Fabrication of bioinspired super-hydrophilic nano-fibrous membrane for oil-water separation and directional water transportation

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Fabrication of bioinspired super-hydrophilic nano-fibrous membrane for oil-water separation and directional water transportation

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School of Civil and Environmental Engineering
2019

Fabrication of bioinspired super-hydrophilic nano-fibrous membrane for oil-water separation and directional water transportation

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School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research,
is free of plagiarised materials, and has not been submitted for a higher degree to any
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Li Zhengtao

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

09/03/2020

Date

DARREN SUN

Name

Authorship Attribution Statement

This thesis contains material from 1 papers published in the following peerreviewed journal(s) where I was the first author.

Parts of Chapter 4 and Chapter 7 are published as Li Zhengtao, Carl M. Tan, Wee Tio, Jeremy Ang, and Darren D. Sun. "Manta ray gill inspired radially distributed nanofibrous membrane for efficient and continuous oil–water separation." *Environmental Science: Nano* 5, no. 6 (2018): 1466-1472. DOI: 10.1039/C8EN00258D.

The contributions of the co-authors are as follows:

- A/Prof D.D. Sun provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Mr. W. Tio and Dr. J. Ang.
- I designed the study performed the laboratory work at the School of Civil and Environmental Engineering with the assistance of Mr. C.M. Tan. I also analyzed the data.
- All characterizations, including FESEM, FTIR, TGA, VCA, were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Mr C.M. Tan assisted in the collection of the oil-water separation data.

09-Mar-2020

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Summary

With the ever-increasing population and economy, energy and water crisis has been the most serious challenge throughout the world. On one hand, the energy source - fossil fuel which is highly relied on is non-renewable, and they fuel a series of environmental problems like climate change and air pollution. On the other hand, most of water technology, including water purification and water transportation, are severely hindered by the huge energy consumption. Therefore, energy efficient water purification and transportation is the key to solve this challenge.

The studies about natural super-wetting phenomena in recent years have provided a brand new idea in water technology, especially in oil-water separation and directional water transportation. Inspired by the special wetting behavior found on the surfaces of lotus leaves and pitcher plant, many super-hydrophobic materials were fabricated and studied for efficient oil-water separation. At the same time, some hydrophobic materials with special surface structures were also designed for directional water movement without external energy. However, for oil-water separation, hydrophobic materials tend to suffer from oil-fouling and low oil permeation flux, while for water transportation, they can only prompt the movement of water droplets. Hydrophilic materials are regarded as the candidate to overcome those shortcomings to achieve efficient oil-water separation and bulk water transportation.

In this study, electrospinning of silk fibroin was first employed to fabricate the super-hydrophilic nano-fibrous membrane. Electrospinning is able to create non-woven nanofibers, which allows the formation of novel membranes with high porosity and rough surfaces to mimic the natural super-wetting structures. As an ancient and environmental-friendly biomaterial, silk fibroin was first utilized in oil-water separation due to its hydrophilicity in this study. The as prepared membrane exhibited super-hydrophilic (water contact angle 0°) and underwater super-oleophobic (oil contact angle 155°). When conducting the oil-water separation, a stable water-oil interface could be formed on the surface of the membrane which allowed water permeation while repelling oil, and thus high oil-water separation efficiency ($\sim 99.9\%$) was achieved.

Another method to fabricate hydrophilic membrane was the modification of hydrophobic surface with hydrophilic material. Nano-sized metal oxide is able to introduce hydrophilicity of the surface and also increase the surface roughness to amplify its hydrophilicity. In this study, electrospinning method and hydrothermal process were combined to fabricate the copper oxide (CuO)-modified polyvinylidene difluoride (PVDF) membrane. Copper acetate was added in the electrospinning precursor as the seed for CuO growth. After electrospinning, CuO nanosheets can be grown easily on the seed-added PVDF nanofiber surface to form hierarchical micro-/nano-structure with large specific surface area via low temperature hydrothermal reaction. Experimental results showed that this approach successfully made the hydrophobic PVDF membrane become hydrophilic. The water contact angle was decreased from 135° to 16°, and underwater oil contact angle is ~150°. This selective wetting property enabled the membrane to separate oil from water. Lab scale oil-water separation test further illustrated that the membrane possessed excellent oil-water separation efficiency (oil removal rate > 99%).

By the similar synthesis process, zinc-oxide (ZnO) nanorod modified polysulfone (PSF) nano-fibrous membrane was also successfully fabricated. Zinc acetate was utilized as the zinc seed in the precursor, and ZnO nanorod was grown on the PSF nanofiber surface by low temperature hydrothermal process. Due to the photo-sensitivity of ZnO nanorods, the membrane obtained the photo-responsive wetting behavior. After dark storage, the membrane was hydrophobic (water contact angle ~135°); after ultraviolet (UV) irradiation, it rendered hydrophilic (water contact angle ~34°). The oil-water separation test further showed that under UV irradiation this membrane performed efficient oil-water separation (oil removal rate >99%). Moreover, this membrane demonstrated self-cleaning property which prompted degradation of foulants and contaminants under UV irradiation.

Subsequently, in order to overcome the fouling issues and noncontinuous operation of traditional gravity-driven dead-end approach, a facile membrane based set-up for oil-water separation was fabricated mimicking the crossflow filtration of manta ray

gill rakers in this study. This crossflow process was fabricated using an aligned electrospun nano-fibrous silk fibroin membrane. In this process, as the oil-water mixture travels in a parallel manner across the super-hydrophilic membrane surface, water permeated through the membrane while oil was rejected by the membrane and collected in the middle pipe. Experimental results showed that oil-water separation was achieved both efficiently and continuously.

Moreover, materials with super-wetting behavior are also regarded as a great candidate for water transportation. Although many researches focused on water directional movement phenomena based on the special surface morphology and surface charge of super-hydrophobic materials, these materials can only transport water droplet by droplet. Inspired from the bulk water transportation of trees, many efforts have been devoted to using hydrophilic materials for the water transportation, but none have delivered a sufficient approach for long-distance bulk water movement. Actually the size does matter, and nano gives the answer. In this study, the novel nano-fibrous matrix was successfully fabricated. It possessed remarkable advantages like small pore size, high porosity with 3D-connected pores, high specific area and high surface charge density. This unique structure and small fiber size of the nanofiber matrix increased its surface energy which maintained the hydration and drove the movement of the polar molecular H_2O to provide a good solution for the long-distance bulk water transportation without external energy. At the same time, in order to achieve the continuous water movement, inspired by the water transportation process of tree, evaporation process was utilized as the driving force of constant water movement, and eventually the energy source was free and unlimited solar energy.

To conclude, different kinds of super-hydrophilic materials have been systematically investigated focusing on the theory, fabrication, optimization, characteristics and its application. The experimental results presented in this study showed their great performance in efficient oil-water separation, and more importantly the long-distance bulk water transportation which has the potential to overcome the hurdle of huge energy consumption in water transportation.

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List of Symbols

<i>Symbol</i>	<i>Description</i>
θ	Contact angle
γ	Surface tension
r	Roughness Factor
h	Rising height
ρ_w	Water density
g	Gravitational constant
L	Wetting perimeter
S	Surface area
R	Oil rejection rate
C_0	Oil concentration of feed oil-water mixture
C_p	Oil concentration of permeate water
J	Water flux
V	Volume of permeated water
t	Time

List of Abbreviation

<i>Abbreviation</i>	<i>Description</i>
AO7	Acid orange 7
ATR	Attenuated total reflection
BET	Brunauer, Emmett, and Teller
DC	Direct Current
DI	Deionized
DFT	Density function theory
DMAC	N, N'-dimethyl acetamide
EDX	Energy dispersive X-ray spectroscopy
FA	Formic acid
FESEM	Field emission scanning electron microscope
FTIR	Fourier-transform infrared spectroscopy
HMTA	Hexamethylenetetramine
MF	Microfiltration
NF	Nanofiltration
PAN	Polyacrylonitrile
PES	Polyethersulfone
PP	Polypropylene
PSF	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene difluoride
RO	Reverse osmosis
SF	Silk fibroin
TGA	Thermal gravimetric analysis
TOC	Total organic carbon
TPNF	TiO ₂ -PVDF nanofiber
UF	Ultrafiltration
UV	Ultraviolet
WCA	Water contact angle

Chapter 1 Introduction

1.1 Background

1.1.1 Water Crisis

Water crisis has been one of the major challenges which is threatening the survival and development of human beings. Driven by the population growth, socio-economic development and changing consumption patterns, water demanding continuously increases, which has resulted in global problems: over 2 billion people live in countries experiencing high water stress; about 4 billion people experience severe water scarcity during at least one month of the year (WWAP 2019). Moreover, by the end of the year 2017, 10% of the world's population have not been able to use basic drinking water services (UNICEF/WHO 2019). Rapid urbanization left many slums without reticular water and sanitation networks; three quarters of people living in extreme poverty live in rural areas and suffer from water shortage and insecurity; displaced people and refugees are severely lack of water-related services (WWAP 2019).

According to the 2019 Revision of World Population Prospects, the world's population is expected to reach 8.5 billion in 2030, to be increased by around 10% from 7.7 billion in the mid of 2019 (UNDESA 2019). Continual rapid population growth has become a great threat to the sustainable development; moreover, the least developed countries are among the world's fastest growing, which adds more pressure on strained resource (UNDESA 2019). There is no doubt that the growth of population, especially population in developing countries, will increase water demand and worsen the water crisis.

Water also plays an important role in the ecosystem, industry, agriculture and economy, which counts a lot for the development of both developed countries and developing countries (WWAP 2016). The water issues are intractable and becoming increasingly complex as it intertwines with world's economy. These spreading global water shortages and inequalities are emphasizing the necessities of research on

creating novel and efficient water technologies would continue to flourish in the coming decades.

1.1.2 Oily Wastewater Treatment

Due to the rapid growth of population and industry, limited fresh water has been further burdened by serious pollution (Lu, Song et al. 2015), as a result of various types of pollutants, such as pathogenic contaminants (WWAP 2016), heavy metals (Yin, Feng et al. 2015), and fertilizers (Zou and He 2016). However, if the polluted water or wastewater can be purified and recycled, the negative influence on the environment can be minimized, and treated water can become a great potential source of fresh water. Among those different pollutants, oil pollution has gained worldwide attention, owing to the large scale oil spill accidents, which were regarded as great man-made catastrophes, in recent years (Tai, Tan et al. 2015). Moreover, oily wastewater from industries like petroleum, textile, food industry is also regarded as a common source of pollutant (Tan, Liu et al. 2016). Therefore, separation of oil from water needs to be studied urgently.

Traditional oil water separation technologies are mainly based on physical, chemical or biological methods, such as gravity separation, coagulation and flocculation, flotation, adsorption, and bio-degradation. (Jamaly, Giwa et al. 2015, Qin, Liu et al. 2015). However, most of these technologies suffer from some limitations such as large footprints, generation of secondary pollution, low efficiency, complicated instrumental setup, and high energy cost (Tan, Tai et al. 2015). Facing these drawbacks and challenges, researchers have been motivated to seek a novel and alternate technology for oil-water separation. Membrane technology, possessing small footprints, high efficiency and simple instrumental setup, has been considered as a promising technology in the future (Kota, Kwon et al. 2012). However, most of the membranes for oil-water separation are hydrophobic, which suffered from severe oil fouling as a result of the adsorption of oil droplets into the pores or on the surface of membranes. It also faces respectively low flux issues, owing to the hydrophobicity of the membrane used (Qin, Liu et al. 2016). These limitations restricted the potential applications of membrane for oil-water separation.

Nature offers a new idea for improving the performance of membranes for oil-water separation. Several plants, insects and animals with super-hydrophobic surfaces have attracted the attention of scientists. One of the most famous examples is super-hydrophobic lotus leaf surface, which possesses water contact angle above 150° and sliding angle at only 2° due to the micro-/nano-structures of hydrophobic waxes (Gao and Jiang 2004). This phenomenon is also named as *lotus effect*. Inspired by these fascinating super-hydrophobic natural surface, quantities of biomimic super-hydrophobic surfaces have been created for self-cleaning materials, anti-icing coatings, anti-corrosion coatings, micro-fluid devices, optical devices and so on (Darmanin and Guittard 2014). According to the wetting theory from Wenzel Model and Cassie Model, the super-hydrophobicity is determined by two factors. One is the intrinsic hydrophobicity of the material; the other is the roughness parameter which is decided by surface roughness and topography (Gao and Jiang 2004). The micro-/nano-structures of these bioinspired surfaces increase the surface roughness significantly and form stable air traps between the liquid-solid interface, which amplify the hydrophobicity. Despite many researches based on lotus leaf, this approach has severe limitations: (1) air traps are easily damaged under pressure; (2) air traps have low resistance to the low surface energy liquid unlike water; (3) the micro/nano structures suffer from mechanical defects and fabrication imperfection. To solve this, researchers used micro-/nano-structural substrate to lock lubricant, instead of air, to form a stable, defect-free and super-hydrophobic surface (Wong, Kang et al. 2011).

However, as for membrane technology, most of the oil-water separation processes are with water as permeate and oil as the liquid to be repelled. Thus, water can be used as the lubricant to assist repelling of oil, as long as the membrane is hydrophilic and micro-/nano-structured. Electrospinning is a promising technology that can fabricate non-woven membranes containing fibers with diameters ranging from micrometers to a few nanometers, which is micro-/nano-structured (Ma, Zhang et al. 2016). Consequently, electrospinning of hydrophilic materials is a promising method to fabricate this lotus-leaf-like super-hydrophilic nano-fibrous membrane.

Therefore, the fabrication of super-hydrophilic nano-fibrous membrane and assesses its applicability in oil-water separation. Silk fibroin was first applied as the raw material for electrospinning to fabricate nano-fibrous membrane. This membrane fabricated was super-hydrophilic and showed potential for oil-water separation. On the other hand, polyvinylidene difluoride (PVDF) and polysulfone (PSF) nano-fibrous membranes were fabricated by electrospinning. In order to modify the surface wetting behavior of PVDF and PSF membrane, a novel in-situ growth process of metal oxide was developed to obtain the hierarchical nano-fibers which increase the hydrophilicity and roughness of the membrane. Due to the special property of the metal oxide, the membrane can also possess anti-fouling and self-cleaning abilities.

Although super-hydrophilic and underwater super-oleophobic membranes can be effectively employed for the gravity-driven dead-end oil-water separation, this method has intrinsic limitations. These membranes can be easily clogged by oil, and the water flux will decrease significantly. Furthermore, the accumulation of oil on the membrane surface renders the separation process cannot be conducted continuously. Large sea creatures like manta rays feeding on suspended food particles are able to filter water rapidly and continuously (Misty Paig-Tran and Summers 2014). However, they have never suffered from the clogging of food particles, even although they have to filter large amount of water all the time, and this phenomenon is owing to their special structured gill rakers (Stewart, Beale et al. 2016). Manta rays separate the food particles from seawater via a crossflow filtration instead of dead-end filtration which prevents the clogging of their gill rakers (Brainerd 2001, Sanderson, Cheer et al. 2001, Paig-Tran, Kleinteich et al. 2013). These rakers allow seawater to pass through but retains the suspended food particles, at the same time these suspended food particles are washed off the gill rakers by the crossflow to avoid clogging. This crossflow filtration is beneficial as the particles and contaminants are less likely to be attached to the gill rakers of manta rays, compared with the dead-end filtration (Dou, Tian et al. 2017). Inspired by unique filtering structure of manta rays, we can solve this problem by combining membrane technology and the structure of manta ray gill rakers. By mimicking manta ray gills, a membrane based oil-water separation set-up can be created to achieve efficient and continuous oil-water separation.

