO membrane surfaces in our experiment while pulling the membrane out of the water fall into a dynamic wettability domain, which involves de-wetting of water from the membrane surfaces. Obviously, the rGO membrane exhibited asymmetrically dynamic wetting behaviors on its two surfaces.
In the dynamic wetting field, the researchers rely on advancing contact angle and receding contact angle measurements to provide important information.\textsuperscript{36-38} Thus, for our rGO membranes produced on the PVDF membrane filters, we carefully measured their advancing and receding angles and found (1) there was no significant difference between the advancing angles of the two surfaces of the same rGO membrane; (2) nevertheless, a drastic difference was observed on the receding angles between the two surfaces of the same rGO membrane, with the receding angle of the bottom surface measured to be 0° while that of the top surface at $\sim 50°$ (Figure 2.8b and c). The receding angle of 0° at the bottom surface is an extreme and interesting case, which indicates the surface's capability to firmly hold water and its unwillingness to let go of the water. This explains why there was a thin water film at the bottom surface of the rGO membrane after it was taken out of water. On the other hand, the 50° receding angle at the top surface indicates its general inclination to let go of the water. The drastically different water dynamic wetting behavior was consistently observed on the two surfaces of the free-standing rGO membranes with a thickness $\geq 250$ nm, as shown in Figure 2.9. To facilitate discussion,
from this point on, the rGO membrane samples with a thickness of 3.5 μm was used for focused discussions unless otherwise noted.

Figure 2.9: The dynamic and static wettability comparison of (a) the top surface and (b) the bottom surface of the rGO membranes with different thicknesses. The red, black and blue spheres stand for advancing contact angle, static contact angle and receding contact angles respectively.
Figure 2.10: C 1s XPS spectra and C/O ratio analysis of GO and rGO membrane. (a) The GO, (b) the top surface, (c) the bottom surface of the rGO membrane, and (d) partially reduced (10 min HI treatment) top surface of the rGO membrane. The atomic ratios of C/O of these samples are 3.06, 13.2, 8.9 and 3.76 respectively.

To find the cause of the asymmetric wetting behavior of the rGO membranes, the surface chemical composition and the surface structure on both the top and bottom surface of the membrane were then analyzed, which are believed to govern the wetting behaviors of the solid surface\textsuperscript{39-40}. Both factors were looked at thoroughly in this study. First, X-ray photoelectron spectroscopy (XPS) measurement was conducted to examine the surface chemistry composition of the rGO membrane. It is believed that the magnitude of residual polar groups (e.g., C–O, C=O) on the rGO membrane partially affects its receding angle, with a higher content of polar residue leading to a smaller receding angle. Figure 2.10 shows the XPS spectra of the GO (Figure 2.10a) and both surfaces (top and
bottom) of the rGO membrane after 2 hour HI treatment (Figure 2.10b and c). Before reduction, the C 1s spectrum of the GO was fitted with six components, located at 284.4, 285.1 eV, 286.4, 287.9, 288.9 eV, and 290.6 eV corresponding to the C=C (sp² hybridized carbon), C–C (sp³ hybridized carbon), C–O–C/C–OH (epoxy and hydroxyl), C=O (carbonyl), O=C–OH (carboxyl) groups and π–π shake-up satellite structure characteristic of conjugated systems, respectively. Meanwhile, the dominant peak at 286.4 eV indicates that the most oxygen-containing functional groups in the GO were hydroxyl and epoxy groups.

After HI treatment, there was an increase in both the intensity of sp² hybridized carbon and the intensity of π–π* shake-up satellite structure, in addition to the decrease of the intensity of hydroxyl and epoxy groups on both surfaces of the rGO membrane, demonstrating the successful reduction. The atomic ratio of C/O was estimated from the survey spectra for these samples. The dramatic increase of the C/O ratio for both surfaces of the rGO membrane confirms the efficient removal of oxygen-containing functionalities by the HI reduction. The treatment by HI beyond 2 hours of the rGO membrane showed negligible change in the XPS spectra and the C/O ratio, indicating sufficient reduction by 2 hour HI treatment. However, the XPS spectra revealed some difference in the residual polar group contents on the two surfaces of the rGO membrane, with the bottom surface having a higher polar residual content than that of the top surface (Figure 2.10b and c).

While 2 hours was determined to be sufficient time to fully reduce the GO to rGO in this study, in one experiment, we kept the GO membrane in the HI vapor for only 10 minutes to purposefully prepare a partially reduced rGO membrane with a higher polar residual content than the fully reduced rGO membrane by 2 hour HI reduction (Figure 2.10d).
The result showed that the top surface of the partially reduced rGO membrane exhibited static and dynamic wettability similar to the top surface of the fully reduced one (Figure 2.11). It is worth pointing out that the top surface of the partially reduced rGO membrane had a much higher polar residual content (C/O ratio ∼3.76) than the bottom surface of the fully reduced one (Figure 2.10d), which implies an insignificant role of surface chemistry difference in inducing different wetting behaviors and specifically different receding angles in this work. Thus, the above results make us believe that, although there is some difference in the polar residual content of the two surfaces of the rGO membranes, the difference is unlikely to be responsible for the drastically different wetting behaviors on two surfaces of the same rGO membrane.

Figure 2.11: Water wettability on the top surface of the partially reduced GO membrane by 10 minutes HI treatment. (a) Static water contact angle of (79°); (b) advancing water contact angle (92°); (c) receding water contact angle (42°).
Next, the surface morphology on both surfaces of the rGO membrane was investigated. First, SEM images of the two surfaces of the rGO membrane were recorded and compared. As shown in Figure 2.12a and b, the top surface of the rGO membrane showed a generally smooth surface. Surprisingly, the bottom surface exhibited drastically different surface morphologies, which was highly rough with many petal-like graphene sheets stretching out upright from the membrane surface (Figure 2.12c and d). We obtained SEM images of the original PVDF and PVDF filter membranes after removing
the overlying rGO membrane and found no rGO residue on the filter surface as well as in the PVDF membrane pores (Figure 2.12e and f), which ruled out the possibility that these rGO surface microstructures were formed during delamination. Furthermore, AFM analysis was conducted to investigate the surface morphology of the rGO membrane. In conducting atomic force microscopy (AFM) measurements, the areas of $2.5 \times 2.5 \, \mu m$ were scanned for both the surfaces, and root-mean-square roughness, $R_q$, which is considered as a reliable parameter in quantifying surface micro-roughness, was then calculated.$^{17,37}$ The $R_q$ values of the top and bottom surfaces of the rGO membrane were calculated to be 31.4 nm and 63.4 nm respectively (Figure 2.13).

![AFM height images of rGO membrane surfaces. (a) Top surface and (b) bottom surface of the rGO membrane prepared on the PVDF membrane filter. The calculated $R_q$ values of the top and bottom surfaces are 31.4 nm and 63.4 nm, respectively.](image)

Clearly, according to the AFM analysis, the bottom surface assumed a rougher surface structure than the top surface of the same rGO membrane, consistent with the SEM imaging results. The relatively rougher structures on the bottom surface of the rGO membranes may allow the water to penetrate into the grooves and generate great resistance to the motion of the three-phase contact line, leading to lower receding
angles\textsuperscript{37, 40}. It is worth pointing out that the asymmetric morphology was also observed on the two surfaces of the GO membrane prepared on the PVDF membrane without the HI reduction (Figure 2.14). Due to the high content of the oxygen containing groups of GO, the receding contact angles of the two surfaces are the same (0\textdegree). Therefore, from the wetting aspect, the GO membranes are symmetric.

![Figure 2.14: SEM image of GO membrane prepared on PVDF membrane filter. (a) Top surface and (b) bottom surface of the GO membrane prepared on the PVDF filter membrane (with a stated pore size of 0.22 μm).](image)

In order to further verify whether surface roughness, or more specifically, the surface petal-like microstructures in this work, is the true cause of the asymmetric wetting behaviors of the rGO membrane, we turned to a polished silicon (Si) wafer, which is considered as a perfectly smooth surface, with an aim at producing a rGO membrane with similar roughness and surface morphology on both surfaces. To prepare such a membrane, a GO suspension was dropped on top of the wafer and placed in a 40 °C convective oven for one week to evaporate water, followed by the same HI vapor reduction. A free-standing rGO membrane was ultimately prepared by carefully peeling it off from the Si wafer surface. XPS measurements show that both the top and the bottom surfaces of the rGO membrane exhibited similar chemistry (Figure 2.15). The SEM
images (Figure 2.16a and b) and AFM (Figure 2.17) analysis show that both surfaces of
the prepared rGO membrane were similarly smooth, with Rq values being 23.6 nm and
20.1 nm on the top and bottom surfaces respectively. As expected, both the top and
bottom surfaces of the rGO membrane produced from the Si wafer were smoother
compared with those of the rGO membrane prepared on the PVDF membranes. At this
point, it came as no surprise that both surfaces of this membrane left behind no water
traces upon out of water contact. The advancing and receding angles of the top surface
were measured to be 89° ± 1° and 49° ± 3°, while those of the bottom surface of the same
rGO membrane produced on the Si wafer were 86° ± 1° and 33° ± 2° (Table 1). Thus, the
fact that, with no difference in the surface roughness, the wetting behavior difference
becomes insignificant, discloses that it is really the different surface roughness that
makes the two surfaces of the same rGO membrane possess different wetting behaviors.