1.1.3 Directional Water Transportation

Water and energy are intricately connected: We use water to help produce energy we need, and energy are also utilized to help us clean and transport water (Olsson 2015). Most of water technologies, including seawater desalination and wastewater purification, are severely hindered by huge energy consumption (Elimelech and Phillip 2011, Logan and Elimelech 2012, Werber, Osuji et al. 2016). Water transportation across micro-/nano-channels is of great importance for designing water purification technology (Zhu, Xie et al. 2016, Qin, Liu et al. 2018). Conventionally, it is believed that the directional movement of water requires hydraulic pressure gradient (Chua, Ji et al. 2015, Karpitschka, Das et al. 2015). Therefore, mechanical pumps are widely used, but they are energy-intensive. As a result, it is a key factor to find out a novel approach to achieve efficient water transportation with little energy consumption.

The water transportation of trees are drawing much attention for its efficient delivery of water from root to the upper crown through trunks (Cochard 2006, Ledford 2008). From the billions of years of evolution, nature created fantastic structures for the trees to transport water. The cellulose-dominated hydrophilic xylem with its multi-channel structure forms the “vessels” for the transportation of water and nutrients; the water and nutrients are then utilized by the transpiration of the trees; this water loss through trans-evaporation from the pores on the leave surfaces creates negative pressure within the “vessels” and drives the water up as the fluid is subjected to the tension caused by the metastable state (Wheeler and Stroock 2008). This is the venerable cohesion-tension theory.

Recently, some studies have been focusing on such tree-inspired designs (Chen, Kuang et al. 2019). However, most of them are focusing on the evaporation of water and thermal insulation of the evaporator, the distance water movement is short (Li, Gao et al. 2017, Li, Gao et al. 2017, Zhu, Li et al. 2017). Although they are well-designed for mimicking the transpiration of trees, the transportation of water is neglected. Either polymer based or natural wood based water pathways are unable to work as the trunk to lift water to several meters high. From the traditional material

point of view, the transportation of water is based on hydrophilic materials with small pores to make the water uphill via capillary forces (Chaudhury 1992). However, current materials are in micron range, and in our opinion, they are not small enough, while size does matter, which is the major obstacle to transport water in long distance. Therefore, nano materials are searched to overcome this limitation. Our super-hydrophilic nano-fibrous materials which possess remarkable advantages like small pore size, high porosity with 3D-connected pores, high specific area and high surface charge density provide a good solution for the long-distance water transportation.

1.2 Research Approach and Hypothesis

The following research approaches or opportunities will be explored in stages to study the fabrication of different kinds of super-hydrophilic nano-fibrous membrane and their applications:

1. The fabrication of silk fibroin nano-fibrous membrane will be explored first. Owing to the hydrophilicity of silk fibroin, it is a good material for the oil-water separation membrane. Furthermore, as a natural material, it exhibits no hazard to the environment. Its great potential for water treatment will be investigated for the first time. Electrospinning as a facile method is chosen for the synthesis of the nano-fibrous membrane, whose hierarchical micro-/nano-structure and interconnected pores show great opportunity for efficient oil-water separation.

2. The fabrication of nano-size metal oxide modified polyvinylidene difluoride (PVDF) and polysulfone (PSF) nano-fibrous membranes will be undertaken. Although silk fibroin membrane has great potential in water treatment, this material is expensive and its chemical resistance is poor. Therefore, traditional polymers PVDF and PSF which are cheap, resistant to chemicals and heat (Mahmoudi, Ng et al. 2015, Park, Jee et al. 2017, Zuo, Chung et al. 2017) are chosen to be the raw material of the nano-fibers. However, both PVDF and PSF are hydrophobic and not optimal for oil-water separation, so it is necessary to make some surface modification to change the surface property (Qin, Li et al. 2015, Zambare, Dhopte et al. 2017). Nano-sized metal oxide with great wetting behavior like zinc oxide (ZnO) and copper

oxide (CuO) is believed to be a good option to help modify the surface property. An in-situ growth method will be explored to obtain the composite nano-fibrous membrane.

3. A manta ray gill inspired oil-water separation set-up will be created. In order to mimic the continuous and efficient crossflow filtration of manta ray gills, we can combine membrane technology and the structure of gill rakers. The membrane with aligned nanofiber will be fabricated by electrospinning on a specially designed collector. During the continuous oil-water separation process, water permeates through the membrane rapidly, while oil is repelled and collected.

4. The directional water movement via super-hydrophilic nano-fibrous matrix will be investigated. The efficiency of water transportation of trees is attractive for an energy-saving water production. Water is 'pumped' from root to leaves via the micro-range hydrophilic xylem vessels. It is always believed that capillary forces and surface energy in the small tubes play an important role for this process, while in nano-sized matrix, smaller pore size, larger surface area and higher surface energy will definitely amplify its ability for water movement. We hypothesize that nanomaterials will add more value to the tree-inspired water transportation process. Therefore, super-hydrophilic nano-fibrous matrix is a good candidate for it.

1.3 Objectives and scope of works

For this study, the fabrication of super-hydrophilic nano-fibrous membrane will be explored by electrospinning method and the novel in-situ hydrothermal growth of metal oxide nanostructures. As synthesized membrane will first be investigated for its oil-water separation efficiency, followed by the creation of the manta ray gill inspired oil-water separation set-up and the water transportation set-up

The objectives of this study are as follows:

- To synthesize silk fibroin nano-fibrous membranes with super-hydrophilic property via electrospinning;

- To synthesis polyvinylidene difluoride nano-fibrous membranes and grow CuO-nanosheet for the modification of the surface property via electrospinning;
- To synthesis polysulfone nano-fibrous membranes and grow ZnO-nanorod for the modification of the surface property via electrospinning;
- To characterize the fabricated nano-fibrous membranes using field emission scanning microscopy (FESEM), Fourier-transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), Brunauer, Emmett, and Teller (BET), density function theory (DFT) method, and energy dispersive X-ray spectrometer (EDX);
- To examine the oil-water separation efficiency.
- To fabricate the manta ray gill inspired oil-water separation set-up and test its efficiency.
- To fabricate the water directional transportation set-up and test its efficiency.

1.4 Organization of the thesis

This thesis comprises nine distinctive chapters.

Chapter One provides an introduction to research background and general information of use of bioinspired nano-technological membrane for oil-water separation and water directional movement. The objectives, scope and organization of the report are also included in this chapter.

Chapter Two presents the literature reviews on wetting theories and bioinspired super-wetting membrane for oil-water separation. The recent advances of silk fibroin copper oxide-modified and zinc oxide-modified membrane are also covered.

Chapter Three describes the materials and methods used in the experimentation process.

Chapter Four to Eight presents the results and discussions of this study.

Chapter Four focuses on the fabrication, characterization and the oil-water separation applications of the electrospun silk fibroin membrane.

Chapter Five discusses the copper oxide modified PVDF nano-fibrous membrane fabricated by the combination of electrospinning and hydrothermal process. Characterization and oil-water separation results of them will be discussed subsequently.

Chapter Six introduces a leaf inspired photo responsive zinc oxide modified PSF nano-fibrous membrane. Characterization and the photo responsive wetting behavior of the membrane will be discussed, followed by its oil-water separation application, photo-catalytic and self-cleaning property.

Chapter Seven presents and analyzed the continuous oil-water separation efficiency and application potential of the manta ray gill inspired radially distributed nano-fibrous membrane (synthesized by a novel aligned electrospinning method).

Chapter Eight discusses the water directional transportation via nano-fibrous matrix and eventually the mechanism of the water movement.

Chapter Nine concludes the scientific achievement of this study and lays out recommendations for future research.

Chapter 2 Review of theory and previous work

2.1 Global challenges from water and energy

Fresh water is necessary for the survival of human beings and sustainable development of the world. Due to the burgeoning of population, living standard, industrialization and urbanization, the demand of this valuable resource has been increased significantly, and water shortage has threatened different countries and districts throughout the world. According to the 2016 Water Report of United Nations, global fresh water withdrawal has increased 1% per annum since the 1980s; with the growth of population and economy, agricultural, industrial and domestic water demand are expected to rise (WWAP 2016). In order to meet the expanding water demand, groundwater abstraction has to increase (WWAP 2012). Although the groundwater can be recharged, the usage in some parts of the world exceeds the rate of replenishment of the aquifer (Amos, Audet et al. 2014). Moreover, fossil groundwater will not be naturally replenished. The over-exploitation of groundwater has caused series of severe impacts such as land subsidence and seawater intrusion. The availability of water has also been threatened by the pollution. Polluted water is not able to be utilized in many areas, and may do great harm to human health, economics and environment. As estimated by researchers, excessive biochemical oxygen demand (BOD) threatens the water quality of one-fifth of the world population, while one-third will be affected by excessive nitrogen and phosphorus in water (IFPRI and VEOLIA 2015).

Oily wastewater from industries such as petroleum, textile, lubricant, metallurgical, food processing has been regarded as one of the most common pollutants throughout the world. Additionally, due to the frequent oil spillage into the ocean, oil pollution has been received increasing concern globally. Oil spills, which often occur during oil exploration, extraction, transportation and storage, are likely to result in mass mortality of the ocean creatures like birds, whales and fishes. Moreover, toxic compounds from oil will accumulated and threaten all of the species along the food chain. Among the numerous historical oil spill accidents from 1967 Torrey Canyon oil spill to the most recent Kuwait oil spill in 2017, the most notorious one was the oil spill disaster which occurred in Gulf of Mexico in 2010 (Wang, Liang et al. 2015).

As the United States (US) government estimated, approximately 4.9 million barrels (equivalent to 210 million US gal or 780,000 m³) of crude oil was spilled into the ocean (US 2011). Reports in the early 2012 indicated that the oil well was still leaking (Jamail 2012). Therefore, treatment of oil polluted water has become a worldwide urgent challenge to be addressed. In addition, if the waste oil can be separated from water efficiently, not only the effects of pollution can be minimized, but oil can also be re-collected and reused in various areas. The development of new technology with high efficiency and low costs is imperative.

2.2 Oil-water separation technologies

2.2.1 Traditional technologies

Traditional oil-water separation technologies include physical, chemical and biological methods.

Physical method employs gravity separation, adsorption and floatation. For spilled oil, booms and skimmers are also utilized (Zhang, Shi et al. 2013, Liu, Wang et al. 2016, Ren, Song et al. 2018). However, the efficiency of gravity separation, floatation, booms and skimmers is not satisfactory, because much oil emulsifies with water and becomes difficult to separate (Ge, Ye et al. 2014, Wang, Yu et al. 2016). As for adsorption, the secondary treatment of the used adsorbent will bring additional treatment cost (Lv, Mei et al. 2017, Jiang, Zhang et al. 2019).

Chemical method involves the use of dispersants (Cai, Fu et al. 2017), solidifiers (Motta, Stoyanov et al. 2018), electro-coagulation (Golzary, Imanian et al. 2015) and burning (Fritt-Rasmussen, Wegeberg et al. 2015). Compared with physical methods, the efficiency of chemical method is much better. However, most of the chemical method is expensive due to the need of large quantity of chemicals (Vibhute, Muvvala et al. 2016). In addition, some of the chemicals used are hazardous to environment and can easily cause secondary contamination (Ma, Cheng et al. 2016).

Biological method often relies on the rate of bio-degradation for the removal of oil (Fingas 2016). There are two ways to achieve the increment: (1) increase the number

of microorganism; (2) supply more nutrients like nitrogen, phosphorus and oxygen to facilitate the increment of bio-degradation (Hazen, Prince et al. 2016). Nevertheless, biological methods require longer treatment time compared to chemical and physical methods. Moreover, nutrients and microorganisms may also result in secondary contamination.

2.2.2 Membrane technology

Since 1960s, membrane technology has been advanced significantly and applied in various areas. Since membrane can repel pollutants while allowing water to pass through, it is regarded as a promising technology to help solve the water crisis throughout the world (Kota and Tuteja 2013, Fane, Wang et al. 2015). Different from the conventional technologies, membrane possesses several advantages: (1) high pollutant removal efficiency; (2) low chemical usage minimizing possibility of secondary contamination; (3) simple and reliable operation; (4) compact system diminishing large footprint; (5) wide suitability for different situations.

Therefore, membrane technologies, including microfiltration and ultrafiltration (MF/UF) which are low pressure-driven and nanofiltration (NF) and reverse osmosis (RO) which are high pressure-driven, have exhibited their promising futures in the fields of water treatment and seawater desalination (Elimelech and Phillip 2011, Fane, Wang et al. 2015). For oil-water separation, in order to achieve the efficient separation at lower cost, membranes are required to possess special properties such as selective wetting behavior, high flux of permeate liquid, easy regeneration and reusability. However, most of the traditional membrane are made of hydrophobic materials; hence it tends to suffer from: (1) low flux due to the high permeate (oil) viscosity, and (2) severe oil-fouling resulted from the hydrophobicity of membrane material (Koltuniewicz, Field et al. 1995, Robinson, Tarleton et al. 2004, Hu and Scott 2008). The fouling due to accumulation of the oil in the pores or on the surface of membrane often results in the reduction of permeate flux and the increase of operational costs. It also reduces the life expectancy of membrane. Furthermore, the quality of water treated by fouled membrane would be relatively low as compared to clean membrane. Fouling now remains to be the main drawback that restricts the

applications of membrane in oil-water separation. Thus, novel membranes with special wetting properties are required to break through the bottle neck.

2.3 Super-hydrophilic Membrane

2.3.1 Theories of wettability

Wettability indicates the tendency of one fluid to spread on or adhere to a solid surface, which refers to the interaction between fluids and solid phases. Wettability is mainly determined by surface energy. When a liquid droplet interacts with the solid surface, the surface energy of this solid-liquid-vapor interphase always remains minimal. The wettability of a solid surface by a liquid plays an important role in surface science and has varieties of applications in anti-icing, self-cleaning, microfluidic devices, textiles, optical devices and so on (Darmanin and Guittard 2014).

Contact angle is the most common way to measure the wettability of a particular surface. Materials with surface water contact angle (WCA) higher than 90° is considered to be hydrophobic, while lower than 90° is hydrophilic. Super-hydrophobic surfaces (WCA higher than 150°) and super-hydrophilic surfaces (WCA almost 0°) has been widely researched in recent years.

From the theoretical point of view, Young's equation forms the foundation of wetting science, which determines the contact angle of the liquid on the ideally smooth solid surface as shown below in Equation 2.1:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta_Y \quad (\text{Equation 2.1})$$

where θ_Y is Young's contact angle, γ_{SA} , γ_{SL} and γ_{LA} are the surface energies of solid-air, solid-liquid and liquid-air (as shown in Figure 2-1). Since water is a high-surface-energy liquid (γ_{LA} is large), γ_{SA} should be high while γ_{SL} should be low to obtain a positive $\cos \theta_Y$, which indicates that the surface is hydrophilic ($\theta_Y < 90^\circ$).

Figure 2-1 Young's model

Young's equation describes the ideal condition, while the roughness of solid surface is a parameter that heavily influences the contact angle. In order to describe the influence of surface roughness to contact angle, Wenzel model and Cassie model were established.