![C 1s XPS spectra of the rGO membrane prepared on silicon wafer.](image)

Figure 2.15: C 1s XPS spectra of the rGO membrane prepared on silicon wafer. (a) Top
surface and (b) the bottom surface of the rGO membrane prepared on the silicon wafer.
The atomic ratios of C/O of the top and bottom surfaces are 7.4 and 6.8 respectively.
2.3.3 Origin of the asymmetry of the vacuum-filtrated rGO membranes

Having confirmed the role of surface roughness being responsible for the difference in water wetting behavior of the rGO membranes, efforts were then made in ascertaining whether the rough bottom surface of the rGO membrane could be reproduced if other filter membranes are used in the otherwise same process. In general, from the nature of the filter membrane preparation, filter membranes popularly used in vacuum filtration can
be classified into two categories: phase-inversion-based polymeric filter membrane and anodic aluminum oxide (AAO). Nylon membrane, along with the PVDF one, falls into the first category.\(^4\) The nylon membrane (with a stated effective pore size of 0.45 μm) was employed in the otherwise same vacuum filtration in this study and the results showed that the smooth top surface and rough bottom surface with petal-like microstructures could be well reproduced with the nylon filter membranes (Figure 2.18).

![SEM images of rGO membrane prepared on nylon filter membrane. (a) Top surface and (b) the bottom surface of the rGO membrane prepared on the nylon filter membrane (with a stated pore size at 0.45 μm).](image)

As expected, the bottom surfaces of the rGO membranes prepared on the nylon filter membranes possessed exactly the same water receding angle (i.e., 0°) as the ones prepared on the PVDF membranes. Next, AAO membrane, fabricated via anodization, was used for the preparation of the rGO membrane by the same process.\(^4\) The AAO membrane has a smooth surface and a uniform and accurate pore size due to its fabrication process. In this work, an AAO membrane with 0.2 μm pore size was employed as a filtration medium to produce the rGO membrane. Intriguingly, the SEM imaging (Figure 2.16c and d) and AFM analysis (Figure 2.19) revealed that the two
surfaces of the so-produced rGO membrane were similarly smooth, with the Rq values of the top and bottom surface being 30.3 nm and 37.8 nm respectively.
Table 2.1: Properties and water wetting behaviors of the rGO membrane prepared from different filter membrane substrate.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Actual pore size</th>
<th>Static contact angle</th>
<th>Advancing contact angle</th>
<th>Receding contact angle</th>
<th>$R_q$</th>
<th>Static contact angle</th>
<th>Advancing contact angle</th>
<th>Receding contact angle</th>
<th>$R_q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>0.5–4 μm</td>
<td>$76^\circ \pm 5^\circ$</td>
<td>$94^\circ \pm 1^\circ$</td>
<td>$45^\circ$</td>
<td>31.4 nm</td>
<td>$75^\circ \pm 1^\circ$</td>
<td>$92^\circ \pm 2^\circ$</td>
<td>0°</td>
<td>63.4 nm</td>
</tr>
<tr>
<td>AAO</td>
<td>0.2 μm</td>
<td>$77^\circ \pm 1^\circ$</td>
<td>$82^\circ \pm 2^\circ$</td>
<td>$41^\circ \pm 3^\circ$</td>
<td>30.3 nm</td>
<td>$73^\circ \pm 1^\circ$</td>
<td>$85^\circ \pm 2^\circ$</td>
<td>$43^\circ \pm 2^\circ$</td>
<td>37.8 nm</td>
</tr>
<tr>
<td>Si wafer</td>
<td>0</td>
<td>$72^\circ \pm 2^\circ$</td>
<td>$89^\circ \pm 1^\circ$</td>
<td>$49^\circ \pm 3^\circ$</td>
<td>23.6 nm</td>
<td>$71^\circ \pm 1^\circ$</td>
<td>$86^\circ \pm 1^\circ$</td>
<td>$33^\circ \pm 2^\circ$</td>
<td>20.1 nm</td>
</tr>
</tbody>
</table>
Figure 2.19: AFM height images of rGO membrane prepared on AAO membrane filter. (a) Top surface and (b) the bottom surface of the rGO membrane prepared on the AAO membrane filter. The calculated $R_q$ values of the top and bottom surfaces are 30.3 nm and 37.8 nm, respectively.

In other words, with the AAO membrane being the filtration medium, the petal-like microstructures were not reproduced on the bottom surface of the rGO membrane. Not surprisingly, the rGO membrane showed no different wetting behaviors between the top and bottom surfaces, with the static and dynamic contact angles all measuring similar on the two surfaces (Table 2.1). Particularly, the receding angles on the top and bottom surfaces of the thus-made rGO membrane were $41^\circ \pm 3^\circ$ and $43^\circ \pm 2^\circ$ respectively. In comparison, although both the polymeric filter membranes used in the study (i.e., PVDF and nylon) have a stated effective pore size of 0.22 $\mu$m and 0.45 $\mu$m, the surfaces of these filter membranes take on irregular and reticular interconnected structures and their actual surface pore sizes are quite heterogeneous and diverse, ranging from several tens of nanometer to 2.0 $\mu$m for the PVDF membrane (Figure 2.12e and f), and from 0.5 $\mu$m to 4.0 $\mu$m for the nylon one (Figure 2.20). A careful comparison revealed that the dimension of the periphery of the petal-like microstructures on the bottom surfaces of the rGO membranes was comparable to some of the surface pores of these polymeric filter membranes. These results now lead us to draw the conclusion that it is the filter
membrane that induces surface petal-like microstructures on the bottom surface of the rGO membrane, provided that the filter membrane surface pore structure is such that it allows the entry of GO sheets into its surface pore space during vacuum filtration. Thus, the surface petal-like microstructures on the bottom surface of the rGO membrane are indeed physical imprints of the filtration membrane, leading to the asymmetry of the rGO membrane.

Figure 2.20: SEM image of the original nylon membrane filter (with a stated pore size ~0.45 μm). The actual surface pore size ranges from 0.5 to 4.0 μm.

To further substantiate that the actual surface pore size of the filter membrane is the dominant factor that controls the filter membrane's imprinting on the bottom surfaces of the rGO membrane and thus the membrane asymmetry, track-etched polycarbonate (PC) membranes were rationally selected. The benefits of using the track-etched membranes are clear: (1) the track etching process is capable of generating very uniform and well-controlled pore size; and (2) the pores are regular in shape. We selected the PC membranes with pore sizes of 0.2 μm(Figure 2.21a), 1.0 μm(Figure 2.21b), and 3.0 μm
(Figure 2.21c) as filtration membranes while keeping the GO mass loading constant at 10 mg during vacuum filtration and compared the surface morphology and wettability behaviors of the two surfaces of the produced rGO membranes.

Figure 2.21: Surface characterization of PC membrane and rGO membrane. SEM image of the PC membrane with a pore size of (a) 0.2 μm, (b) 1 μm and (c) 3 μm; top view of the top surface of the rGO membranes produced by (a1) 0.2 μm, (b1) 1 μm and (c1) 3 μm PC membranes; top view of the bottom surface of the rGO membranes obtained by (a2) 0.2 μm, (b2) 1 μm and (c2) 3 μm PC membranes; tilt view of the bottom surface of the rGO membranes fabricated on by (a3) 0.2 μm, (b3) 1 μm and (c3) 3 μm PC membranes. All scale bars correspond to 10 μm, except for that in (a).