In Wenzel model, as shown in Figure 2-2a, liquid fills all the valleys on the surface. As a result, the liquid-solid interface area is enlarged. Factor r , defined as the ratio of real surface area of the apparent one describing the roughness, is employed to modified the Young's equation. The real contact angle is illustrated as shown below in Equation 2.2:

$$\cos\theta_w = r\cos\theta_Y \text{ (Equation 2.2)}$$

Equation 2.2 suggests that when a surface is hydrophobic ($\theta_Y > 90^\circ$, $\cos\theta_Y < 0$), $\cos\theta_w$ will decrease as the roughness increases (the value of r increases), and θ_w will increase. On the contrary, when a surface is hydrophilic, θ_w will decrease as the roughness increases. In other words, roughness of a surface will make hydrophobic surface more hydrophobic and hydrophilic surface more hydrophilic.

Figure 2-2 Wenzel model (a) and Cassie model (b)

In Cassie model, as shown in Figure 2-2b, liquid does not fill all the valleys on the surface. Liquid is only in contact with top of the solid surface, and air “pockets” are trapped between the solid and liquid. That is to say, on this surface, the interface is not only liquid-solid but also liquid-air. Therefore, Cassie model is described as shown below in Equation 2.3:

$$\cos\theta_C = f_s \cos\theta_s + f_a \cos\theta_a \quad (\text{Equation 2.3})$$

where f_s and f_a are the area fraction of solid and air on the surface. Since $f_s + f_a = 1$; $\theta_s = \theta_Y$ and $\theta_a = 180^\circ$, Equation 2.3 can be rewritten as shown below in Equation 2.4:

$$\cos\theta_C = f_s \cos\theta_Y + f_s - 1 \quad (\text{Equation 2.4})$$

Meanwhile, we can combine Wenzel model and Cassie model, so Equation 2.4 can be written as shown below in Equation 2.5:

$$\cos\theta_C = f_s r \cos\theta_Y + f_s - 1 \quad (\text{Equation 2.5})$$

r refers to the roughness ratio of the solid surface in contact with the liquid. When f_s is 1, Equation 2.5 will be the same as Equation 2.2 as Wenzel model. However, f_s is smaller than 1 most of time, so θ_C will be larger than θ_Y .

While under water, the vapor phase in the former models will be changed to water as shown in Figure 2-3, hence the new Young's equation is shown below:

$$\gamma_{SW} = \gamma_{SO} + \gamma_{OW} \cos \theta_{OW} \quad (\text{Equation 2.6})$$

$$\cos \theta_{OW} = \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}} \quad (\text{Equation 2.7})$$

where γ_{SW} , γ_{SO} and γ_{OW} are the surface energies of solid-water, solid-oil and oil-water. According to Young's equation in the air:

$$\gamma_{SW} = \gamma_{SA} - \gamma_{WA} \cos \theta_W \quad (\text{Equation 2.8})$$

$$\gamma_{SO} = \gamma_{SA} - \gamma_{OA} \cos \theta_O \quad (\text{Equation 2.9})$$

Equation 2.7 can be changed as:

$$\cos \theta_{OW} = \frac{\gamma_{OA} \cos \theta_O - \gamma_{WA} \cos \theta_W}{\gamma_{OW}} \quad (\text{Equation 2.10})$$

where θ_O and θ_W are the contact angle of oil and water in air.

Figure 2-3 Young's model underwater

As shown in Equation 2.10, if the solid surface is hydrophilic ($\cos \theta_O > \cos \theta_W > 0$), since the surface energy of oil-air is much smaller than that of water-air ($\gamma_{OA} \ll \gamma_{WA}$), the value of $\cos \theta_{OW}$ is negative. Thus, the underwater oil contact angle is above 90° . The in-air-hydrophilic surface shows oleophobicity underwater.

As for a hydrophobic and oleophilic surface ($\cos\theta_o > 0 > \cos\theta_w$), the value of $\cos\theta_{ow}$ is positive, so this surface is underwater oleophilic.

2.3.2 Natural super-hydrophobicity

In nature, many surfaces demonstrated excellent non-wetting behavior. Among them, lotus leaf is one of the most well-known examples, on which raindrops can easily roll away and carry the dirt away. The water contact angle is above 150° , and sliding angle is less than 2° (Liu, Yao et al. 2010). Such a super-hydrophobicity and the excellent low adhesion capability are regarded as “lotus effect”. Due to the progression of surface science and bionics, a new idea for efficient oil-water separation is offered by mimicking this natural super-hydrophobic surfaces.

Super-hydrophobicity of some natural material was firstly believed to be caused by the surface tension effect of the secreted wax. In 2004, based on the research of water repelling legs of water striders, Gao and Jiang discovered its water resistance is induced by the hierarchical micro-/nano- structure of the legs (Gao and Jiang 2004). Since there are many oriented tiny hairs (microsetae) and fine nano-frooves on the water strider legs as shown in Figure 2-4(a), many air gaps are locked in the hierarchical structures and prompt the water repelling property. It was then more natural materials were studied.

It was reported that the unique super-hydrophobic self-cleaning property of the lotus leaves is attributed to the epicuticle wax and the micro-/nano-scale structures on the surface (Liu, Yao et al. 2010) as shown in Figure 2-4(b). Owing to the special T structures on the surface, some arthropods such as pringtails (*Orthonychiurus stachianus* and *Tetrodontophora bilanensis*) possessing omniphobicity are even able to repel low surface energy liquid (Hensel, Finn et al. 2014) as shown in Figure 2-4(c). Due to the nanoscale nipples covering the micro-hemisphere, the mosquito eyes show striking super-hydrophobic anti-fogging properties (Gao, Yan et al. 2007) as shown in Figure 2-4(d). The microstructure of moth eyes and cicada wings are also remarkably similar to the mosquito eyes, which demonstrate similar super-

hydrophobic anti-fogging and antireflection properties (Sun, Jiang et al. 2008, Ivanova, Hasan et al. 2012) as shown in Figure 2-4(e). Other species like water strider and gecko are able to walk or slip on water, which is also because of the micro-/nano-structures on their surfaces (Hu, Chan et al. 2003, Gao and Jiang 2004, Hansen and Autumn 2005, Lee, Lee et al. 2012) as shown in Figure 2-4(f).

Figure 2-4 Natural super wetting surfaces: (a) water strider (Hu, Chan et al. 2003, Gao and Jiang 2004); (b) lotus leaf (Liu, Yao et al. 2010); (c) *Folsomia candida* (Hensel, Finn et al. 2014); (d) mosquito eyes (Gao, Yan et al. 2007); (e) cicada wings (Ivanova, Hasan et al. 2012); (f) gecko (Lee, Lee et al. 2012).

According to the theories introduced before, the super-hydrophobicity of these natural surfaces is mainly due to the hierarchical micro-/nano-structures which significantly increase the roughness of the surface and form the air pocket between water and solid.

2.3.3 From super-hydrophobicity to super-hydrophilicity

Inspired by these natural super-hydrophobic materials, scientists began to fabricate biomimic material with micro-/nano-structures for oil-water separation.

Super-hydrophobic and super-oleophilic materials are typically used for removing oil. This property will make oil spread easily and then absorbed (for porous sponge-like material) or penetrated (for filter material), while it repels water, thus achieving the oil-water separation. As discussed in the theory part, wettability of surface is determined by the chemical composition and the surface structure. As a result, there are two strategies to fabricate the super-hydrophobic and super-oleophilic materials. One is to modify the surface roughness with hydrophobic materials; the other is to build a rough surface of hydrophobic materials.

In 2004, Feng et al. first fabricated super-hydrophobic and super-oleophilic surfaces on stainless steel mesh via spray-and-dry method (Feng, Zhang et al. 2004). Water will form a droplet on the surface and can easily roll off, while oil can penetrate the mesh within only 240 milliseconds. It indicated that this surface-modified mesh can separate oil and water efficiently. Since then, various methods and materials were employed to fabricate super-hydrophobic and super-oleophilic meshes. Apart from inorganic porous meshes, soft and flexible organic fabric materials and sponge or foam based materials are also widely studied.

However, there are also some challenges faced with the use of these materials. Firstly, these materials are only suitable for the layered oil-water mixture. As for emulsified oil-water mixture, these materials are not effective in the separation. In order to solve this problem, membrane technology may be an ideal choice. Due to its small pore

size and high separation efficiency, membranes with modified super-wetting surface would likely be a promising choice for oil-water separation.

Secondly, since oil always floats on water due to the density difference, it is a challenge to make oil contact with the separation surface, resulting in low separation efficiency and complex process. Moreover, owing to the high permeate viscosity, the flux of oil would be lower. Oil fouling on the surface poses another great limitation. Therefore, compared with hydrophobic surface, if the surface is hydrophilic which can allow water pass through while repelling oil, all of these problems can be solved.

Thirdly, the roughness surface can be easily damaged, which can result in the loss of super-hydrophobicity and also decrease the separation efficiency. Inspired by *Nepenthes pitcher* plants, Wong et al. adopted different method to obtain the self-repairing slippery surfaces with pressure-stable omniphobicity (Wong, Kang et al. 2011). Their concept is different from lotus leaf effect. In order to avoid the damage of surface structures and maintain the super-omniphobicity, lubricating fluid is managed to be locked within the micro-nanostructures on surfaces. The schematics is shown in Figure 2-5. This slippery liquid-infused porous surface (SLIPS) is based on three criteria: (1) the lubricating liquid must fully wet the substrate and stably adhere with in it; (2) the substrate prefers being wetted by lubricating liquid rather than the liquid to be repelled; (3) the repelled liquid and lubricating liquid are immiscible. Thus, if a special material uses water as the lubricating liquid, it will have a promising future for oil-water separation. To satisfy these three criteria, it is the most important to fabricate a micro-nanostructured hydrophilic surface.

Figure 2-5 Schematic image of slippery liquid- infused porous surface(s) (SLIPS)
(Wong, Kang et al. 2011).

To conclude, in order to overcome the three limitations, we can fabricate a super-hydrophilic membrane with micro-nanostructured surface, which uses water as lubricating liquid to help repelling oil. There are two methods proposed to develop this membrane. One is to fabricate a micro-nanostructured surface of super-hydrophilic materials. The other is to modify the micro-/nano-structured surface with super-hydrophilic materials. Electrospinning shows promising potential as the technology to fabricate these membranes with special surfaces.

2.4 Electrospinning

2.4.1 Introduction and application of electrospinning

Electrospinning is a versatile and inexpensive technique, which produces continuous fibers at micrometer and even nanometer scale. The electrospinning process involves the substantial elongation of viscoelastic polymer solution jet, which is driven by electrical forces of free charges on the surface or inside the solution. Under the applied high voltage, the electrical force is strong enough to overcome the surface tension of the polymeric solution, a thin polymer jet would be formed from the needle tip and stretched in uniaxial direction. The stretch elongates the jet and makes it thinner to a scale of micron meter and even nanometer. At the same time, the evaporation of solvent in the polymeric solution accelerates the thinning process, leaving the nanofibers of the polymer. The stretched fibers would deposit on a collector and form a nonwoven mat or membrane (Teo and Ramakrishna 2006). A schematic diagram (as shown in Figure 2-6) shows the basic principle of electrospinning.

Figure 2-6 Schematic diagram of electrospinning (Li and Xia 2004)

The concept of electrospinning can be tracked back to 18th century; it has been widely studied since 1990s (Reneker and Chun 1996). With electrospinning technology, nanofiber components can be manipulated. This makes the fabrication of membrane with desirable functionalities possible. Thereafter, numerous electrospinning fibers possessing different structures like hollow, core-shell and honeycomb have been reported (Li, Wang et al. 2003, Li and Xia 2004, Dalton, Klee et al. 2005). Moreover, the one-dimensional nanofibers made via electrospinning obtain excellent structural mechanical strength, nanoscale pore size and large specific surface area coupled with remarkable porosity due to the interconnected pore structure. After decades of development, electrospun fibers have been utilized in many areas such as filtration (Liu, Wang et al. 2013), tissue engineering (Zhan, Liu et al. 2016), electronic and photonic devices (Li, Wang et al. 2016) and also sensor technology (Senthamizhan, Celebioglu et al. 2014).

Electrospinning has enormous potential in water treatment. Electrospun nano-fibrous materials can reach very small pore size range which is capable for application of microfiltration and ultrafiltration. Meanwhile they can be utilized in nano-composite membrane as the supporting layer. Compared with traditional phase inversion method, electrospun nano-fibrous materials have higher porosity and low tortuosity. Thus the eletrospun materials have higher flux compared to phase inversion membrane. For example, Song *et al.* used electrospun nanofibers as the supporting layer of forward

osmosis membrane to break the bottleneck of internal concentration polarization (Song, Liu et al. 2011). The high porosity and low tortuosity of electrospun nanofibrous layer resulted from interconnected pore structure favored the salt diffusion in the support layer, and the effect of internal concentration polarization was minimized, which resulted in a higher flux performance.

Electrospun filters are also employed in the air purification area. Liu *et al.* introduced a transparent air filter for indoor air protection through windows that uses natural passive ventilation to effectively protect the indoor air quality (Liu, Hsu et al. 2015). This electrospun filter was highly effective because of its small diameter and special surface. They manipulated the surface chemistry to make the nanofiber obtain strong particulate matter (PM) adhesion. At the same time, due to the porous structure of the nanofibers, their ability to capture PM was increased as well. Hence, the electrospun air filter showed practical applicability to the removal of PM_{2.5}.

The sensor application can be exemplified by a research of real-time selective visual monitoring of mercury ion (Hg^{2+}) detection at ppt level conducted by Senthamizhan *et al.* Golden clusters engraved with ligand was used as the functional material (Senthamizhan, Celebioglu et al. 2015). Electrospun nanofibers, on which various ligands were able to be effectively grafted to enhance the attachment of nanoparticles, were adopted to form a stable platform for holding and protecting the golden clusters. Meanwhile, the large specific surface area of nanofibers significantly decreases the need of materials, and a small piece of it will be able to work well. In addition, extensive applications of nanofibrous materials are promising due to their high porosity, large surface area and ability to be functionalized on surface.

Electrospun nanofibers with high specific surface areas, nanoscale pore sizes and highly interconnected pore structures have promising application in oil-water separation (Ma, Zhang et al. 2016). Moreover, active nanoscale structures can be induced on the surface of nanofibers to obtain different properties (Li, Wang et al. 2016). Thus, they have the potential to work like the micro-/nano-structured superhydrophilic surfaces using water as lubricating liquid to repel oil.

2.4.2 Morphology of electrospun nanofibers

The morphology of electrospun fibers is decided by a number of processing parameters which includes the intrinsic properties of the raw materials or precursor solution with different solvent/solute systems and the operating conditions.

The influence of intrinsic properties has been investigated by many scientists, which includes the physical and chemical properties of the polymer, concentration, viscosity, conductivity, and surface tension of the solution. A systematic electrospinning parameter research about concentration, viscosity and conductivity was carried out by Tan et al. When the concentration is low, the fibers formed would not be uniform and contained a lot of beads on the fiber, which is unfavorable (Tan, Inai et al. 2005). The reason leading to bead-on-string morphology could be the higher surface tension, lower viscosity and conductivity of the lower concentration solution (Yuan, Zhang et al. 2004). The formation of fibers is due to the electric force overcoming the surface tension. When a low molecular weight liquid is driven by electric force, droplets will form due to the capillary breakup of the spinning jet, which is known as electrospraying (Fong, Chun et al. 1999). For polymer solutions, the capillary breakup is different. Fibers will be formed between droplets, and thus a stable beads-on-string structure is developed. As the viscosity of the solution increases, beads will become less prominent, and their shape will become changes from spherical to spindle-like. When surface tension increases, the solution tends to keep spherical shape in order to minimize the surface energy and forms more beads on the surface. While, increasing the conductivity can also make the fibers thinner and at the same time decreases the number of beads. Under the same electric field, the solution with higher conductivity exhibits more charge density. Therefore, the electric force will be larger, and a higher degree of elongation will be triggered.

Operating conditions includes the applied voltage, the distance between spinneret and collector, feeding rate of solution, temperature and humidity. In the case of electrospinning, applied voltage is regarded as the driving force. If the voltage is too low, the electric force is not strong enough to overcome the surface tension, and thus

there will be no jets formation. On the other hand, if the voltage is too high, the jets will become unstable and the fiber beads density will increase (Deitzel, Kleinmeyer et al. 2001, Lee, Kim et al. 2003). According to Yuan et al, increasing the distance between spinneret and collector can have more time for the solvent to evaporate and for the charged fluids to split, so the electrospun fibers can be thinner (Yuan, Zhang et al. 2004). However, the distance is also an impact factor of the electric field strength. If the distance is too large, the electric field strength will be too small to stretch the solution to form the jets. Changing the feeding rate of solution can also influence the electrospinning. The feeding rate that is smaller or larger than the spinning rate will cause the jet to become unstable and lead to the formation of more beads or solution droplets. The ideal condition is that there is an equilibrium of the solution mass between spinning and feeding. Nevertheless, some researchers also indicated that slower feeding rate benefited the evaporation of solvent and this avoided beads formation (Yuan, Zhang et al. 2004). The influences of temperature and humidity on electrospinning process are also investigated by scientists. Demir et al. reported that higher temperature accelerated the electrospinning and influenced the morphology of electrospun fibers formed which were relatively uniform (Demir, Yilgor et al. 2002). Moreover, Mit-uppatham et al. also investigated that higher temperature decreased the viscosity of solution, which lead to the reduction of fiber diameter (Mit-uppatham, Nithitanakul et al. 2004). Some researchers had found that humidity had effect on the morphology of electrospun fibers as well (Li and Xia 2004, Li, Mondrinos et al. 2005, Bhardwaj and Kundu 2010). The table below summarized the parameters and their effect on the morphology of nano-fibers.

Table 2-1 Summary of parameters affecting properties of nanofibers

Parameters		Effect
<i>Solution</i>	Viscosity of Solution	Increase viscosity increases fiber diameter
	Concentration of Polymer Solution	Increase concentration results in higher amount of polymer deposited
	Applied Voltage	Increase voltage decreases fiber diameter

<i>Operation</i>	Distance of the collector from spinneret	Increase distance reduces fiber diameter
	Pumping Rate	Too low may stop development of Taylor's cone, too high may cause pulsing
<i>Ambient</i>	Temperature	Increase temperature increases fiber diameter
	Humidity	Increase humidity reduces fiber strength

For various applications, the required morphology of eletrospun fibers are different. In order to obtain the optimized material, all of the parameters mentioned before need to be considered, and the most suitable solution properties as well as the best operating conditions are required.

2.5 Silk fibroin

A number of animals can generate silk for specific tasks (Omenetto and Kaplan 2010). Silkworms and spiders are the most well-known examples. The farming *Bombyx mori* (*B. mori*) silkworms which produce cocoons from silk composite fibers to protect them from predators during their metamorphosis into moths can be traced back millennia (Fu, Shao et al. 2009). Such silk has been utilized by humans for applications including currency, hunting (bow strings, cross hairs, fishing lines or nets), textiles, paper and wound dressings (Hardy and Scheibel 2010). The mechanical properties of silk are superior to most artificial fibers including Nylon, Kevlar and high-tensile steel (Shao and Vollrath 2002, Omenetto and Kaplan 2010, Su and Buehler 2016).

Figure 2-7 Schematic diagram showing the structure of silk fiber (Zhao and Asakura 2001).

Silkworm cocoon silk consists of two structural proteins, the heavy chain (~350 kDa) and the light chain (~25 kDa), which are conglomerated by a family of hydrophilic sericin proteins (Vollrath and Knight 2001, Jin and Kaplan 2003). The proportion of two kinds of fibroin is 1:1, and they are linked by a single disulfide bond (Silva, Vilela et al. 2014). Sericin proteins can be easily removed from cocoons by boiling in aqueous alkaline solution (Ho, Wang et al. 2012). The amino-acid molecules form hydrogen-bonded polypeptide strands that crystallize into β -sheet nanocrystals. These nanocrystals constitute silk fibrils, and the multilayered silk fibroin fibers are covered by the sericin as shown in Figure 2-7 (Zhao and Asakura 2001, Ketten, Xu et al. 2010, Ude, Eshkoor et al. 2014). The hierarchical structures are regarded as the reason why silk possesses the special strength and stiffness.

In recent years, the applications of silk were widely expanded. Silk protein based materials, especially degummed silk fibroin materials are playing increasingly important roles in biomedical engineering, photonic devices and electronics (Tao, Kaplan et al. 2012, Kundu, Kurland et al. 2014). The superior physical and chemical properties as well as excellent biocompatibility, controllable biodegradability and limited bacteria adhesion presented by silk protein offer unlimited opportunity in diverse fields (Lu, Wang et al. 2011, Tao, Kaplan et al. 2012, Zhang, You et al. 2015). Meanwhile, silk is explored to be transformed into a variety of new material formats

like films, hydrogels, capsules, scaffolds, threads, nanoparticles, nanofibers and coatings for various applications by the regeneration process (Hu, Gupta et al. 2013, Liu, Zhang et al. 2015, Xiao, Lu et al. 2016).

In order to acquire the regenerated silk protein based materials, degummed silk fibroin will be dissolved in solutions such as Lithium bromide (LiBr) aqueous solutions (Yun, Cho et al. 2013), Calcium chloride (CaCl_2) - ethanol ($\text{C}_2\text{H}_5\text{OH}$) - water (H_2O) solutions (Guo, Ke et al. 2014), CaCl_2 -formic acid solution (Zhang, You et al. 2015). Electrospinning, as one of the promising technology which is able to produce nanofibers, is also an option in the regeneration of silk fibroin. Electrospinning of silk fibroin was first reported by Zarkoob et al. which used hexafluoro-2-propanol (HFIP) as solvent (Sukigara, Gandhi et al. 2003). However, fabrication of silk fibroin fibers with narrow diameters and without any beads formation remains a big challenge. As a result, silk fibroin is usually electrospun with the addition of other polymers like polyethylene oxide (PEO) (Jin, Fridrikh et al. 2002), or with high concentration which will lead to thick fibers (Min, Lee et al. 2004).

Zhang et al. indicated that the features of electrospun fibers were influenced greatly by the nano-structure of silk fibroin in solution, and the self-assembly of silk fibroin from nanospheres to nanofibers was crucial in a successful electrospinning process (Zhang, Zuo et al. 2012). As their experiments showed, after dissolved by LiBr aqueous solutions, if the silk fibroin solution evaporated slower, the silk fibroin filaments would be assembled by silk fibroin spheres, which is observed by Atomic Force Microscopy (AFM). Electrospinning of filament-silk fibroin exhibits better results with thinner diameter and fewer beads than sphere-silk fibroin.

Liu et al. used CaCl_2 -formic acid solution instead of LiBr aqueous solutions or CaCl_2 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O solutions to dissolve the degummed silk fibroin (Liu, Zhang et al. 2015). The regenerated silk fibroin solution exhibited high viscosity which improved the electrospinning significantly. The interpretation of this phenomenon was that

there were still some native silk fibrils remaining in the solution, which lead to better electrospinning.

Moreover, ethanol is always utilized for the post-treatment of electrospinning. Since the solvent cannot totally volatilize during the electrospinning process, ethanol treatment is used to induce a conformation transition to β -sheet structure, which is insoluble in water (Cao, Chen et al. 2009). The mechanism of this transition is hydrogen bond rearrangement in ethanol (Chen, Zhou et al. 2003). Because of the swelling of nanofibers in ethanol, there will be enough space for the molecule chain to rearrange.

Besides the good mechanical and biological properties, regenerated silk fibroin materials also possess hydrophilicity. Researches of Zhang et al. and Zhou et al. indicate that the regenerated silk fibroin films are hydrophilic (Zhou, Zhang et al. 2014, Zhang, You et al. 2015). Water contact angle of electrospun poly(lactide-co-glycolic acid) (PLGA) can decrease by inducing silk fibroin due to its hydrophilicity (Shahverdi, Hajimiri et al. 2014). Therefore, electrospun nano-fibrous silk fibroin membrane will be a good choice for this research.

2.6 Metal oxide modified polymeric membrane

Membranes synthesized from polymers including polysulfone (PSF), polypropylene (PP), polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), polyethersulfone (PES) and polytetrafluoroethylene (PTFE) have been commonly used for water treatment (Lonsdale 1982, Gin and Noble 2011, Pendergast and Hoek 2011, Fane, Wang et al. 2015).

PVDF and PSF are both widely used polymers in different area including membrane technology due to their excellent thermal and chemical resistance (Gopal, Kaur et al. 2007, Chakrabarty, Ghoshal et al. 2008, Chen, Tian et al. 2017, Zambianchi, Durso et al. 2017). Phase inversion is the traditional method to develop polymeric membrane (Kim, Lee et al. 2002, Munirasu, Banat et al. 2017). To date, considerable amount of studies on electrospun nano-fibrous membranes have been conducted, and

the variables influencing electrospinning process have been explored (Chang and Lin 2009, Ahmed, Lalia et al. 2015, Obaid, Barakat et al. 2015, Zhou and Wu 2015, An, Guo et al. 2017). According to the literature, N, N'-dimethyl acetamide (DMAC) is one of the most widely used solvents for the electrospinning of PSF and PVDF; in order to increase the viscosity and volatility of the solvent, acetone is always introduced into the DMAC solution (Yuan, Zhang et al. 2004, Su, Li et al. 2016).

However, as hydrophobic materials, according to what we discussed above, the usage of PVDF and PSF in membrane technology, especially in oil-water separation, are limited (Boo, Lee et al. 2016, Peng, Lei et al. 2016, Ji, Xiao et al. 2018). As a result, surface modification of the membrane is necessary to obtain better wetting behavior (Chakrabarty, Ghoshal et al. 2008, Maphutha, Moothi et al. 2013, Obaid, Barakat et al. 2015).

Surface modification is conducted by graft polymerization method, chemical cross-linking, chemical treatment and surface coating (Fane, Wang et al. 2015). One common approach to obtain hydrophilic surfaces is to coat hydrophilic metal oxide. At the same time, as discussed in the theory part, imparting surface roughness is another way to help improve the wettability. Therefore, nano-sized metal oxide has gained much attention. Nanoparticles can be coated on the surface by many methods as diverse as dip coating, sputtering, electrochemical deposition, lithographic techniques and solution growth (Lu, Zhang et al. 2016, Chen, Zhou et al. 2017, Xu and Wang 2018).

Metal oxide like titanium dioxide (TiO_2) (Tan, Liu et al. 2016), silica (SiO_2) (Tai, Tan et al. 2015), copper oxide (CuO) (Baghbanzadeh, Rana et al. 2015), and zinc oxide (ZnO) (Ennaceri, Wang et al. 2016) are widely studied due to their especial wetting behaviors. Those metal oxide materials were reported with excellent water affinity and strong underwater stability, so they were regarded as a suitable candidate for oil-water separation (Li, Yan et al. 2015, Li, Yan et al. 2016, Tian, Li et al. 2019). Furthermore, nano-sized metal oxides were also developed to increase the roughness of the surface which could further improved the hydrophilicity of the membrane (Ji,

He et al. 2018, Ghadimi, Azad et al. 2019, Song and Lu 2020), and some of the metal oxide demonstrated self-cleaning and anti-fouling property, which was also of great benefit to oil-water separation (Du, You et al. 2017, Yuan, Chen et al. 2017, Kang, Cheng et al. 2018). However, most of metal oxide modified membrane are based on metal mesh, which has many limitations like large pore size and poor flexibility when applied for oil-water separation (Qin, Liu et al. 2016). Therefore, metal oxide modified polymer membrane has promising potential for efficient application in oil-water separation.

Copper has been widely applied to for water treatment due to its antimicrobial properties (Ruparelia, Chatterjee et al. 2008, Meghana, Kabra et al. 2015). With the development nanotechnology, many researches are focusing on the combination of copper or copper oxide nanoparticles and membrane technology to achieve the biofouling resistance (Ben-Sasson, Zodrow et al. 2014, Ma, Soroush et al. 2016, Zhu, Wang et al. 2017), while there is few research using CuO for its hydrophilicity. In 2013, Cu(OH)₂ nanowire-haired copper mesh membrane was first reported for its super-hydrophilicity and underwater super-oleophobicity (Zhang, Zhang et al. 2013). They used a facile (NH₄)₂S₂O₈ oxidation method to fabricate the Cu(OH)₂ nanowire directly on a copper mesh, and this membrane exhibited excellent hydrophilicity and underwater oleophobicity, which leads to high oil-water separation efficiency. Therefore, copper oxide can be a good candidate for the surfure modification of PSF nano-fibrous membrane. At the same time, it possesses many advantages like low cost, chemical stability, abundance, and ease of synthesis in nanoscale (Zhang, Feng et al. 2016).

A number of methods can be utilized for the synthesis of copper oxide (CuO) nanoparticles, such as electrochemical method, oxidation and hydrothermal method (Zhang, Sun et al. 2005). The electrochemical method is based on the reaction between sacrifice Cu anode and electrolyte (Grigore, Biscu et al. 2016). In 2002, Jiang et al. reported a vapor-phase approach to synthesis copper oxide nanowire in air at 300-800°C using oxidation method (Jiang, Herricks et al. 2002). However, these methods are required copper mesh or high temperature, which is not suitable for

membrane modification. Hydrothermal methods are widely employed to achieve different morphology of CuO micro-/nano-structures in different conditions (Sun, Sun et al. 2015). For membrane modification, it is necessary to synthesis CuO nanoparticles at lower temperature due to the 177°C melting point of PSF. Gou et al. synthesized CuO nanoribbons from the hydrothermal reactions of copper sulfide (CuSO_4) and sodium hydroxide (NaOH) with the presence of surfactant sodium dodecylbenzenesulfonate at 120°C (Gou, Wang et al. 2008). Ananth et al. also reported the synthesis procedure of CuO nanoparticles with different morphology from copper nitrate ($\text{Cu}(\text{NO}_3)_2$), NaOH and Polyethylene glycol (PEG) at different temperature (Ananth, Dharaneedharan et al. 2015). Recently, Liu et al. fabricated CuO nano-sheet modified PVDF-HFP membrane by hydrothermal method using cupric acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) and ammonium hydroxide (NH_4OH) as reagent (Liu, Qin et al. 2019). In this research, hydrothermal growth of CuO on the PVDF nanofibers will be studied for the surface modification to obtain hydrophilicity for oil-water separation.

Zinc oxide is another promising candidate for hydrophilic modification of membrane. Apart from its application as semiconductor, controllable wettability of aligned ZnO nanorod films was first reported in 2004 (Feng, Feng et al. 2004). Under ultraviolet (UV) irradiation or dark storage, the films show different wettability, which can be reversible switched. After storage in dark, ZnO nanorod films is super-hydrophobic owing to the roughness structure and low surface energy. However, after UV irradiation, electron-hole pairs will be generated on the surface of ZnO, and thus some defective site would form, which can absorb water from air. Therefore, ZnO nanorod, covered by a very thin water film, are switched to be super-hydrophilic (Tian, Zhang et al. 2011).