Figure 2.22: Schematic Illustration of GO stacking mechanism on different pore sized PC membrane, (a) 0.2 μm (b) 3.0 μm.
As expected, the SEM images showed smooth morphology on the top surfaces of all rGO samples as shown in Figure 2.21a1, b1 and c1, which resulted in similar surface wettability on all top surfaces (Table 2.2). On the other hand, due to small pore size of the PC membrane, GO sheets, generally with sizes ranging from 0.5 to 5 μm, are denied entry into the 0.2 μm pores and they end up stacking up on the membrane surface, leading to a petal-like microstructure-free smooth bottom surface of the rGO membrane as schematically illustrated in Figure 2.21a. A smooth surface morphology was observed on the bottom surface of the rGO membrane prepared on the PC membrane with 0.2 μm pore size (Figure 2.21a2 and a3). However, when the PC membrane pore size was 1.0 μm, irregular petal-like microstructures were visible on the bottom surface of the rGO membrane (Figure 2.21b2 and b3). Interestingly enough, when the PC filter membrane pore size was 3.0 μm, round-shaped petal microstructures were clearly observed on the bottom surfaces of the rGO membranes and the sizes of the petal-like microstructures perfectly matched with the pore size of the corresponding PC filter membranes (Figure 2.21c2 and c3). The tilted-view SEM images of the bottom surfaces indicate that the height of the petal-like microstructures ranged from several ten nanometers to one micrometer. Such a large surface pore size of these filter membranes allows the GO nanosheets with similar lateral dimension to partially penetrate, thus forming the petal-like structure (Figure 2.22b). Different from the top surfaces of the rGO membranes, a clear and gradual transition with increasing PC filter membrane pore size was observed in the receding angles on the bottom surfaces of the rGO (Table 2.2). More specifically, a clear transition from a symmetry to asymmetry in the wetting behaviors of the both surfaces of the rGO membranes was obtained as the pore size of the PC filter membranes
increased from 0.2 to 3.0 μm, with the receding angles on the bottom surface reduced to 0° at 3.0 μm PC filter membrane pore size. XPS analysis showed no significant difference in surface chemistry on the two surfaces (Figure 2.23a and b). Thus, the results from the PC membrane experiments clearly demonstrate that (1) the pore size of filtration membrane controls the surface roughness, in the form of surface petal-like microstructures, on the bottom surface of the so-produced rGO membrane; (2) with suitable pore size, surface petal-like microstructures result on the bottom surface of rGO membrane, which mimic the surface pore structures and thus are the physical imprints of the filtration membrane; (3) the surface petal-like microstructures, once present, induces a strong interaction of the surface to water, leading to the decreased water receding angle.

Figure 2.23: C 1s XPS spectra of the bottom surfaces of the rGO membrane obtained by PC membrane with a pore size of (a) 0.2 μm and (b) 3 μm.

2.4 Conclusions
This work revealed the asymmetric wetting behaviors on the two surfaces of the vacuum-filtrated rGO membrane, and have disclosed that the asymmetry is originated from the filter membrane's physical imprint on the bottom surface of the rGO membrane. This work also revealed that it is the actual surface pore size of the filter membrane that
controls its imprinting during the filtration, with the filter membrane imprinting taking place only when the filter surface pores have similar dimension to GO sheets. The results in this chapter contributes a significant effort to rGO based membrane research as it looks at a generally overlooked side of vacuum-filtration based rGO membrane preparation and provides scientific insight behind it. It also opens up a new avenue of engineering and designing surface micro-structures on rGO membranes by the substrate imprinting concept for potential future applications, which will be discussed in the Chapter 3.
Table 2.3: Properties and water wetting behaviors of the rGO membrane prepared by the PC membranes with different pore sizes.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Top surface of the rGO membranes</th>
<th>Bottom surface of rGO membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Static contact angle</td>
<td>Advancing contact angle</td>
</tr>
<tr>
<td>PC (0.2 μm)</td>
<td>71° ± 1°</td>
<td>89°</td>
</tr>
<tr>
<td>PC (1 μm)</td>
<td>74° ± 3°</td>
<td>90° ± 1°</td>
</tr>
<tr>
<td>PC (3 μm)</td>
<td>72° ± 4°</td>
<td>91° ± 1°</td>
</tr>
</tbody>
</table>
References


CHAPTER 3: APPLICATION OF ASYMMETRIC RGO SUBSTRATE TO FOG COLLECTION AND FABRICATION OF PRE-DESIGNED PATTERNS ON SELECTIVE SURFACE OF RGO THIN FILM

3.1 Introduction

As described in Chapter 2, it has been discovered that with similar size of the pores to the dimension of GO, the filter membranes would leave its physical imprint on the bottom surface of the rGO film in the form of petal-like microstructures, leading to asymmetry of the rGO films. It is these microstructures that are the origin of drastically different dynamic water wetting behaviors on the two surfaces of the rGO films. Excited at this result, we made efforts in Chapter 3 to explore potential applications of this discovery.

First, since surface water wettability is a key parameter in several applications, including fog harvesting\(^1\)-\(^9\), anti-fouling coating\(^10\)-\(^13\), anti-corrosion coating\(^14\)-\(^17\), self-cleaning surface\(^18\)-\(^22\), and so on, the difference in dynamic water wettability of the two surfaces of the same rGO films may offer some interesting applications. Especially true is the fact that the two surfaces of the rGO films have the same chemical composition, which has been confirmed and discussed in Chapter 2, and their differed dynamic water wetting behaviors are solely from surface roughness (i.e., surface microstructures). Therefore, the two surfaces of the rGO films offer a unique opportunity to examine the sole effect of roughness-induced hysteresis on water related phenomena. In the first half of Chapter 3, the two surfaces of the rGO films with different wettability were fabricated by using PVDF membrane as filter substrate, and they were subsequently utilized for fog water harvesting. Drastic differences were observed on the two surfaces of the same rGO films
for water condensation, droplet growth, etc. It turned out that the captured fog water droplets followed a film-wise collection on the bottom surface while a drop-wise collection on the top surface of the rGO films, which led to quite contrasting fog water collection efficiencies on the two surfaces.

Secondly, the mechanism of physical imprint of the filter membrane onto the bottom surface of rGO film can be pushed a step further to rationally print pre-designed pattern onto the rGO film by simple vacuum filtration of GO aqueous solution. This idea involves first fabricating a filter substrate with pre-designed pattern consisting of holes with similar size to the flake size of GO to be filtered. To demonstrate, in the second half of Chapter 3, a silicon wafer with pre-designed pore size and pore arrangement pattern was fabricated and then utilized to print the pre-designed pattern selectively on the bottom surface of rGO film via vacuum filtration. The bottom surface of the synthesized rGO film possessed pre-designed and vertically aligned rGO microstructures. The possibility of using this special material for cold field emission application was discussed, although not tested in this chapter.

3.2 Fog harvesting using both surfaces of asymmetric rGO film substrate

Fog, suspended water droplets in air, is a potential alternative freshwater source in the dry regions where humidity is high\(^1\text{-}^2\). Fog can be harvested through specially designed collection systems and the captured water can be used for agricultural and domestic uses\(^1\text{-}^2,^6,^8\). The fog collection system can also be applied to water collection in mountainous areas when the water is in the form of stratocumulus clouds, at altitudes of approximately 400 m to 1,200 m\(^5\text{-}^9\). The development of various fog harvesting materials/surfaces,
mostly inspired by the behavior of Namib Desert beetles\textsuperscript{2, 23} and other natural species (spider silk\textsuperscript{24-25}, cactus\textsuperscript{26} etc.), has attracted significant research attention in the past few decades as the water scarcity has been emerging as a global challenge\textsuperscript{23, 27-29}.

Technologically, fog harvesting is both a heat and mass transfer process which involves tiny water droplets in the wind stream encountering with and thus attaching onto a substrate. During the process, both water droplet growth and coalescence would take place, which are affected by the geometry\textsuperscript{5} and surface wettability\textsuperscript{9, 30} of the water collection substrate and which have been extensively investigated in the past decades. A popular example demonstrating the effect of surface wettability on fog harvesting efficiency is the well-known hydrophilic-hydrophobic patterned surface inspired by the Namib beetles, surviving in the extremely dry Namib Dessert\textsuperscript{23}. The Beetles have been found to have great capability of collecting morning fog as their vital water source. There are several beetle species in the Namib Dessert and they all show such capability. In 2001, a paper\textsuperscript{23} published on Nature specialized on \textit{Stenocara sp.} and reported its special wax-free (hydrophilic) region on the top of wax covered (hydrophobic) bumps on the elytra. It is now believed that the hydrophilic-hydrophobic patterns can enhance water droplet coalescence by inducing directional movement of water droplets on the surface from hydrophobic regions to hydrophilic regions, which enhances the overall fog collection efficiency\textsuperscript{7}. Various methods have been developed to fabricate wettability patterned surfaces for highly efficient fog water collection and to study detailed water droplet behaviors on such surfaces\textsuperscript{7, 31-32}. Figure 3.1 presents comparisons of water droplet growth and droplet coalescence behaviors on five different surfaces, including
uniformly hydrophobic (Figure 3.1a), uniformly hydrophilic (Figure 3.1b), and wettability patterned surfaces (Figure 3.1c to e). 