Moreover, due to its low cost, non-toxicity and environmental friendliness, ZnO nanorod materials with photo-responsive wettability possess a significant potential in various fields (Zhang 2017). Some researchers developed ZnO-coated steel mesh for oil-water separation (Tian, Zhang et al. 2012), but there are few researches about ZnO-modified nanofibers. In 2016, Li *et al.* first combined hydrothermal method and

electrospinning to develop ZnO-modified carbon nanofibers as supercapacitor (Li, Wang et al. 2016). For this topic, modification of the PSF nano-fibrous membrane with ZnO to obtain special wettability for oil-water separation will be studied.

There are two common methods to fabrication ZnO nanostructures; One is vapor-phase reaction; the other is liquid-phase reaction (Zhang and Liao 2017). Vapor-phase reaction uses physical or chemical process to produce a vapor of material which is then deposit on the objects (Zhang and Liao 2017). For ZnO, there are two steps for vapor-phase synthesis: (1) evaporation and (2) deposition. Mostly, Zn powder is utilized as the raw material, and the reaction and phase transition are shown below (Zhang and Liao 2017):

in which (g) represents gas; (l) means liquid, and (s) refers to solid.

However, in order to produce vapor-phase ZnO, high temperature is necessary. Although there are many methods to create ZnO vapor, like thermal evaporation with catalyst or without catalyst (Yao, Chan et al. 2002, Xu, Li et al. 2015), pulsed laser deposition (Sun and Kwok 1999, Krämer, Engel et al. 2017) and molecular beam epitaxy (Look, Reynolds et al. 2002, Ying, Wang et al. 2016), all of them require 300-800°C which is beyond the thermal resistance of PSF.

Hydrothermal growth method is also commonly employed to fabricate the ZnO nanorod (Ou, Sanchez-Jimenez et al. 2016). More importantly, zinc oxide nanorod is able to grow on the different surfaces easily at low temperature which benefits the synthesis process (Zhang and Liao 2017). In 2001, ZnO nanorods were first synthesized via hydrothermal reaction (Vayssieres, Keis et al. 2001, Vayssieres 2003). $\text{Zn(NO}_3)_2$ and hexamethylenetetramine (HMTA, $(\text{CH}_2)_6\text{N}_4$) were mixed to obtain the

reaction solution. After several hours under 95°C, ZnO nanorod arrays were grown on the substrate. The reactions are shown below (Xu and Wang 2011):

ZnO nanostructures can also form from the reaction of Zn salt and other alkaline solutions like NaOH, KOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Demianets, Kostomarov et al. 2002). The reactions are commonly believed as below (Xu and Wang 2011):

In these reactions illustrated above, Zn^{2+} and OH^- ions will coordinate with each other and agglomerate in the form of $[\text{Zn}(\text{OH})_4]^{2-}$ complex. With the dehydration, H_2O molecules will migrate into solution; O^{2-} ions will form; and the nucleation of ZnO structure occurs in the interior of aggregates. As the result of further association and dehydration, nanostructure will grow from the ZnO core.

As a weak base, $\text{NH}_3 \cdot \text{H}_2\text{O}$ is not only providing the alkali condition but also able to mediate heterogeneous nucleation of ZnO nanostructures (Liu, Huang et al. 2007). $\text{NH}_3 \cdot \text{H}_2\text{O}$ can stabilize the Zn^{2+} by the reversible reaction below:

When the reaction consumes Zn^{2+} , this zinc–ammonia complex will decompose and release Zn^{2+} . As a result, the concentration of Zn^{2+} will maintain which leads to heterogeneous growth and suppresses homogeneous nucleation in the solution.

Hence, in this study, low-temperature hydrothermal method will be studied to modify the surface property of PSF nano-fibrous membrane. Moreover, ZnO is a semiconducting material with a broad direct band gap of 3.37 eV, large exciton binding energy of 60meV and deep violet/borderline ultraviolet (UV) absorption at room temperature (Özgür, Alivov et al. 2005, Ong, Ng et al. 2018). Among various semiconductors, ZnO are well-known as a good photo-catalysts for several contaminants (Xia, Wang et al. 2016). The photo-catalysis degradation process with semiconductors like ZnO can be briefly described as four steps: (1) UV irradiation; (2) exciton generation; (3) formation of oxidative species; and (4) oxidation of organic compounds or oxidation of water (Xia, Wang et al. 2016). Under UV irradiation, electrons will be promoted from the valence band to the conduction band, forming a pair of positive hole (h_{VB}^+) and electron (e_{CB}^-) on the surface of ZnO; both the electron and the hole can undergo the redox reactions with other specie; those reactions are shown below (Lee, Lai et al. 2016):

The superoxide anions and hydroxyl radical will further react with organic contaminant to form carbon dioxide and water as end products. Thus, ZnO nanomaterials are widely applied in water treatment technology. In this research, the self-cleaning of ZnO modified membrane will be studied.

2.7 Manta Ray Gill and crossflow filtration

As mentioned above, super-hydrophilic membranes obtain many advantages for efficient oil-water separation. Most of the researches are focusing on dead-end

separation using perpendicular gravity-driving approach (Chu, Feng et al. 2015, Li, Yan et al. 2015, Gu, Xiao et al. 2017). However, during the separation process, oil will accumulate on the membrane surface and clog the membrane. As a result, this approach is suffering from the pore clogging of oil, which will further cause the decline of water flux and discontinuity of the process.

Nature offers a different idea to solve this problem. Large suspension-feeding sea creatures filter water rapidly and continuously to have enough food, but surprisingly, they have never suffer from any clogging (Paig-Tran, Kleinteich et al. 2013, Paig-Tran and Summers 2014). Actually this phenomenon is thanks to their special structured gill rakers which function not via dead-end filtration but via the remarkable crossflow filtration (Sanderson, Cheer et al. 2001). Compared with the dead-end filtration, this crossflow filtration is beneficial as the particles and contaminants are less likely to be attached to the gill rakers (Werth and Potvin 2016). This unique filtering structure from nature is inspiring for water treatment.

Inspired by these natural process, crossflow filtration has been widely studied in membrane technology (Koltuniewicz, Field et al. 1995, Henry 2018). Some researchers have proved that crossflow filtration in membrane technology is able to minimize the accumulation of particles at the filter surface and thus increase the filtration rate (Yeats, Strain et al. 1990, Choi, Zhang et al. 2005, Shamsuddin, Das et al. 2015). In traditional nanofiltration (NF) and reverse osmosis (RO) membranes, crossflow filtration is necessary to limit the salt concentration polarization and reduce the fouling issue from dissolved natural organic matter and small colloids (Hoek, Kim et al. 2002). Four main types of silicon-based microfilters, including weir, pillar, crossflow and membrane, for isolation of white blood cells from red blood cells were fabricated by Ji et al (Ji, Samper et al. 2007). Based on their experimental results, the crossflow microfilter performed highest separation capacity and efficiency, because less white blood cells would be clogging the filter. Araus et al. used crossflow reverse osmosis membrane coupled supercritical carbon dioxide to separate bioactive components present in vegetable oil (Araus and Temelli 2018). Yim et al. presented a crossflow membrane filtration for separating two-dimensional graphene quantum

dots; this crossflow membrane filtration system was exhibiting stable flux with less fouling, higher selectivity and higher permeability compared to a dead-end filtration (Yim, Kim et al. 2018). Moreover, continuous process of crossflow filtration also attracted much attention in different fields. In 2015, Shamsuddin et al. reported a commercially available, continuously operating, dynamic cross-flow filtration device for continuous filtration of pharmaceutical ingredients (Shamsuddin, Das et al. 2015). Rodrigues et al. successfully fabricated a novel microfluidic device by using crossflow microfilters which is able to perform continuously and simultaneously separation of a certain amount of blood cells from an initial blood sample and avoid clogging or jamming (Rodrigues, Pinho et al. 2015). Dou et al. designed a Co_3O_4 coated stainless steel mesh for continuous spilled oil collection via crossflow (Dou, Tian et al. 2017). Considering those progress based on crossflow filtration, this method is also a promising strategy to achieve efficient and continuous oil-water separation.

2.8 Directional Water Movement

Water transportation plays curial roles in many applications, especially water technology. Long-range water transportation with less energy consumption is the key to overcome the limitation of existing energy-intensive water technology.

Materials with specially wettability have been widely studied for the transportation of water droplets. There are two main methods to achieve directional water movement. One is special topographic surface structure which creates gradient of Laplace pressure (Lorenceanu and Qur 2004, Chu, Xiao et al. 2010, Karpitschka, Das et al. 2015), and the other is the chemical gradient of the surface (Daniel, Chaudhury et al. 2001, Ju, Zheng et al. 2014). The Laplace pressure gradient or chemical gradient is able to induce the non-equilibrium of the surface energy, which sets the water droplet into an unbalanced state, and thus helps them to break the contact line with the surface and move along a particular distance (Sandre, Gorre-Talini et al. 1999, Pollack, Shenderov et al. 2002, Vialetto, Hayakawa et al. 2017). “Bead on string” structure which is similar to the spindle-knots was studied for the water directional movement on it (Zheng, Bai et al. 2010, Du, Zhao et al. 2016). This special

asymmetric structure resulted in a difference of Laplace pressure and the surface energy gradient around the beads and knots, which led to the continuous movement of water droplets. In 2016, Chen et al. reported the continuous directional water transportation phenomenon on the peristome surface of *Nepenthes alata* (Chen, Zhang et al. 2016). The special multiscale structure with two-order microgrooves and hydrophilicity of the surface prompted the continuous unidirectional water flow and prevented backflow. Another design of the directional water-harvesting surface which combining the macroscopic bump topography from beetles, asymmetry slope of cactus and molecular-scale smooth lubricant on nanoscale texture from pitcher plants was fabricated by Park et al. (Park, Kim et al. 2016).

Nonetheless, these super-wetting material can only transport water droplet by droplet. In order to achieve the bulk water transportation, researchers got some inspiration from trees due to their ability to deliver water from root to the upper crown through trunks via their hydrophilic cellulose-dominated xylem (Scholander, Bradstreet et al. 1965, Cochard 2006, Surridge 2008, Wheeler and Stroock 2008). Therefore, tree-inspired materials are attracting more attentions. In a recent research, tree-inspired design, natural basswood was utilized to extract water from ground or seawater for evaporation (Zhu, Li et al. 2017). The mesoporous channels and hydrophilic cellulose microfibers of the natural wood successfully pumped the water vertically and maintained continuous flow. Another research adopted hydrophilic cellulose nanofibers aerogel for the water absorber (Jiang, Liu et al. 2018). The aerogel was fabricated by freeze dry method to obtain 3D-connected pores at a scale of 200–300 μm . Vertically aligned graphene sheets are also utilized for the water extraction due to its run-through channels facilitating the water transport (Zhang, Li et al. 2017).

However, since most of these researches are focusing on the evaporation process, hydrophilic-material-based bulk water transportation remains un-studied and just regarded as a small part of the water evaporator to facilitate the water transportation and thermal insulation. Moreover, the distance of water transportation is limited as most of them are at micrometer range and not small enough. From the material point

of view, the transportation of water is based on hydrophilic materials with small pores to make the water uphill via capillary forces (Chaudhury 1992).

Considering the traditional capillary effect in micron-range tube, according to venerable Jurin's law (Caupin, Cole et al. 2008), the rising height h is

$$h = \frac{2\pi r \gamma \cos\theta}{\pi r^2 \rho_w g} = \frac{L}{S} \cdot \frac{\gamma \cos\theta}{\rho_w g} = \frac{2}{r} \cdot \frac{\gamma \cos\theta}{\rho_w g} \quad (\text{Equation 2.29})$$

where γ , ρ_w , θ and g are the surface tension, the density of water, the water contact angle and the gravitational constant, respectively. L is the wetting perimeter; S is the surface area of the tube; r is the diameter of the tube.

An interesting question to address is whether this equation makes sense when the value of r is nanometer range. This equation suggests that h is $\sim 1.5\text{km}$ when L/S is large enough ($r \sim 100\text{nm}$), but such value of H seems impossible and unreliable. However, some researches have proved that this result is plausible because the driving forces is large enough compared to the neglectable gravity forces (Caupin, Cole et al. 2008). Therefore, in order to make the long distance water transportation, it is the necessary to fabricate the porous matrix for larger L/S . As a result, Nano-sized material shows great potential in the long distance water transportation.

2.9 Conclusion

To conclude, the shortage of water and energy has become the great hurdle on the sustainable development of human beings. Super-hydrophilic material has been regarded as a promising material to alleviate those water and energy crisis. According to the basic theories and natural phenomena, surface energy and roughness are important to the wettability. Natural surfaces with special wetting behaviors give us the inspiration that water can be induced in the micro-/nano-structures of the material surface as a lubricating liquid to help achieve the oil-water separation.

In order to obtain the super-hydrophilic materials, electrospinning is the key driver for the fabrication of the materials with hierarchical micro-/nano-structural surfaces. Both naturally hydrophilic silk fibroin and metal oxide-modified polymeric have the potential to be utilized as the raw material. These the super-hydrophilic materials may open the door for applications both in oil-water separation and directional water movement.

Chapter 3 Methodology

3.1 Introduction

This chapter is an overview of all the experimental details of this study. First, the materials and methods for the fabrication of nano-fibrous membranes would be explained. Secondly, the characterization techniques would be covered. Finally, the methods for testing the oil-water separation would be introduced.

3.2 Chemicals

Chemicals utilized in this research has been listed in the following table.

Table 3-1 Chemical list

Item	Source	Remarks
Raw <i>Bombyx mori</i> Silk Cocoons	Alibaba	Used to obtain silk fibroin film for electrospinning
Polysulfone (PSF)	Sigma Aldrich	Molecular weight (MW) ~22,000
Polyvinylidene fluoride (PVDF)	Sigma Aldrich	Pellets, Mw ~180,000
Polyvinylidene fluoride (PVDF)	Arkema	Kynar® 761
Zinc Acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$)	Sigma Aldrich	Anhydrous, $\geq 99.9\%$
Copper Sulfate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	Sigma Aldrich	$\geq 98\%$
Copper Acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$)	Sigma Aldrich	Anhydrous, powder, $\geq 98\%$

Sodium Carbonate (Na_2CO_3)	Sigma Aldrich	Anhydrous, powder, $\geq 99.5\%$
Calcium Chloride (CaCl_2)	Sigma Aldrich	Anhydrous, powder, $\geq 97\%$
Formic acid (FA, HCOOH)	Sigma Aldrich	$\geq 96\%$
Dimethylacetamide (DMAC, $\text{CH}_3\text{CON}(\text{CH}_3)_2$)	Sigma Aldrich	Anhydrous, 99.8%
Acetone ($\text{CO}(\text{CH}_3)_2$)	Sigma Aldrich	$\geq 99.5\%$
Ammonium hydroxide solution (NH_4OH)	Sigma Aldrich	28.0-30.0% NH_3
Deionized (DI) Ultra Pure Water	produced by Millipore® ultra-pure water machine	Resistivity 18.2 $\text{M}\Omega/\text{cm}$ at 25 °C and TOC = 2 ppb

3.3 Membrane Fabrication

3.3.1 Fabrication of silk fibroin nano-fibrous membrane

3.3.1.1 Preparation of regenerated silk fibroin film

Silk cocoons were boiled in aqueous solution of 0.05 wt.% Na_2CO_3 and then wash by deionized water to extract the sericin proteins. The degummed silk was directly dissolved in CaCl_2 -formic acid (FA) solution. The solution was poured in polystyrene Petri dishes (diameter 30 mm) which were placed in the fume hood for the evaporation of FA to obtain the regenerated silk fibroin film. The film was immersed in deionized water to remove CaCl_2 and residual FA and subsequently dried in air.