Figure 3.1: Water collection processes on various kinds of surfaces. (a) On the superhydrophilic surface, water droplets spread over the surface and quickly form a thin water film (arrow). (b) On the superhydrophobic surface, the tiny captured droplets coalesce randomly (dashed circles). As the sizes of these droplets grow beyond a certain threshold, the droplets roll off the superhydrophobic surface. The droplets spontaneously move and coalesce into the superhydrophilic polydopamine micropatterns (dashed circles and arrows) on (c) the superhydrophobic surface with 500 mm polydopamine patterns and 1000 mm separation, (d) the superhydrophobic surface with 200 mm polydopamine patterns and 400 mm separation and (e) the superhydrophobic surface with 200 mm polydopamine patterns and 1000 mm separation. Some of the polydopamine
micropatterns are outlined with black dashes. All scale bars = 500 mm. Note: polydopamine patterns on these surfaces are superhydrophilic.

Recent advances in preparing surfaces with low contact angle hysteresis (CAH), advancing contact angle (ACA) minus receding contact angle (RCA) (ACA - RCA), include oil-infused slippery surfaces and polydimethylsiloxane (PDMS) brush surfaces and these surfaces have been utilized for fog water collection. Lubricant oil infused nanostructure, due to the property of the infused liquid oil, can lead to a CAH as low as 1° (Figure 3.2a) and it allows oil to wet the surface and at the same time repels water. Similarly, the PDMS brush functionalized slippery surface is achieved by growing uniform PDMS chains onto a substrate which act like liquids (Figure 3.2b). The advantage of such low CAH surfaces is that they allow smaller droplets to move by the force of gravity and thus permit faster turnover rate of fog collection cycle. There are a few studies that have demonstrated desirable fog collection efficiency of the low CAH surfaces. For example, the nanomat fabricated by electrospinning of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) initially had very high retention force which prevented a droplet with a diameter smaller than 4.2 mm from sliding vertically while oil-infused nanomat reduced the critical water sliding size to 2.1 mm as shown in Figure 3.3a. Such oil-infused surface was shown to have enhanced fog harvesting efficiency (Figure 3.3b). Thus, the surfaces with low CAH are preferable for fog water collection.
Figure 3.2: (a) Preparation of lubricant oil-infused slippery surface; (b) preparation of PDMS brush mediated slippery surface, dynamic contact angle measurement, AFM image of surface and scheme of PDMS chain grafting.\textsuperscript{33}
Figure 3.3: (a) Optical images of differently sized water drops on the vertical surface of a nanomat and a nanomat impregnated with total quartz oil; (b) water collection rate of Nanomat, Total-Nanomat and Krytox-Nanomat.

Given the general hydrophobicity and asymmetry of our rGO films, with its two surface having contrasting CAH, it is natural that we would like to test the fog water collection by the two surfaces of the rGO film. Given the fact that the two surfaces of the same rGO films have the same chemical composition, their differed dynamic water wetting behaviors are solely from surface roughness (i.e., surface microstructures). Therefore, the two surfaces of the rGO films offer a unique opportunity to examine the sole effect of roughness-induced hysteresis on fog water collection.
3.2.1 Surface wettability of rGO film substrate

The rGO films were fabricated in Chapter 3 following the methods reported in Chapter 2 and the thickness of the rGO films were kept constant at 10 micrometers for fog water collection experiments. For the purpose of confirmation and comparison, a variety of filter membranes were used in making rGO films and the water wettability measurements on the two surfaces of thus-prepared rGO films were measured first. More specifically, polycarbonate (PC) (with a pore size of 0.2 µm, 1 µm, 3 µm and 5 µm), AAO membrane (with a pore size 0.2 µm), and PVDF (with a stated pore size of 0.22 um) membranes were used as the filter substrates to fabricate rGO films. The ACA, static contact angle (SCA) and RCA of the rGO films prepared on AAO and PVDF were measured and presented (Figure 3.4 to 3.5) as examples. The detailed contact angle values of the rGO film prepared on all mentioned substrates are shown in Table 3.1. The results were consistent with the results in Chapter 2. However, in conducting fog water collection experiments, only the rGO films fabricated on the PVDF filter membrane were used for the purpose of more focused discussion.

Figure 3.4: The ACA, SCA and RCA of the rGO membrane fabricated on AAO (0.2 um) membrane support, from left to right respectively. The measured ACA, SCA and RCA
for top surface were 92°, 76° and 45° respectively. The measured ACA, SCA and RCA for bottom surface were 87°, 72° and 44° respectively.

Figure 3.5: The ACA, SCA and RCA of the rGO film fabricated on PVDF (0.22 um) membrane support, from left to right respectively. The measured ACA, SCA and RCA for top surface were 93°, 73° and 45° respectively. The measured ACA, SCA and RCA for bottom surface were 95°, 70° and 0° respectively.

Table 3.1: The contact angle measurements of the rGO membranes fabricated on different substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Top surface</th>
<th>Bottom surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ACA</td>
<td>CA</td>
</tr>
<tr>
<td>PC (0.2 um)</td>
<td>91°</td>
<td>68°</td>
</tr>
<tr>
<td>PC (1 um)</td>
<td>91°</td>
<td>73°</td>
</tr>
<tr>
<td>PC (3 um)</td>
<td>93°</td>
<td>69°</td>
</tr>
<tr>
<td>PC (5 um)</td>
<td>90°</td>
<td>67°</td>
</tr>
<tr>
<td>AAO (0.2 um)</td>
<td>92°</td>
<td>76°</td>
</tr>
<tr>
<td>PVDF (0.22 um)</td>
<td>93°</td>
<td>73°</td>
</tr>
</tbody>
</table>
3.2.2 Fog collection system setup

A homemade fog collection system, schematically shown in Figure 3.6a, was used to evaluate the fog harvesting performance. The rGO film sample (2.5 cm × 2.5 cm) was fixed on a glass substrate with the same size. The sample was hung with its surface perpendicular to the horizontal plane. A simulated fog flow (flow rate ∼12 cm s\(^{-1}\)) was produced by a commercial humidifier and was captured by the vertically placed substrate surfaces (Figure 3.6a and b). The experimental temperature was 21 °C and the relative humidity was around 90–95%. The distance between the fog generator and the sample surface was ∼9 cm. The captured water droplets were drained by gravity and were collected by a container located on top of the digital balance below the sample. A digital optical microscope (Dino-Lite) was used to record the capture and movement behaviors of water.

![Diagram of experimental setup](image.png)

Figure 3.6: The demonstration of the fog harvesting experiment. (a) The schematic diagram of the experimental setup by using simulated fog generated by the home made humidifier and the captured droplet is collected in the analytical balance connecting to the computer\(^8\). (b) The digital image of the experimental setup for fog harvesting experiment.
3.2.3 Water behaviors on two surfaces and fog collection efficiency

Figure 3.7 present the images of the captured water droplets on the two surfaces at different time points, which show the droplet growth behaviors as a function of time. As can be clearly seen, the water behaved quite differently on the two surfaces of the same rGO film, which can be explained by the difference in their wetting properties. On the bottom surface of the rGO film, whose RCA is zero, the captured water droplets gradually coalesce into a water film and are thus hesitant to leave the surface (Figure 3.7a). When droplets coalesce on the bottom surface, the retention force is too large and droplets tend to deform into a spread thin films rather than round shape droplets. While, on the top surface of the rGO film, the captured water droplets tend to coalesce into bigger ones that are later cleared off the surface due to the high water receding angle on the surface, meaning less retention force (Figure 3.7b).

![Figure 3.7: Water collection process on two surfaces of the rGO film prepared on PVDF substrate. (a) Film-wise water collection process on the bottom surface of the rGO film. (b) Drop-wise water collection process on the top surface of the rGO film. The scale bar corresponds to 2 mm.](image)
Detailed analysis of the water surface coverage on the both surfaces is presented in Figure 3.8. Analysis of water surface coverage indicates that bottom surface of the film was nearly fully covered by water film (around 96%) while the surface coverage of the top surface of the film was around 60% at equilibrium. Water droplets growing on the top surface during fog harvesting process showed similar behavior to those in condensation process, namely self-similar growth\textsuperscript{36}. Water surface coverage is constant during steady state for a given surface with specific contact angle. However, due to the large hysteresis, water droplets growing on the bottom surface cannot maintain their self-similar growth behavior and thus form a thin layer of water film which totally covers the film surface. Overall, our results demonstrate that the two surfaces of the asymmetric rGO membranes prepared on the PVDF film substrate exhibited markedly different performances in fog collection and the top surface had a higher efficiency compared to the bottom surface, with the top and bottom surfaces achieving efficiency at 260 and 152 g m\textsuperscript{-2} h\textsuperscript{-1} respectively, which directly shows the disadvantage of water films in fog collection.
Moreover, it is observed that water droplets growth is always much larger on the edges, where there is higher air velocity\(^3\), than those on the non-edge areas during fog harvesting process (Figure 3.9). The fog droplets (with radius \(r_{\text{fog}}\)) have a tendency to hit the substrate due to their high inertia\(^5\). The efficiency of fog droplets intercepted by the substrate is controlled by the Stokes number: 
\[
\text{St} = \frac{t_{\text{particle}}}{t_{\text{flow}}} = \frac{2\rho_{\text{water}}r_{\text{fog}}^2/9\mu_{\text{air}}}{(R/v_0)},
\]
where \(\rho_{\text{water}}\) is water density, \(r_{\text{fog}}\) is the radius of fog droplets, \(\mu_{\text{air}}\) is air viscosity, \(R\) is the substrate dimensions and \(v_0\) is air velocity. From the Stokes number, higher interception efficiency is expected with higher air velocity. Our result is in an agreement with the model prediction and it implies that creating more edge areas can facilitate the growth of water droplets and can thus enhance the overall fog harvesting efficiency.
In all, our results convincingly confirm that, with the same chemical composition, the surface roughness induced hysteresis leads to significantly different water behaviors on the surfaces and thus play a significant role in fog water collection.

Figure 3.9: Optical images showing the faster growth of water droplets on the edges of the substrates on both top and bottom surface. The green markers indicate the edge areas.

3.3. Engineering pre-designed micropatterns selectively on bottom surface of rGO film substrate

The newfound imprinting mechanism also inspired us to take it to the level of deliberately and selectively engineering only the bottom surface of thin rGO films. To this end, we made an effort on fabricating a silicon wafer with a pre-designed pore arrangement pattern (i.e., KAUST in capital letters) of a through-micropore array with a pore size of 5.0 μm (Figure 3.10) by lithography, and used it as template for fabricating of rGO film with the same surface pattern38-39.
3.3.1 Fabrication of micropatterned Si wafer as filtration membrane substrate

In detail, the Si wafer with patterned micropores used for the pattern imprinting experiment was prepared using standard photo lithography and etching processes\textsuperscript{38-40}. To build Si wafer as a filter substrate that possesses the precisely designed pattern, the Si wafer has to be thin enough so that the etching process can drill through-pores. In our experiment, silicon on insulator (SOI) wafer was used, which consists of three parts: device layer (20 um thick in our case), buried silicon oxide layer (SiO\textsubscript{2}) and handle layer (400 um thick in our case) (Figure 3.11). The buried layer separates the devise layer and handle layer into two separate parts. The pattern is made on the device layer and once the pattern is obtained, the device layer is separated from the buried layer and thus used as the filter membrane substrate.

The detailed fabrication flow diagram of the patterned Si wafer is presented in Figure 3.11. The pattern of ‘KAUST’ in capital letters was designed with L-edit software, followed by exporting design file and sending to mask writer\textsuperscript{40}. 

Figure 3.10: (a) Mask design pattern of KAUST and (b) ultimately obtained KAUST patterned Si wafer.
The SOI wafer was first cleaned in the mixture of concentrated sulfuric acid and hydrogen peroxide at 120 °C for 10 minutes followed by DI water rinsing. The as cleaned SOI wafer was immediately spin coated by photo resist (PR) AZ9260. 10 µm of AZ9260 was first coated on the top of the handle layer, followed by baking at 110 °C for 3 minutes to solidify the coated PR before moving to contact aligner for exposure. The exposed wafer was then moved to a developer MIF 726 bath. Then, a 3 µm of AZ 3027 PR was coated on the top of device layer, followed with the same baking and solidifying as the previous step. Upon the exposure and develop step, this wafer was ready for etching process.

During the exposure step, the Si wafer with the PR coating was moved into a direct contact aligner and exposed with certain dose of UV light with the pre-designed pattern.
mask on top. The exposed PR was then removed with the developer. The UV exposure was done on the both sides of the device layer and handle layer.

Deep reactive-ion etching (DRIE) technique was then employed\textsuperscript{38}. We first etched the handle layer until the handler was thoroughly penetrated and the SiO\textsubscript{2} layer was exposed. Then, the device layer was etched with similar process. At the end of the etching process, the SiO\textsubscript{2} layer was removed by immersing in buffered oxide etch solution (BOE) solution containing dilute HF, leaving behind a free-standing device layer with the pre-designed patterned micropore array. It is worth empathizing that after removing the handle layer and SiO\textsubscript{2} layers, the patterned device layer is very fragile and the post cleaning process must be handled carefully. After removing the residual PR, the Si wafer with the pre-designed pattern is ready to be used for GO filtration (Figure 3.12).

Figure 3.13a shows the pattern of KAUST on the Si wafer, consisting of properly spaced micropores with a uniform diameter of ~5.0 \textmu m. Given the size of the graphene flake sizes, the size of the pore on the Si wafer is proper for GO filtration and thus for imprinting on to the final rGO film.
3.3.2 Printing of pre-desinged pattern onto the bottom surface of rGO film by vacuum filtration

The patterned Si wafer was then used in the vacuum-assisted GO suspension filtration using similar procedure. The mass of the GO in suspension was 10 mg and size of the GO sheets was in the range of 1 -10 um. In this case, when the GO aqueous solution was passing through the Si wafer membrane substrate, the GO sheets were retained on top of the Si wafer membrane substrate since the diameter of the membrane holes was smaller than the size of the GO sheets. The HI induced reduction was then conducted to the GO film to convert it to rGO film. The rGO film was then peeled off from the Si wafer membrane substrate carefully for characterization.
Figure 3.13: Top view of SEM image of the Si wafer and the bottom surface of rGO film. (a) The image of micropattern KAUST on the Si wafer used as filtration membrane substrate; (b) the imprint of the pattern with microstructures on the bottom surface of rGO film.

Figure 3.13b presents the SEM images of the bottom surface of the thus-produced rGO film, clearly showing that exactly the same pattern was faithfully imprinted on the rGO film bottom surface and the pattern was made of discrete petal-like microstructures with the diameter around 5.0 μm. The titled SEM images in Figure 3.14a and b clearly show the structures of the surface pattern on the rGO film. Figure 3.15a and b present the SEM images of the Si wafer after removing the rGO film, showing no significant residue of rGO sheets. This results successful demonstrate the imprinting of pre-designed pattern from the filter membrane onto the rGO film’s bottom surface.
3.3.3 Potential application of the patterned rGO surface for field emission

The electrons inside a solid can be emitted out by thermal excitation at high temperature or by a sufficiently large electric field, and the later one is known as field emission (FE) or cold cathode filed emission\(^{41}\). The field emission can be operated at room temperature and provide high emission current density at low electric fields\(^{41}\). Therefore, it is widely used as electron sources for many applications include construction of bright electron sources for high-resolution electron microscopes and field emission display (FED)\(^{42}\). For a pure metal, the field emission only occurs under very high electric fields, which are
typically higher than 1000V/μm\textsuperscript{43-44}. High aspect ratio materials such as sharp metallic tips and carbon nanotubes exhibit excellent electron emission characteristics due to the great local field enhancement at their tip and edge, which significantly decreases the barrier width and allows electrons to tunnel into vacuum at relatively low electric fields. Low threshold fields (∼1 V/μm) have been reported for several carbon-based materials\textsuperscript{42,45-48}.

There has been lots of interest in cold cathode field emission from various carbon materials including diamond, vertically aligned carbon nanotubes\textsuperscript{41}, carbon nanosheets\textsuperscript{49-50}, graphene\textsuperscript{45-48,51} and reduced graphene oxide (rGO)\textsuperscript{43-44}. Among them, it has been widely believed that the geometrical features of graphene and rGO should increase field enhancement with a lower threshold electric field for the extraction of electrons. Theoretically, the electric field enhancement factor for a single layer graphene may be of the order of a few thousand. In order to utilize this high field enhancement, the graphene sheets should stand perpendicular to the substrate. Nearly vertically oriented graphene and rGO with good field emission properties has been reported especially in recent years. However, most of them involve very complicated synthesis method.