3.3.1.2 Electrospinning of silk fibroin nano-fibrous membrane

Homogenous precursor solution of formic acid (FA) with different concentrations of SF from 4 wt.% to 12 wt.% was prepared by magnetic stirring for 3 hours. SF was electrospun using a custom-established rotating drum electrospinning device shown in Figure 3-1. A piece of aluminum foil wrapped on the rotating drum acted the collector. Subsequently, the solution was electrospun in a closed chamber. The conditions of SF electrospinning are illustrated in Table 3-2. The electrical potential was applied by high voltage DC supply (Dongwen High Voltage Power Supply, China). For post-treatment, the SF membrane was immersed in ethanol for 1 hour and then dried in air.

Table 3-2 Conditions of SF electrospinning

Electrospinning Conditions	
Voltage	24 kV
Tip-collector distance	15 cm
Needle tip diameter	1.2 mm
Feeding rate	0.4 mL/h
Humidity	<50%

Figure 3-1 Schematic diagram of electrospinning setup

3.3.2 Fabrication of CuO modified PVDF nano-fibrous membrane

3.3.2.1 Electrospinning of nano-fibrous membrane

1.5 g PVDF was dissolved in 8.5 g solution with 80 wt.% dimethylacetamide (DMAC) and 20 wt.% acetone by magnetic stirring at 70 °C for 12hr. Thereafter, 0.15 g copper acetate was added into the solution. And the homogenous solution was obtained by stirring at 70 °C for 15 min. The solution was used for electrospinning with a custom-established rotating drum electrospinning device shown in Figure 3-1. A piece of aluminum foil wrapped on the rotating drum acted the collector. Subsequently, the solution was electrospun in a closed chamber. The electrical potential was 20 kV applied by high voltage DC supply (Dongwen High Voltage Power Supply, China). The conditions of PVDF electrospinning are illustrated in Table 3-3. For post-treatment, the membrane was stabilized in furnace at 188 °C for 3hr. A sample without any copper acetate was also prepared as a control sample for the following test.

Table 3-3 Conditions of PVDF electrospinning

Electrospinning Conditions	
Voltage	20 kV
Tip-collector distance	20 cm
Needle tip diameter	1.2 mm
Feeding rate	1.0 mL/h
Humidity	<50%

3.3.2.2 Hydrothermal process for CuO growth

The as prepared membrane was immersed into an aqueous solution of ammonia (1 mol/L) and copper sulfate (0.1 mol/L). Then the CuO nanosheets with different morphology were grown on the surface of nanofibers at 70 °C from 4hr to 48hr. The control sample with copper acetate was also prepared for comparison.

3.3.3 Fabrication of ZnO modified PSF nano-fibrous membrane

The fabrication method of ZnO modified PSF nano-fibrous membrane is similar to the CuO modified PVDF membrane using the combination of electrospinning and hydrothermal reaction.

3.3.3.1 Electrospinning of nano-fibrous membrane

2 g PSF was dissolved in 8 g solution with 80 wt.% dimethylacetamide (DMAC) and 20 wt.% acetone by magnetic stirring at 70 °C for 12hr. Thereafter, 0.2 g zinc acetate was added into the solution. And the homogenous solution was obtained by stirring at 70 °C for 15 min. The solution was used for electrospinning with the same custom-established rotating drum electrospinning device shown in Figure 3-1. A piece of aluminum foil wrapped on the rotating drum acted the collector. Subsequently, the solution was electrospun in a closed chamber. The electrical potential was 20 kV applied by high voltage DC supply (Dongwen High Voltage Power Supply, China). The conditions of PSF electrospinning are illustrated in Table 3-4. For post-treatment, the membrane was stabilized in furnace at 160 °C for 3hr. A sample without any zinc acetate was also prepared as a control sample for the following test.

Table 3-4 Conditions of PSF electrospinning

Electrospinning Conditions	
Voltage	20 kV
Tip-collector distance	20 cm
Needle tip diameter	1.2 mm
Feeding rate	1.0 mL/h
Humidity	<50%

3.3.3.2 Hydrothermal process for ZnO growth

The as prepared membrane was immersed into an aqueous solution of ammonia (1 mol/L) and zinc acetate (0.1 mol/L). Then the ZnO nanorods with different

morphology were grown on the surface of nanofibers at 70 °C from 1hr to 3hr. The control sample with zinc acetate was also prepared for comparison.

3.4 Membrane Characterization

3.4.1 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM, Jeol JSM-7600F) was used to observe the morphology of membranes. The energy dispersive detector (EDX) (Oxford, 80 mm²) attached to the FESEM (Jeol JSM-7600F) was used to measure the element composition of membranes. Before FESEM, auto fine coater (Jeol JFC-1600) was utilized for 30 s platinum coating of the samples at 20 mA current to increase their conductivity.

3.4.2 Thermal Gravimetric Analysis (TGA)

Thermal stability of nanofibers was determined by Thermal Gravimetric Analysis (TGA, Perkin Elmer TGA-7). The measurement was performed from 30 °C to 700 °C, at a heating rate of 10 °C min⁻¹ in N₂ atmosphere.

3.4.3 Video Contact angles (VCA)

Contact angles were determined by Video Contact Angle (VCA) device (AST product Inc. Optima series) at room temperature. A video camera was used to capture the video and snapshot of a liquid droplet contacting the solid surface. The contact angle was then measured to determine the wetting property of the individual membrane surface. Three results were measured for each membrane to achieve the average result. 2 µL DI water in air or 2 µL 1,2-dichloromethane under water were used as the probe liquids.

3.4.4 Brunauer, Emmett, and Teller (BET)

The BET specific surface area were determined at liquid nitrogen temperature (77K) using a Micromeritics ASAP 2040 system. The samples were degassed at 200°C for 3 hours prior to measurement. The density functional theory (DFT) method was employed to obtain the pore size distribution of the electrospun nanofibers.

3.4.5 Fourier transform infrared (FTIR) spectra

Fourier transform infrared (FTIR) spectra of the samples was measured with the Perkin Elmer spectrum GX FTIR spectrometer in the range of 400 to 4000 cm^{-1} with an attenuated total reflection (ATR) accessory

3.5 Testing of oil-water separation

The oil-water separation was conducted by a dead-end filtration setup as shown in Figure 3-2. The oil-water mixture was prepared by mixing different types of oil with water in a volume ratio of 9:1. The membrane sample was pre-wetted by DI water and then secured on the membrane holder. Thereafter, oil-water mixture was discharged into the filtration cup. The Erlenmeyer was utilized to collect the water permeation. The oil rejected by the membrane remained in the filtration cup. Total organic carbon (TOC) measured by Shimadzu TOC-VCSH TOC Analyzer was used to analyze oil concentration. The separation efficiency can be calculated by oil rejection ratio ($R\%$):

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \text{ (Equation 3.1)}$$

where C_0 and C_p are the oil concentration of the feed oil-water mixture and the permeate water.

Figure 3-2 Dead-end filtration setup for oil-water separation

3.6 Testing of pure water flux

Pure water flux test was conducted by another dead-end filtration setup as shown in Figure 3-3. Nitrogen gas cylinder with a controlling valve was utilized to provide the pressure. Before the test, membrane was immersed in DI water for 30 min to eliminate air gaps. Thereafter, the wetted membrane was placed on the base of the filtration cell and DI water was discharged into the filtration cell. After sealing the setup, the valve of gas cylinder was adjusted to control the pressure as 0.9 bar. As 0.9 bar is relatively low, the influence of membrane compaction of flux was not observed. Some reference also indicated that the compaction of membrane was not obvious from 2.5psi to 30psi (0.17bar to 2.1bar) (Wang, Liu et al. 2012, Liu, Wang et al. 2013). Water permeated through the membrane and was collected in the beaker. The time taken to collect 50g water was utilized to calculate the flux. The flux was calculated using the following equation:

$$J = \frac{V}{t \times S} \text{ (Equation 3.2)}$$

where J is the water flux ($\text{L/m}^2\text{-hr}$); V is the volume of permeated water (L); t is the time (s) and S is the membrane area (m^2).

The flux test was repeated three times to obtain average values.

Figure 3-3 Dead-end filtration setup for pure water flux test

3.7 Testing of photocatalytic oxidation

The photocatalytic ability of the synthesized samples was tested. Figure 3-4 shows the schematic illustration of the setup. The experiment was carried out in a closed chamber. Acid orange 7 (AO7) was used as a target pollutant. The membrane ($3 \text{ cm} \times 3 \text{ cm}$) was added into the 10 ppm AO7 solution and placed in the dark chamber for 1 hr to ensure adsorption equilibrium. 2 mL samples were collected before the start of experiment, 1 hr later and another 10 mins later to ascertain complete adsorption. Thereafter, UV irradiation was switched on and the samples were collected at every 20 mins interval. The samples were analysed using the UV-vis spectrophotometer by obtaining the absorbance reading scanned over a wavelength range of 300 nm to 600 nm. The absorbance reading can be converted into concentration (mg/L) by using the standard curve for AO7.

Figure 3-4 Schematic illustration of photocatalytic oxidation setup

Chapter 4 Super-hydrophilic nano-fibrous silk fibroin membrane

4.1 Introduction

Electrospinning is a promising technology to fabricate nanofibers which can form a porous membrane with interconnected pores and high specific area. As discussed in Chapter 2, electrospun nano-fibrous membrane can be an ideal candidate for oil-water separation because of its nano-structure. Silk fibroin as a hydrophilic material possessing good mechanical property, is suitable for making electrospun membrane and ultimately used for oil-water separation. This chapter will present the results and discussion comprising: (1) preparation of electrospun silk fibroin membrane, (2) characterization of the membrane, (3) oil-water separation testing.

4.2 Electrospinning of silk fibroin nano-fibrous membrane

As described in Chapter 3, silk fibroin films were obtained after degumming, dissolving, washing and drying process. Subsequently, silk fibroin-formic acid solutions with different concentration were prepared for electrospinning.

Field emission scanning electron microscopy (FESEM) was employed to study the morphology of silk fibroin nanofibers. Figure 4-1 shows the morphology of electrospun silk fibroin nanofiber from different precursor concentration. It was observed that with the increase of silk fibroin concentration, the beads formation was lessened and fibers formed were thicker. When silk fibroin solution concentration was 4%, it was found that the jet was easy to break up into droplets and the fiber was rarely formed shown in Figure 4-1(a). Since viscosity and conductivity is not high enough at low concentration, chain entanglements of polymers are not sufficient to stabilize the jet, which leads to a bead-like structure (Cao, Chen et al. 2009). With increasing concentration, the solution obtained higher viscosity and conductivity, and thus the jet was stable, resulting in uniform fiber formation (Figure 4-1(b-d)). As observed in Figure 4-1, the fiber formation is optimized when the concentration is at the range of 8 wt.% to 10 wt.%. On the other hand, further increase in concentration resulted high solution viscosity which disrupted the electrospinning process due to

the jamming of the spinneret. In addition, higher concentration always leads to thicker fibers and larger pore size of the membrane. As a result, 10 wt.% of SF solution is the optimal choice.

Figure 4-1 FESEM images of silk fibroin membrane (a) 4% (b) 6% (c) 8% (d) 10%

4.3 Post-treatment of the membrane

After electrospinning, smooth, uniform and flexible membranes can be achieved as shown in Figure 4-2. In order to stabilize the membrane and make it insoluble in water, post-treatment is required. As shown in Figure 4-3(a), the nanofiber structure of the membrane without post-treatment was damaged by water. After the treatment in ethanol, the nanofiber structure revealed stability and was not influenced after immersing in water for one week.

Figure 4-2 Digital image of SF membrane

Figure 4-3 FESEM images of silk fibroin membrane treated in water. (a) Without any treatment, after immersing in water for 3hr, the nano-fiber structure was damaged; (B) With the treatment in ethanol, after immersing in water for 1 week, the nano-fiber structure was not influenced.

This phenomenon was attributed to the β -sheet crystal structure of silk fibroin, which was induced by ethanol treatment and eliminated the water solubility of silk fibroin (Huemmerich, Slotta et al. 2005, Li, Vepari et al. 2006, Melke, Midha et al. 2016). Before the ethanol treatment, some of the protein chains without β -sheet structure were soluble in water, resulting in the defect of nanofibers, while after ethanol treatment, insoluble β -sheet structure was formed and the membrane was no longer soluble.

Zhang et al. used FTIR analysis to investigate the structural changes of silk fibroin before and after ethanol treatment, and their results proved the conformation transition with absorption peaks moving from 1656 cm^{-1} to 1630 cm^{-1} and from 1540 cm^{-1} to 1525 cm^{-1} after ethanol treatment (Zhang, Zuo et al. 2012). Su et al. and Zheng et al. also reported similar FTIR analysis result after ethanol treatment (Su, Yao et al. 2017, Zheng, Wu et al. 2018). Figure 4-4 shows the FTIR spectrum of the silk fibroin membrane. Peaks were observed at 3300 cm^{-1} , 1630 cm^{-1} , 1530 cm^{-1} and 1265 cm^{-1} . The three notable peaks or troughs 1630 cm^{-1} and 1530 cm^{-1} showed the formation of β -sheet structure after ethanol treatment, and the peak 1265 cm^{-1} is consistent with silk fibroin fibers (Liu, Zhang et al. 2015, Zhang, You et al. 2015). The point where the vibration is 3300 cm^{-1} depicts adsorbed water in the silk fibroin membrane. The thermogravimetric curve of as-prepared membrane is shown in Figure 4-5. The first stage of weight loss below 150°C is due to the evaporation of water, while the second stage from 300°C is associated with the degradation of silk fibroin (Kweon, Um et al. 2000, Zhou, Zhang et al. 2014). Silk fibroin fibers with these profiles exhibit better stability in water and better mechanical properties as compared to silk fibroin fibers that have not undergone ethanol treatment (Zhang, Lu et al. 2014).

Figure 4-4 FTIR spectrum of silk fibroin membrane.

Figure 4-5 Thermogravimetric curve of silk fibroin membrane.

4.4 Wetting behavior of the membrane

The wetting behavior of the membrane was assessed by water contact angle and underwater oil contact angle, which is presented in Figure 4-6. During the contact angle testing, as the water droplet contacted with the membrane surface, it quickly spread, and the water contact angle was 0° (as shown in Figure 4-6(a)), which illustrated super-hydrophilicity of the membrane. Meanwhile, according to Figure 4-6(b), the membrane acquired super-oleophobicity with 154° underwater oil contact angle.

Figure 4-6 Water Contact Angle of silk fibroin membrane (a) and Underwater Oil Contact Angle of silk fibroin membrane (b)

Generally, the wettability properties are determined by the surface morphology and the chemical composition. The micro-/nano-structure of electrospun membrane as well as the hydrophilicity of silk fibroin accounts for the super-hydrophilicity and underwater super-oleophobicity of the membrane. Due to the special wetting behavior of the membrane, water is able to pass through it while oil can be rejected. As a result, the membrane is a perfect candidate for oil-water separation.

4.5 Oil-water separation test

In order to investigate the oil-water separation ability of the membrane, several types of oil-water mixture were prepared using vegetable oil, olive oil and silicon oil. The setup, test procedure and calculation equation for oil removal rate were the same as the description in Section 3.5. For each testing, 100 mL of oil-water mixture was used, and the separation efficiency was evaluated by TOC (total organic carbon) testing.