In our synthesis, the nearly vertically oriented rGO can be easily achieved by the vacuum assisted filtration method by using commercially available PVDF membrane or a specially designed porous Si wafer, using GO aqueous solution as precursor as described in Chapter 2 and in this chapter. Our method is very simple and provides lots of advantages in controlling the rGO layer density and distribution. As a simple demonstration described above, a Si wafer with pre-patterned micropores was used as the filtration membrane substrate and a cylindrical rGO tube was replicated from each hole
of the Si wafer membrane substrate onto the bottom surface of rGO film. The rGO tubes were generally composed of single layer of rGO and were almost perfectly perpendicular to the rGO film. This structure is highly desirable for a cold field emission device. In addition, since the diameter of the holes, the distance between the holes, the arrangement of the holes can be rationally controlled, the size of the rGO tube, the distribution of the rGO tube and the patterned array can all be well controlled, which is a great advantage of this method. The cold field emission property of the rGO tube array fabricated by our method deserves further research attention.
References


CHAPTER 4: WATER FILTRATION BY REDUCED GRAPHENE OXIDE MEMBRANES

4.1 Introduction

While there are many literature reports on stacked GO membranes for water filtration\textsuperscript{1-31}, the number of the research work on stacked rGO membranes is very limited\textsuperscript{32-35}. The transport mechanisms in stacked GO membranes are largely three-pronged, with none being dominant (Chapter 1) while the transport mechanisms in stacked rGO membranes are largely unknown\textsuperscript{14, 17, 36-37}.

In the past several years, several groups reported the fabrication of rGO membranes and their nanofiltration performances. In 2013, Han et al. fabricated stacked rGO membranes with thickness of 22 nm directly from base-refluxing rGO dispersion via vacuum-assisted filtration\textsuperscript{18, 38}. The rGO membranes showed high water flux of 21.8 L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1}, high rejection rate over 99% for organic dyes and moderate rejection from 20% to 60% for salt ions\textsuperscript{38}. However, in 2014, Geim et al. reported that a 1 micrometer thick stacked rGO membrane was impermeable to water\textsuperscript{39}. In 2015, Liu et al. showed rapid transport of water through stacked 100 nm thick rGO membrane in a FO filtration process with a water flux of 57 L m\textsuperscript{-2} h\textsuperscript{-1}\textsuperscript{32}. The discrepancy in the literatures regarding the water permeability and species rejections of rGO membranes will most likely persist for a while. However, given the attractive properties of rGO, especially its high water stability, and the ease with which stacked rGO membranes can be made via vacuum-driven filtration, the future perspective of the rGO membrane for water filtration should not be underestimated\textsuperscript{40}. 
Some researchers even go as far as arguing that since the interlayer spacing of stacked rGO sheets can be potentially reduce down to ~6 Å, which is smaller than the size of sodium ion, rGO membrane holds great hope for direct seawater desalination\textsuperscript{9}. Unfortunately there hasn’t been any convincing experiment results so far to support this argument.

Since in most of the rGO membrane fabrication cases, GO water suspension is starting material in vacuum-driven filtration, followed by reduction of the GO membrane to rGO, the interaction of individual GO sheets within the GO membrane might significantly affect the final filtration performance by the final rGO membrane\textsuperscript{4, 9, 17, 25}. In most literature reports, constant water flux through GO and rGO membranes throughout the filtration experiments are normally reported\textsuperscript{4, 10, 33, 35, 41}. The water flux kinetics generally slips the research attention in most of the previous works arguably due to the general belief the adjacent GO or rGO flakes in the stacked membranes are held tight by strong interlayer interaction therein\textsuperscript{2, 42}.

Although large lateral size of GO sheets, individual sheets are very thin, one or a few layer only. It is possible that the flexibility of GO sheets may lead to bending or even folding GO structure during the membrane fabrication process. The bended or even folded GO sheets, if present, might response to the applied pressure during water filtration\textsuperscript{23}.

During water filtration operation, a pressure (one atmosphere or higher in GO or rGO membrane based filtration) is usually applied to drive water or other species to pass the membrane (Figure 4.1). In the case with stacked GO membranes, there has been only one
report that reported serious water flux attenuation and obvious changes in surface morphology due to hydraulic pressure applied in water filtration\textsuperscript{23}. It was assumed that the structural defects were formed during vacuum-driven membrane fabrication when the GO sheets were in contact with the membrane substrate. It was also reported that the defect structures further developed into surface wrinkles (Figure 4.2)\textsuperscript{23}. Most importantly, it was observed that the water flux decreased while the rejection rate against divalent salt increased with time within a long testing period\textsuperscript{23}. The deceasing water flux with increasing ion rejection rate was attributed to the bended or folded GO defect structures formed during membrane fabrication step. These defect structures would, under pressure, gradually smooth out, leading to an unstable water flux and rejection within an initial stabilization step. The results from this report are helpful in explaining some of the discrepancy in the vastly different water flux by stacked GO membranes reported in literature\textsuperscript{4, 23}. 
Figure 4.1: The schematic diagram of the pressurized filtration process using laminated GO/rGO membranes. The dark blue shows solute molecules and light blue represents water molecules.

Figure 4.2: Schematic diagram of the formation of surface wrinkle from initial wrinkle (a), folding (b) and stacking (c) of GO nanosheets and the deformation of wrinkle after compaction (d)²³.

However, no such a phenomenon, namely, water flux and rejection kinetics with respect to time, has been noticed and reported on stacked rGO membranes. Given there is a
reduction process which reduces GO to rGO in producing stacked rGO membrane.

Would the reduction lead to sheet realignment and thus structural defect free stacking in rGO membrane? The answer to this question remains to be explored. Thus, Chapter 4 aims to study the water filtration performance of the rGO membrane and special attention is paid to the water flux and species rejection as a function of applied pressure during the filtration to investigate the defects evolution behavior.

4.2 Materials and methods

4.2.1 GO synthesis and rGO membrane fabrication

It is worth mentioning that, different than the GO synthesis in Chapter 2, the GO in this chapter was synthesized by improved Hummers method. The detailed method for the regular Hummers method can be found in Chapter 2. As to the improved method, in brief, concentrated H$_2$SO$_4$ and H$_3$PO$_4$ was mixed with volume ratio of 9:1 and the graphite was mixed with KMnO$_4$ with a weight ratio of 1:6. For every 1.0 g of graphite, 120 ml of H$_2$SO$_4$ and 13.3 ml of H$_3$PO$_4$ was used. The reaction took up to 12 h with stirring and the temperature was maintained at 50 °C. After the reaction completion, ~150 g of ice was added into the mixture with ~2-3 ml of 30% H$_2$O$_2$. Then the filtrate was centrifuged for 2 hour at 4000 rpm, and the supernatant was discarded$^{43}$. The GO membrane was fabricated using the same method (vacuum-filtration on PVDF membrane) mentioned in Chapter 2 and then reduced by HI vapor.

4.2.2 Water filtration experiments

The schematic representation of the water filtration setup is presented in Figure 4.3a and as can be seen, pressure-driven method was utilized in water filtration in a dead-end
configuration. Figure 4.3b is a photo of the real filtration experimental setup used in this work. In more details, nitrogen gas was used as the pressurizer to accelerate the filtration process. The permeate was collected at the drain of the pressurized system and the mass of the permeate was real time monitored on an electrical balance which was connected a computer. A magnetic stir was used and kept on at 450 rpm inside the stainless water container during the filtration experiment to reduce the effect of concentration polarization. The dye and ion concentrations in the permeate were determined by UV-vis spectrum and conductivity meter respectively.

Figure 4.3: Demonstration of the filtration setup. (a) The schematic diagram of the pressurized filtration setup design; (b) the digital image of the experimental filtration setup.
4.3 Results and discussions

4.3.1 Material and membrane characterization

The advantages of the improved Hummers method include (1) the addition of phosphoric acid in the oxidation step would reduce the defects in the basal plane of the product GO; (2) more hydrophilic functional groups would be added to the product GO, which could improve the GO’s ability to disperse more homogeneously in water; (3) the final yield of GO by the improved method can reach up to 90% which is significantly higher than the regular Hummer’s method of 10~20%.

The SEM (Figure 4.4a) and TEM (Figure 4.4b) images show that the GO flakes synthesized by the improved method are well exfoliated. Also, as expected, from XPS data in Figure 4.5, the C/O ratio of GO (Figure 4.5a) produced by the improved method has lower value (C/O ratio=2.1) than that is produced via the regular Hummers method (C/O ratio=3.06) (Figure 2.10).