Figure 4-7 shows the result of olive oil-water separation test. The membrane was pre-wetted by water at the beginning and placed on the filter holder as shown in Figure 4-7(a). Thereafter, oil-water mixture was discharged into the filtration cup. Subsequently, vacuum pump was turned on to allow suction of water through the membrane while repelling the oil. As illustrated in Figure 4-7(b), oil remained on the top of the membrane (Figure 4-7(c)), while water percolated through the membrane (Figure 4-7(d)).

Figure 4-7 Olive oil-water separation by silk fibroin membrane

The membrane showed remarkable oil removal efficiency. Figure 4-8 exhibits the very high oil removal efficiency of the silk fibroin membrane (99.92% for olive oil-water mixture, 99.89% for silicone oil-water emulsion and 99.97% for vegetable oil-water emulsion).

Figure 4-8 Removal efficiency of oil-water mixtures (a) Six different kinds of oil; (b) Recycle 8 times.

4.6 Conclusion

To conclude, silk fibroin nano-fibrous membrane was successfully fabricated via electrospinning. Due to the natural hydrophilicity and micro-/nano-hierarchical structure of the nano-fibers, the as-prepared membrane exhibited super-hydrophilicity (water contact angle = 0°) and underwater super-oleophobicity (underwater oil contact angle $> 150^\circ$). The following oil-water separation test proved that this super-hydrophilic membrane obtained the remarkable oil-water separation ability.

Chapter 5 CuO nanosheets modified PVDF nano-fibrous membrane

5.1 Introduction

Chapter 4 has presented an advancement in our research domain through the nano-fibrous silk fibroin membrane synthesized via electrospinning for the efficient oil-water separation. In light of that, this nano-fibrous membrane has demonstrated super-hydrophilicity and good oil-water separation ability, and silk fibroin as a natural material was first utilized in the water treatment. Nevertheless, challenge remains where the chemical and thermal resistance of protein-based silk fibroin was not optimal in some cases like acidic or basic condition and it is relatively expensive. In order to overcome the limitation of silk fibroin, traditional polymer materials like polyvinylidene difluoride (PVDF) with excellent chemical and thermal resistance is an alternative option. However, its hydrophobicity renders it unsuitable for oil-water separation as we discussed in the previous chapter. Thus, modification of PVDF membrane is necessary. Metal oxide that processes hydrophilicity is promising to modify the membrane. A combination method of electrospinning and hydrothermal growth was utilized for the fabrication. Copper oxide modified PVDF nano-fibrous membrane are studied in this chapter. This chapter presents all results and discussion comprising: (1) Synthesis of CuO-nanosheets modified PVDF membrane, (2) characterization of the membrane, (3) oil-water separation efficiency of the membrane.

5.2 Fabrication of CuO modified PVDF membrane

A facile synthesis process combining electrospinning and *in-situ* hydrothermal growth was utilized in this study. In order to show the process clearly, a schematic diagram was shown in Figure 5-1. At first, PVDF nano-fibrous membrane was fabricated by electrospinning from the PVDF and DMAC/acetone precursor solution. Copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) was added in the precursor solution as the seed of Cu to obtain uniform CuO nano-particle growth in the following steps. Secondly, the electrospun nano-fibrous membrane was posttreated in the oven at 160°C. This step is for the solidification of PSF as well as the formation of CuO nucleus for CuO growth. The following is hydrothermal reaction. $\text{Cu}(\text{CH}_3\text{COO})_2$ was dissolved in

ammonia water to form the hydrothermal reaction solution. In this solution, Cu^{2+} will form the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to avoid the formation of $\text{Cu}(\text{OH})_2$ sediment. Then the as-prepared nano-fibrous membrane with CuO seeds was immersed in the solution and placed in the 70°C oven. As reactions proceeded, the Cu^{2+} in the solution would react with OH^- and transformed into $\text{Cu}(\text{OH})_2$ and then CuO which grew on the CuO seeds on the nano-fiber surface and formed CuO nanosheets.

Because of the presence of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the reaction rate was limited and CuO could grow at nano-size. Since the CuO nano-particles were *in-situ* grown on the nano-fiber surface, the attachment of CuO was stable, and flexibility of the membrane was not affected.

Figure 5-1 Schematic illustration of the synthesis procedure of CuO nanosheets modified PVDF nano-fibrous membrane.

5.3 Morphology of CuO modified PVDF membrane

Figure 5-2 shows the digital image of the as-prepare membrane. Figure 5-2(a) is the membrane before post-treatment. Due to the presence of copper acetate, the membrane has a light blue color. After post-treatment as shown in Figure 5-2(b), the membrane became brown color, which indicated the formation of CuO seeds. Figure 5-2(c-f) show the membrane after 4hr, 8hr, 24hr and 48hr hydrothermal growth. It can be easily observed that the membrane became black color owing to the growth of CuO nano-sheets, and there were also some brown color defects on 4hr and 8hr samples which demonstrated the insufficient growth of CuO.

Figure 5-2 Digital image of CuO modified PVDF membrane (a) before post-treatment (b) after post-treatment (c) 4hr hydrothermal duration (d) 8hr hydrothermal duration (e) 24hr hydrothermal duration and (f) 48hr hydrothermal duration

The morphology of CuO modified PVDF nano-fibrous membrane was measured by FESEM. Figure 5-3 shows the FESEM images of the PVDF nano-fibrous membranes before post-treatment and after post-treatment which is smooth and there is no observable CuO growth. Figure 5-4 shows the FESEM image of PVDF nano-fibrous membrane with different CuO hydrothermal duration. It is obvious that with the increase of hydrothermal duration, more CuO was grown on the surface of PVDF nanofibers, so the CuO nanosheets became larger and thicker. For 48hr sample, too long hydrothermal duration resulted in overgrowth of the CuO nanosheets and some nanosheets started to aggregate. Large CuO could have influence the membrane

performance. Therefore, the optimal hydrothermal duration is 24hr hydrothermal process, as the nanofibers were well covered with CuO nanosheets.

Figure 5-3 FESEM image of PVDF nano-fibrous membrane without CuO growth (a) before post-treatment, (b) after post-treatment.

Figure 5-4 FESEM images of CuO modified PVDF membrane with different hydrothermal duration (a) 4hr, (b) 8hr, (c) 24hr and (d) 48hr

The hydrothermal reaction was also conducted for the PVDF nano-fibrous membrane without Cu seeds for comparison. As shown in Figure 5-5(a), after 4hr, there were only few small particles deposited on the nanofiber without CuO seeds. After 24hr hydrothermal reaction, many CuO particles coagulated together and attached on the membrane surface (Figure 5-5(c)). The FESEM image of 4hr hydrothermal membrane with Cu seeds is shown in Figure 5-5(b), CuO nanosheets was able to grow directly on the nanofiber surface with guidance of Cu seeds. After 24hr hydrothermal reaction, as shown in Figure 5-5(d), the CuO nanosheets growth on the nanofiber surface was well regulated by the seeds. These results indicated that Cu seeds can be regarded as the anchor for CuO growth on the nanofiber surface, which is able to prompt the *in-situ* growth of CuO nanosheet.

Figure 5-5 FESEM images of CuO modified membranes (a) 4hr hydrothermal without Cu seed; (b) 4hr hydrothermal with Cu seed; (c) 24hr hydrothermal without Cu seed; (d) 24hr hydrothermal with Cu seed.

EDX element mapping was adopted to determine the surface composition of the membrane surface. EDX spectrum and elemental mapping images shown in Figure 5-6, indicated that the nanosheets on the nanofiber surface was comprised of CuO.

Figure 5-6 EDX result of CuO modified membrane (a) FESEM image of the membrane, (b) EDX spectrum, (c) Elemental mapping image of oxygen; (d) Elemental mapping image of copper.

5.4 Wetting property of CuO modified PVDF membrane

Water contact angle and underwater oil contact angle were measured to evaluate the wetting behavior of the membrane. In this underwater oil contact angle test, 1,3-dichloromethane was used as the oil.

Figure 5-7 shows the water contact angle of the blank membrane. Figure 5-7(a) is before posttreatment; (b) is after posttreatment. Both sample exhibited high contact angle 135° , which indicates they are hydrophobic. As shown in Figure 5-8, after the growth of CuO, the membrane turned from hydrophobicity to hydrophilicity. With different duration of hydrothermal process, the contact angle changed. From 4hr to 24hr the contact angle decreased from 55.7° to 16.7° was measured. However, the

water contact angle started to increase when the hydrothermal growth duration increased. 48hr hydrothermal duration resulted the membrane to possess a contact angle of 36.0° . According to the wetting theory discussed in the pervious chapters, the surface composition and its morphology decide the wetting behavior of the surface. In this study, since CuO is naturally hydrophilic, CuO modification of PVDF membrane will render its surface become hydrophilic. The nano-structure of CuO will make it more hydrophilic. As the CuO nanosheets were grown from 1hr to 24hr, the surface roughness increased and further led to the decrease of water contact angle. As for 48hr reaction, when the growth of CuO was too dense and leading to the aggregation of nano-structures, consequently the surface roughness decreased, which resulted in the increase of water contact angle.

Moreover, hydrophilic surface will show underwater oleophobic property due to the “water gap” locked in the nano-structure. The underwater oil contact angle was tested for CuO modified membranes to evaluate their underwater oleophobicity. Figure 5-9 shows the underwater oil contact angle of 24hr hydrothermal membrane and the 48hr one. Both of them exhibited super-oleophobicity ($\sim 150^\circ$). Due to the super-hydrophilicity and underwater super-oleophobicity of this membrane, it favors water permeation while rejecting oil. Therefore, it is a good candidate for efficient oil-water separation.

Figure 5-7 Water contact angle of blank membrane without CuO growth (a) before posttreatment; (b) after posttreatment.

Figure 5-8 Water contact angle of the membranes with different CuO growth duration (a) 4hr; (b) 8hr; (c) 24hr; (d) 48hr.

Figure 5-9 Underwater oil contact angle of the CuO modified PVDF membrane (a) 24hr hydrothermal duration; (b) 48hr hydrothermal duration.

5.5 Oil-water separation efficiency test

Oil water separation test was conducted to evaluate the oil-water separation efficiency. As described in Chapter 3, the filtration setup was used for the test. Five types of oil-water mixture were prepared for testing, including cooking oil, olive oil, silicon oil, diesel and engine oil. Figure 5-10 shows the result of olive oil-water separation test. Figure 5-10(c) and (d) demonstrate the rejected oil and permeated water, respectively.

Figure 5-10 Olive oil-water separation by CuO modified PVDF membrane (a) before the separation (b) after the separation (c) oil remained in the filtration cup (d) permeate water collected

The separation efficiency of 5 types of oil-water mixture was shown in Figure 5-11. 4hr, 8hr, 24hr, 48hr hydrothermal duration membrane was tested respectively.

This result demonstrated that the vegetable oil and olive oil both were well-rejected by 4 kinds of membrane with very high removal rate. The average removal rate of vegetable oil was 99.88%, and the olive oil removal rate was 99.65%. All 4hr, 8hr, 24hr and 48hr-hydrothermal membranes demonstrated similar removal rate over 99.5%.

However, for silicon oil, diesel and engine oil, the removal rates were not as good as vegetable oil and olive oil. When the experiment was conducted, it was observed that these three kinds of oil were more easily adhered on the membrane surface, disrupted the “water gap” and formed some small “oil paths” on the membrane surface. Some oil droplets could permeate through the membrane via these small “oil paths”. On the contrary, vegetable oil and olive oil were less likely to attached on the membrane surface during the experiment, so the removal rate of them was much higher.

Figure 5-11 Different types of oil removal efficiency for membranes with different hydrothermal duration.

Membranes with 24hr and 48hr CuO growth exhibited better rejection rate than that of 4hr and 8hr. The oil removal rate of 4hr hydrothermal membrane was only 93.41% for silicon oil, 88.21% for diesel and 88.51% for engine oil, and the oil removal rate for 8hr hydrothermal membrane was 93.94% for silicon oil, 86.88% for diesel and 91.20% for engine oil, while 24hr and 48hr samples had better removal rate from 94% to 98% (24hr: 96.64% for silicon oil, 95.43% for diesel and 97.44% for engine oil; 48hr: 97.60% for silicon oil, 94.69% for diesel and 97.64% for engine oil). This difference could be explained that 24hr and 48hr samples were well covered by CuO nanosheets and more hydrophilic. Thus, the oil rejecting “water gap” on the membrane surface was disrupted less and less oil could permeate through the membrane.

In summary, 24hr and 48hr samples demonstrated excellent oil-removal efficiency due to their super-hydrophilicity and underwater super-oleophobicity. An oil-

rejecting “water gap” could be easily formed on the membrane surface, which allowed water to pass through the membrane while oil was rejected. The well-growth of CuO nanosheet influenced the oil-water separation to a greater extend.

5.6 Water flux test

The pure water flux of the membranes was determined to evaluate their permeability. A dead-end filtration setup was adopted to conduct the test as shown in Figure 3-3. The testing process and calculation equation were the same as the description in Section 3.6 The permeation flux of pure water was tested for four kinds of membranes with different hydrothermal duration.

Figure 5-12 shows the water flux of four kinds of membrane. All membranes maintain high flux above 6000 L/m²-hr. It can also be observed that pure water flux declined with the increase of hydrothermal duration. 4hr hydrothermal membrane has the highest flux 7176 L/m²-hr, while 48hr hydrothermal membrane has the lowest flux 6129 L/m²-hr. Although the membrane became more hydrophilic with longer hydrothermal duration, the membrane also turned thicker and the pore size became smaller due to the growth of CuO nanosheets. Therefore, according to Hagen Poiseuille equation, the thicker membrane and smaller pore size led to the decrement of water flux.

Membranes with 24hr and 48hr hydrothermal reaction demonstrated similar flux (6177 L/m²-hr and 6129 L/m²-hr, respectively), which indicated that the flux did not keep decreasing after 24hr hydrothermal reaction. Thus, after 24hr, the membrane surface was saturated with CuO nanosheets, and the further growth of CuO nanosheets was not obvious. Actually, we also noticed that there were many black particles suspended in the reaction bottle, which suggested that the continue formation of CuO nanosheets was not on the nanofiber surface. As a result, the prolongation of hydrothermal reaction did not further lead to the flux decrease.

Figure 5-12 Pure water flux of membranes with different hydrothermal duration.

5.7 Conclusion

To conclude, a CuO nanosheets modified PVDF nano-fibrous membrane was successfully fabricated. A novel method combining electrospinning and low-temperature hydrothermal reaction was adopted to synthesis the membrane. PVDF nano-fibrous membrane was first electrospun to obtain the membrane substrate. Subsequently, CuO was introduced on the nano-fiber surface by hydrothermal reaction to modify the hydrophobic membrane to render hydrophilic. The as-prepared membrane exhibited super-hydrophilicity and underwater oleophobicity. This property made the membrane a promising material for oil-water separation. The following test results indicated that the membrane displayed very high oil removal rate and water permeation flux. It is anticipated that this membrane will have numerous applications in water treatment especially oil-water separation and this synthesis method can also be adopted to fabricated different materials with their unique properties in distinct applications.