Figure 4.4: The image of the exfoliated GO flakes. (a) SEM of the GO flakes on silicon mica support; (b) TEM image of the exfoliated GO flake on the carbon substrate.
The GO membranes were produced via vacuum filtration method which is described in Chapter 2 in details. Considering the purpose of our membrane to be used for pressure-driven water filtration, a flexible and strong membrane support is desired. In Chapter 4, PVDF membrane was chosen deliberately as the support for GO membrane fabrication. After the GO filtration was completed, the membrane was kept in the ambient condition for half day in order to remove water residue. Then the GO membrane was transferred into a HI vapor flask for reduction. The membrane was kept on the PVDF support for the entire process (Figure 4.6). The thickness of the membranes, which can be controlled by varying the loading amount of GO during vacuum filtration, was determined by cross sectional SEM images of the membranes (Figure 4.7).

According to Raman spectrum (Figure 4.8), the intensity of the G band increased while the D band decreased after reduction. The explanation for this phenomena could be the restoration of the sp2 hybridization domain after the successful reduction of graphene oxide by HI. In order to further confirm the reduction, the membranes were also
characterized with XPS, which showed the C/O was around 2.1 and 7.6 for the GO and rGO (Figure 4.5b), indicating the significant removal of the oxygen functional group by HI reduction.

As expected, the static water contact angels on the GO and rGO membranes were greatly changed (37.2 for GO and 70.9 for rGO) (Figure 4.9), implying the removal of certain degree of oxygenation by HI reduction and thus indicating reduced hydrophilicity and enhanced hydrophobicity of the rGO membrane. The increase in hydrophobicity of the rGO makes the rGO membranes more stable in water than the GO ones.

Since membrane water stability is an essential factor in the filtration process\textsuperscript{44-45}. The stability of GO and rGO membrane was tested in pure water at stationary state. In the water stability test, the GO and rGO membranes with the same size and thickness were put into DI water. The GO membranes disassembled into small fragments after 5 hour and broke into very small pieces after one day, indicated by light dark brown color of the water in the end. In a sharp contrast, the rGO membrane remained stable and no significant morphology change was observed even after 2 days contact with water (Figure 4.10). This test supports our hypothesis that rGO membrane is more stable than GO membrane in water, and therefore the rGO membrane is more advantageous in water filtration than GO membrane.
Figure 4.6: The digital image of GO (left) and rGO (right) membrane of PVDF support.

Figure 4.7: The rGO membrane thickness as the function of the GO mass loading. The insets are cross section of the rGO membranes showing different thickness.
Figure 4.8: The Raman spectrum of (a) GO and (b) rGO membranes. The D and G represent the corresponding D band and G band.

Figure 4.9: The static contact angle of water droplet on (a) GO and (b) rGO membrane surface.
Figure 4.10: Stability test of GO and rGO membrane in water. Top, left, GO membrane is placed into DI water; mid, the status of the GO membrane after 5 hour exposure in water; right, GO membrane after 1 day exposure in water., Bottom, left, rGO membrane is placed into DI water; mid, rGO membrane after 5 hour exposure in water; right, rGO membrane after 2 day exposure in water.

4.3.2 Water filtration

The pure water permeability of the rGO membrane as a function of time is firstly tested. Two membranes of different thickness (65, 100nm) were tested first in the pressurized dead-end filtration setup shown in Figure 4.3b. The flux of the 65 nm thick membrane produced an initial high flux level at ~ 4000 L m⁻² h⁻¹ which dropped to ~3000 L m⁻² h⁻¹ after 30 mins under 5 bar pressure. However, it was later found that the 65 nm rGO membrane showed no significant species rejection in the initial tests and thus no further effort was put on this membrane. On the other hand, the 100 nm thick rGO membrane produced a very high initial water flux of ~2800 L m⁻² h⁻¹ under 5 bar and the water flux decreased significantly to ~500 L m⁻² h⁻¹ at the end of 25 mins as presented in Figure
4.11. The decrease in water flux slowed down beyond 25 mins and a relatively stable water flux (~115 L m\(^{-2}\) h\(^{-1}\)) was obtained after 5 hour continuous operation under a constant pressure at 5 bar.

Figure 4.11 also compares the water flux kinetics of the 100 nm thick rGO membranes under three different pressures (1, 3, 5 bars). It is found that the 5 bar pressure led to the highest initial water flux, following by 3 bar and then 1 bar. The water flux becomes stable after 5 hour filtration.

Figure 4.12 presents the permeance of water based on pressure of the 100 thick rGO membranes under 1, 3, and 5 bar pressure. As can be seen, lower pressure favored higher water permeance generally.

The observed water flux as a strong function of time for rGO membrane is indeed similar to the literature report on GO one. During the membrane fabrication, GO suspension is first vacuum-filtered to produce GO membrane. In this step, the GO laminates are stacked together under one bar (i.e., vacuum), which is assumed not sufficiently compact. There is possibility of bending and folding defect structures formed. During the subsequent HI-vapor induced reduction, some of the oxygen functional groups are removed in the form of water or water vapor, which is believed to lead to a more tight interlayer space. However, the strong relationship between the water flux and time for all three pressures applied indicates that the HI induced reduction process of GO to rGO membrane fails to remove the bended and folded defect structures and the defect structures persists through the entire process of rGO membrane fabrication.
The defect structure containing rGO membrane, when used for water filtration, gives high initial water flux, which, however, is transient. The water flux quickly drops as the rGO membrane responds to the applied pressure by realigning the rGO sheets to form more smooth and compact stacking.

Figure 4.13 presents a continuous 60 hours water permeance measurement on a 100nm thick rGO membrane under 5 bar, which shows a steady water flux of 23 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and proves the longevity of the rGO membrane for water filtration.

Figure 4.11: Water flux as the function of time of rGO membrane with the thickness of ~100 nm under 1, 3 and 5 bar pressure.
Figure 4.12: Water permeance as the function of during time of rGO membrane with the thickness of ~100 nm under 1, 3 and 5 bar pressure.
Figure 4.13: The water permeance of 100nm thick rGO membrane of 60 hours filtration test using pure water under the pressure of 5 bar.

Another question now remains: would the compacted rGO membrane become uncompact once the pressure is released? The answer to this question is critical for rGO membrane’s practical applications as some filtration processes involves alternating pressurization and depressurization. Thus, efforts were made to study the reversibility of the rGO membrane compaction process.

To this end, an rGO membrane with a thickness of ~100 nm was used for pressurized water filtration first. The membrane was initially operated under 1 bar for ~7 hour, during which the flux dropped by 6 folds. According to Figure 4.14, by this stage, it is believed
that the membrane had completed the compaction process at 1 bar which is indicated by the membrane’s very stable flux (Figure 4.15).

The pressure was then increased to 2 bar, and according to Figure 4.14, the initial flux rose to 1700 L m$^{-2}$ h$^{-1}$ due to increased pressure. After 1.5 hour filtration, the flux dropped to $\sim$900 L m$^{-2}$ h$^{-1}$ and the pressure was then released and the membrane was left under ambient temperature in pure water for over $\sim$40 hours.

Then the same pressure of 2 bar was applied again to restart the water filtration and interestingly, the flux of the membrane did not rise and followed and continued the same trend of the test before the pressure release. This result convincingly indicates that the rGO membrane does not loose up after the pressure release and the pressure-driven compaction process is irreversible.

Furthermore, upon achieving a stable water flux under 2 bar, the pressure was released and the membrane was left idle in water for $\sim$50 hours before water filtration under 5 bar. Under 5 bar, an immediately increased water flux was observed, although with much less magnitude in flux increase, followed by gradually decreasing flux thereafter until a stable flux was obtained.
After the membrane flux reached a steady state under 5 bar, the pressure was again released and the membrane was kept under ambient condition in water for 40 hours. Unlike the previous steps, a smaller pressure of 1 bar was applied this time. A very steady flux was obtained and the flux was almost 1/5 of the steady flux under 5 bar. After idle time, the 5 bar pressure was reapplied and a steady flux of $70 \pm 5 \text{ L m}^{-2} \text{ h}^{-1}$ was obtained.

The deliberately designed experiment provides evidences supporting the dynamic compaction process of the rGO membranes under differing pressure. The whole process can be explained as follows: under pressure, the stacked membrane gets compacted as the interlayer distance between the rGO laminates decreases and the compaction is pressure-dependent. The higher pressure leads to more compact rGO membrane. rGO has much less oxygen functional groups and thus stronger $\pi-\pi$ interactions than GO and therefore once the GO laminates are pushed within $\pi-\pi$ interaction distance, they stay close permanently\textsuperscript{39}. When the pressure is released, the $\pi-\pi$ interaction is strong enough to hold...
the adjacent laminates in place, giving rise to an irreversible compaction process of rGO membrane.

In one extension, a 100 nm thick rGO membrane was compacted under 8 bar and subsequently tested for water flux under pressures from 1 to 8 bar. The results show an almost linear relationship between water flux and pressure for the membrane, which is considered as another evidence supporting irreversible compaction of rGO membrane under pressure (Figure 4.15).

Figure 4.15: The water flux of the rGO membrane that has been pre-compacted with the pressure of 8 bar.

The rejection test of the 100nm rGO membrane was carried out first with Evans blue (EB) solution under 5 bar pressure. The water flux and EB concentration in the permeate were monitored throughout the experiments. According to Figure 4.16a, the water permeance dropped quickly from ~650 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) to ~50 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) in the first 10 minutes, during which the dye rejection was below 20%. The EB rejection rate reached ~90% at 200 mins when the water permeance was becoming stabilized. The rejection rate reached to ~100% when the stable water permeance was obtained at ~7 L
m$^{-2}$ h$^{-1}$ bar$^{-1}$. In comparison to the water permeance kinetics of the same membrane in the absence of the dye in the feed, the water permeance was lower at any time point with the EB than without it due to potential water channel blockage and also cake layer formation on top of the membrane.

At the end of the filtration experiment, EB concentration in the retentate was measured on UV-vis spectrophotometer at wavelength of 608 nm and the results showed that the EB concentration in the retentate was higher than that in the initial feed (Figure 4.16b), implying the rejection effect of the rGO membrane for EB. The EB in the retentate gets concentrated with time as some EB molecules are rejected by the membrane while water is allowed passage. The fact that a perfect rejection of EB was achieved when a stable permeance was obtained points out the promise of the rGO membrane for NF application.

Figure 4.16: The rejection kinetics of rGO membrane with a thickness of 100 nm against EB dye. (a) The permeance and rejection rate as the function of time. (b) The UV visible spectrum of the absorbance of the feed, retentate and permeate collected at the same time points as those in (a).
This phenomena is also confirmed by filtrating EB through a 120 nm thick rGO membrane under 5 bar. Due to the higher thickness, the initial permeance of the membrane, ~350 L m⁻² h⁻¹ bar⁻¹, was less than the 100 nm thick rGO membrane. The rejection of EB also increased as the filtration went on. However, by comparing Figure 4.16a and Figure 4.17a, it took longer time for 120 nm rGO membrane to reach 100% EB rejection than the 100nm thick one. It is worth pointing out that, in our experiments, we carefully studied the effect of dye adsorption onto the rGO membrane and PVDF support and found the adsorption was insignificant to affect the rejection experiments.

Figure 4.17: The rejection kinetics of rGO membrane with a thickness of 120 nm against EB dye. (a) The permeance and rejection rate as the function of time. (b) The UV visible spectrum of the absorbance of the feed, retentate and permeate collected at the same time points as those in (a).
Table 4.1 Stable permeance and rejection 100 nm thick rGO membrane against dyes and ions.

<table>
<thead>
<tr>
<th>Solute</th>
<th>2000 ppm Na₂SO₄</th>
<th>20 ppm EB</th>
<th>20 ppm Rb</th>
<th>20 ppm MB</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical structure</strong></td>
<td><img src="image1" alt="Structure" /></td>
<td><img src="image2" alt="Structure" /></td>
<td><img src="image3" alt="Structure" /></td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>142.04</td>
<td>960.809</td>
<td>479.01</td>
<td>319.85</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 bar</td>
<td>18.91</td>
<td>80 ± 3</td>
<td>69.23</td>
<td>51 ± 1</td>
</tr>
<tr>
<td>3 bar</td>
<td>37.14</td>
<td>24 ± 1</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>5 bar</td>
<td>62.92</td>
<td>10 ± 1</td>
<td>100</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>8 bar</td>
<td>68.66</td>
<td>3</td>
<td>100</td>
<td>2</td>
</tr>
</tbody>
</table>
The rejection rate of two other dye molecules (EB and MB) and sodium and sulfate ions by the 100 nm thick rGO membrane were also studied and the stable rejection rates are listed in Table 4.1, along with the stable water permeance. In measuring the stable rejection rates, the stable pure water permeance was obtained first with pure water permeation experiments under the corresponding pressure. The feed water was then replaced with the corresponding dye or salt solutions for rejection tests. The results show that when the applied pressure was equal and greater than 5 bar, a full rejection of all three dyes could be achieved on the membrane. The 100nm thick rGO membrane shows a moderate rejection (>62%) toward Na$_2$SO$_4$ under 3 and 5 bar, showing certain promise of using rGO membrane for water desalination.

After the EB dye rejection experiment, the membrane was characterized with SEM and a clear cake layer could be identified on top of rGO membrane (Figure 4.18). This also serves as an evidence that the membrane was rejecting the dye molecules.

Figure 4.18: The cake layer of EB that is formed on top of rGO membrane after rejection test under 5 bar.
4.3 Conclusions

This chapter revealed for the first time that rGO membrane, during pressure-driven water filtration, possessed significant water flux and species rejection kinetics. The water flux dropped quickly within an initial stage and obtained a stable value under sufficiently high applied pressure. Our results can be of help in explaining the discrepancy in the literature on the inconsistent water flux and rejection by stacked rGO membranes.
References


CHAPTER 5: CONCLUSIONS AND FUTURE PERSPECTIVES

5.1 Conclusions

The following are the major conclusions of this dissertation:

(1) The asymmetric water wetting behavior of the two surfaces of rGO membrane prepared by vacuum filtration method was revealed. We found that the asymmetry is originated from the filter membrane’s physical imprint, in the form of surface rGO microstructures, on the bottom surface of the as-made rGO membrane and the actual surface pore size of the membrane substrate is the key that controls the imprint during the filtration process. The microstructures are formed only when the pore size of the substrate has the similar dimension to the flake size of GO sheet used in the vacuum filtration. The microstructures, once formed, leads to higher water contact angle hysteresis, on the bottom surface of the rGO membrane than its top surface. This part of the dissertation contributes a significant effort to rGO based membrane research as it looks at a generally overlooked side of vacuum-filtration based rGO membrane preparation process and provides scientific insight behind it.

(2) Drastic differences were observed on the two surfaces of the same rGO membranes for water condensation and droplet growth. It turned out that the captured fog water droplets followed a film-wise collection on the bottom surface while a drop-wise collection on the top surface of the rGO membranes, which led to quite contrasting fog water collection efficiencies on the two surfaces. Furthermore, the mechanism of physical imprint was employed to rationally print pre-designed pattern selectively onto the bottom surface of the rGO membrane by simple vacuum filtration of GO aqueous solution. The idea was demonstrated by fabricating a silicon wafer with pre-
designed pore size and pore arrangement pattern (letters of ‘KAUST’) and utilizing it to fabricate the predesigned microstructured pattern of rGO selectively only on the bottom surface of rGO membrane via vacuum filtration. Thus, this dissertation contributes a significant effort in employing stacked rGO membrane for the applications other than water filtration.

(3) It was revealed for the first time that rGO membrane, during pressure-driven water filtration, possessed significant water flux kinetics. The membrane got more compact during the pressure-driven water filtration and both water flux and species rejection were highly dependent on the compactness of the membranes. Our results can be of help in explaining the discrepancy in the literature on the inconsistent water flux and special rejection by stacked rGO membranes.

5.2 Future perspectives

The suggested future work includes:

(1) The application of surface microstructures selectively on one surface of rGO membrane should be further explored. Besides, cold field emission, since the bottom surface of the rGO membrane has an ability to hold down to water, indicated by its high water hysteresis, its application to chemical reaction involving accurate control of water amount can be investigated. We also believe that the physical imprinting mechanism discovered in this dissertation can be further extended to other 2D materials, including but not limited to, MoS$_2$, WS$_2$, boron nitride, layered clays.
(2) The mechanism of the water transport through stacked rGO membrane deserves more research attention. Innovative approaches are much needed to engineer stacked rGO membrane to further increase its water flux and at the same time its molecular rejections. The attentions should also be paid to investigate the potential of using rGO membrane for water desalination and thus more efforts in ion rejection by rGO membrane should be invested.

(3) There has been a MD simulation on MoS$_2$ as potential water desalination membrane, but so far no any experimental proof exists. Therefore, research efforts should be made to other emerging 2D material based membranes for water filtration, especially for water desalination.