Chapter 6 Leaf-inspired photo responsive ZnO nanorods modified PSF membrane

6.1 Introduction

Smart membrane which is able to alter its wettability in response to external stimuli have great potential in the design and fabrication of intelligent materials for advanced applications and especially controllable oil-water separation (Li, Zhou et al. 2015, Ma, Cheng et al. 2016). Considerable efforts have been devoted to achieving switchable wettability by different stimuli like pH (Zhang, Zhang et al. 2012), magnetic (Wu, Wang et al. 2015), light (Liu, Wang et al. 2015), carbon dioxide (Che, Huo et al. 2015), photo-thermal (Hu, Gao et al. 2015). The transpiration of leaves has provided us another inspiration. The stomata of leaves provide many pore-like structures on the leaf surface and help to regulate the water exchange between leaves and the atmosphere. At daytime, under solar light, the stomata on the leaf surface will open and water vapour will pass through them; while at night without light, those pores will shrink to reduce the water loss (Waggoner and Bravdo 1967, Zhu, Li et al. 2017). Combining this photo responsive water transportation and the surface wetting science, is it possible for us to fabricate a material with photo-responsive wetting behaviour? Therefore, micro-/nano- structural surface and photo-responsive material are the two key factors. Inspired by the stomata of leaves, we successfully fabricated a smart photo-sensitive ZnO nanorod-modified polysulfone (PSF) nano-fibrous membrane by the combination of electrospinning and hydrothermal reaction. The schematic illustration of photo-responsive water permeate and stomata and the wetting behaviour of ZnO-modified PSF membrane is shown in Figure 6-1.

Figure 6-1 Schematic illustration of the photo-responsive water permeation of stomata and ZnO nanorod modified PSF membrane.

As a facile and versatile technology, electrospinning is widely utilized to fabricate nanofibers with high specific surface areas, highly interconnected pore structures, nanoscale pore sizes, the potential to incorporate active chemistry at nanoscale and low initial solidifies (Ma, Zhang et al. 2016). Using electrospinning of PSF, a nanofibrous membrane was synthesized as a substrate for the hierarchical micro-/nano-structural surface.

In order to induce the photo-responsive property, surface modification like graft polymerization method, chemical cross-linking, chemical treatment and surface coating is necessary (Fane, Wang et al. 2015). Nano-sized metal oxide has gained much attention, because metal oxide alters the surface property and also increases the surface roughness to create micro-/nano- structures (Zan and Wu 2016). Metal oxide like titanium dioxide (TiO_2) (Tan, Liu et al. 2016), silica (SiO_2) (Tai, Tan et al. 2015), copper oxide (CuO) (Baghbanzadeh, Rana et al. 2015), and zinc oxide (ZnO) (Ennaceri, Wang et al. 2016) are widely studied due to their especial wetting behaviors. However, most of these metal oxide modified membranes are based on metal mesh, which has many limitations like large pore size and poor flexibility when

applied for oil-water separation (Qin, Liu et al. 2016). Therefore, metal oxide modified PSF has promising potential for efficient application in oil-water separation

As a low-cost, non-toxic and environmental-friendly material, zinc oxide is considered as a promising candidate for the modification of PSF nano-fibrous membrane (Zhang 2017). Controllable wettability of aligned ZnO nanorod films was first reported in 2004 (Feng, Feng et al. 2004). Under UV irradiation or dark storage, the films alter its wettability, which can be reversible switched. After storage in dark, ZnO nanorod films is hydrophobic owing to the roughness structure and low surface energy. However, after UV irradiation, electron-hole pairs will be generated on the surface of ZnO, and thus some defective site would form, which can absorb water from air. Therefore, ZnO nanorod are covered by a very thin water film, which renders the surface to be super-hydrophilic and shows great potential in the photo-responsive oil-water separation (Tian, Zhang et al. 2011). Moreover, since ZnO is a semiconducting material with a broad direct band gap of 3.37 eV, large exciton binding energy of 60meV and deep violet/borderline UV absorption at room temperature (Özgür, Alivov et al. 2005, Ong, Ng et al. 2018), it is also well-known as a good photo-catalysts for several contaminants (Xia, Wang et al. 2016). Thus, ZnO modified PSF membrane possesses great potential in self-cleaning of oil contaminant.

To modify the PSF membrane with ZnO nano-materials, hydrothermal growth is chosen in this research. As one of the most commonly employed methods, hydrothermal growth of ZnO nanorod is able to grow on the different surfaces easily at low temperature which benefits the synthesis process (Ou, Sanchez-Jimenez et al. 2016). Some researchers developed ZnO-coated steel mesh for oil-water separation (Tian, Zhang et al. 2011, Tian, Zhang et al. 2012), but there are few researches about ZnO-modified nanofibers. Li et al. first combined hydrothermal method and electrospinning to develop ZnO-modified carbon nanofibers as supercapacitor (Li, Wang et al. 2016).

In this research, via hydrothermal growth method, modification of the electrospun PSF nano-fibrous membrane with ZnO nanorod was achieved to obtain special wettability and self-cleaning property for oil-water separation.

6.2 Fabrication of ZnO nanorod modified PSF membrane

Figure 6-2 presents the schematic illustration of the synthesis procedure of ZnO modified PSF nano-fibrous membrane. By electrospinning method, PSF nano-fibers was synthesized. In order to have the Zn seed on the nanofibers, zinc acetate was dissolved in the electrospinning precursor. Zinc acetate provided the uniform zinc seeds on the nanofiber surface and also guided the growth of ZnO nanorods via hydrothermal reaction. Figure 6-3(a) shows the FESEM image of electrospun PSF nanofibers with Zn seed.

Figure 6-2 Schematic illustration of the synthesis procedure of ZnO nanorod modified PSF nano-fibrous membrane.

For the modification of the PSF nanofibrous membrane, hydrothermal method was utilized for the ZnO growth on the surface of nanofibers. Initially, zinc acetate on the nanofiber surface reacted with OH⁻ to form Zn(OH)₂ which then was converted to ZnO as the seeds. As reactions proceeded, the zinc ions in the hydrothermal solution were transformed into Zn(OH)₂ then ZnO and grew on the ZnO seeds leading to the ZnO nanorods.

Figure 6-3 Morphology and surface composition of the membrane. (a) FESEM image of PSF nanofibers without ZnO growth; (b) PSF membrane after 3hr ZnO growth; (c) enlarged image of ZnO nanorods; (d) EDX spectrum of ZnO modified PSF membrane; (e) Elemental mapping image of oxygen; (f) Elemental mapping image of zinc.

6.3 Characterization of ZnO nanorods modified membrane

The FESEM images shown in Figure 6-3(b) illustrates that ZnO nanorods grew on the fiber surfaces forming a micro-/nano-structure together with polysulfone. An EDX element mapping indicates that the nanorod was comprised of ZnO as shown in Figure 6-3(d-f). Our experimental results also demonstrate that the reaction time

had a great influence of the ZnO morphology. After one hour of hydrothermal reaction, Figure 6-4(a) shows insufficient growth of ZnO nanorods. After 3hr, uniform growth of nanorods can be observed, while a duration of 5hr made some nanorods elongated while some aggregated to form thicker nanorods. By 24hr, highly dense nanorods were obtained with smoother surface, in which the hexagonal shape becomes more apparent.

Figure 6-4 FESEM images of ZnO modified PSF nano-fibrous membrane with different hydrothermal duration. (A) 1hr; (B) 3hr; (C) 5hr; (D) 24hr.

To further verify the effect of reaction time, we conducted the Brunauer-Emmett-Teller (BET) surface area analysis to determine the specific surface area of ZnO nanorods modified membranes with different hydrothermal durations. Figure 6-5 compares the BET surface areas (DFT method) for the various hydrothermal growth duration with 3hr growth displaying the highest specific surface area, followed by 1hr, 5hr and 24hr. With regards to 3hr having the highest surface area, this can be explained by the most ideal growth of ZnO nanorods which contributes to a higher

specific surface area. For 1hr duration, due to insufficient growth of ZnO nanorods, its specific surface was lower than that of 3hr. With increasing hydrothermal duration, the specific surface area decreased due to overlapping of nanorods. In addition, Figure 6-6 presents the pore size distribution of 3hr which indicates the texture of the fibers. A narrow pore size distribution was obtained which indicates the uniform texture on the fibers for 3hr. This is in good agreement with FESEM images. Therefore, the 3hr hydrothermal growth which yields the best morphology is expected to yield the best performance for photo-catalytic oxidation and self-cleaning.

Figure 6-5 BET specific surface (DFT method) of ZnO modified PSF nano-fibrous membrane with different hydrothermal duration.

Figure 6-6 Pore size distribution of ZnO modified PSF nano-fibrous membrane with 3hr hydrothermal duration.

Surface wetting property is the key factor to determine the ability of oil-water separation. The surface wettability of the as prepared ZnO modified PSF membrane was investigated after dark storage and UV irradiation. The UV lamp used in this research had a wave length 365 nm. As shown in Figure 6-7, the membrane after dark storage showed hydrophobicity (contact angle 135°), while after 4-hour UV-irradiation, the water contact angle of the membrane was 34° , which was hydrophilic. During the test, we observed that the water contact angle decreased with the increase time of UV irradiation, but after 4 hours, the decrease was not obvious any more. This contact angle change could be cyclical. After storage in darkness overnight (around 12 hours), the membrane became hydrophobic again, and after UV irradiation it became hydrophilic. Therefore, the membrane renders hydrophilic under UV irradiation, and water will be able to spread on the membrane surface. When more water is added, the water droplet will spread and permeate through the membrane (Tian, Zhang et al. 2012). Due to some limitation of the testing equipment, the underwater oil contact angle could not be measured for this membrane. However, with the accordance of the wetting theories, the in-air-hydrophilic surface always shows oleophobicity underwater, which leads to its ability to let water pass through while reject oil (Wang, Liang et al. 2015). This suggests that this membrane is a good candidate of photo-responsive oil-water separation.

Figure 6-7 Water contact angle change. (a) After dark storage, contact angle is 135° , which is hydrophobic; (b) After UV irradiation, water contact angle is 34° , which is hydrophilic.

6.4 Oil-water separation test

The oil-water separation efficiency of the novel ZnO modified PSF membrane was investigated by a series of tests. Figure 6-8(a) shows the schematic illustration of the UV-responsive oil-water separation. As shown in Figure 6-8(b), the as-prepared membrane was placed on the filter holder. After the whole setup was stored in dark for 24hr, the oil-water mixture was discharged into the filter cup. The water-oil mixture was stable in the upper glass cup and could not penetrate through the membrane, due to its hydrophobicity and the “air gap” locked in the micro-/nano-structures. Subsequently the UV light was turned on, which irradiated the membrane to “switch” from its hydrophobic characteristics to hydrophilic. Water permeation was observed shortly after the exposing the membrane to UV irradiation, while the oil was repelled due to the “water gap” on the membrane surface and remained in filter cup. As a result, the photo-responsive water-oil separation was achieved by the ZnO-modified PSF membrane. Several types of oil-in-water mixtures including cooking oil, olive oil, silicon oil, diesel and engine oil were prepared to evaluate the photo responsive oil-water separation ability as shown in Figure 6-9.

Figure 6-8 UV-responsive oil-water separation. (a) Schematic Illustration of the UV responsive oil-water separation; (b) both oil and water could not permeate through the membrane because of the presence of “air gap”; (c) after UV irradiation, water permeated through the membrane while oil was rejected, due to the “water gap”; (d) oil remained on the top of membrane; (e) water collected.

Figure 6-9 Separation efficiencies of different types of oil-water mixture in term of oil rejection.

6.5 Photocatalytic and self cleaning test

Membrane fouling remains to be one of the greatest hurdle to its application in oil-water separation and water treatment. This is caused by the deposition of organic matters on the membrane surface, which induced the decrease of flux (Tian, Zhang et al. 2012). As highlighted before, the photo-catalysis degradation process with semiconductors like ZnO can be briefly described as four steps: (1) UV irradiation; (2) exciton generation; (3) formation of oxidative species; and (4) oxidation of organic compounds or oxidation of water (Xia, Wang et al. 2016). Under UV irradiation, electrons will be promoted from the valence band to the conduction band, forming a pair of positive hole (h_{VB}^+) and electron (e_{CB}^-) on the surface of ZnO; both the electron and the hole can undergo the redox reactions with other specie; those reactions are shown below(Lee, Lai et al. 2016):

The superoxide anions and hydroxyl radical will further react with organic contaminant to form carbon dioxide and water as end products. Thus, ZnO

nanomaterials are widely applied in water treatment technology due to its photocatalytic property.

In this research, the photocatalytic and self-cleaning property of ZnO modified membrane was studied. Photo catalytic oxidation (PCO) of acid orange 7 (AO7) was tested for membranes with different hydrothermal duration at first. Table 6-1 and Figure 6-10(a) show the changes of AO7 concentration for different hydrothermal durations (c/c_0 vs. Time). Table 6-2 and Figure 6-10(b) compare the photo-degradation rate of AO7 as the first order reaction ($-\ln(c/c_0)$ vs. time). All of the ZnO modified membrane showed better photo-degradation rate than the blank sample. The sample with 3hr ZnO nanorods growth was able to achieve the highest photo-degradation efficiency 96.70% after 240 min of UV irradiation and the highest rate constant with $k = 0.0145 \text{ min}^{-1}$, while efficiency of the blank sample without ZnO was only 81.81%, and the reaction constant k (0.0073 min^{-1}) is the lowest. As for 1hr hydrothermal growth, due to the insufficient ZnO nanorods formation, the reaction rate was slower than 3hr. By increasing the hydrothermal duration to 5hr and 24hr, the reaction rate constant decreases to 0.0097 min^{-1} and 0.0087 min^{-1} . This result also matches the FESEM image of the membrane morphology as shown in Figure 6-4 and the specific surface area result as shown in Figure 6-5. Therefore, this PCO test result indicates that the 3hr-hydrothermal ZnO modified nano-fibrous membrane demonstrated the best AO7 degradation efficiency, which matched the results of FESEM and surface area analysis discussed above. Therefore, the 3hr-hydrothermal membrane had the best potential for application in photo-catalysis and self-cleaning, and it was utilized for the following test.

Table 6-1 AO7 degradation efficiency of 240min for membranes with different hydrothermal duration.

Hydrothermal Duration (hr)	Degradation Efficiency (%)
1	92.85
3	96.70
5	87.40
24	85.52
Blank	81.81

Table 6-2 Photo-degradation rate constant and R^2 of AO7 for membranes with different hydrothermal duration.

Hydrothermal Duration (h)	Rate Constant (min^{-1})	R^2
1	0.0119	0.9849
3	0.0145	0.9867
5	0.0097	0.9926
24	0.0087	0.9937
Blank	0.0073	0.9954

Figure 6-10 (a) Changes of AO7 concentration and (b) photo-degradation rate for different hydrothermal duration

Self-cleaning property of oil contaminated membrane was tested subsequently. Two samples of PSF nano-fibrous membrane were utilized in this test. One was ZnO modified after 3hr hydrothermal growth; the other was the blank membrane without any ZnO. The test was carried out by first immersing the membrane into an olive oil/acetone solution for 10 min to contaminate it. Then the two membranes were placed under UV irradiation for 4hr. As shown in Figure 6-11, by observing the water contact angle change every hour, gradual decrement of water contact angle of the membrane was observed with increase exposure time to UV irradiation. During the first two hours of UV irradiation, there was no observable change of water contact angle of both membranes as the oil was not degraded. However, large decrement of the water contact angle was observed on ZnO modified membrane from 137° to 109°

after 3hr UV irradiation, which indicated the membrane became more hydrophilic and the degradation of oil contaminant started. After 4hr UV irradiation, the ZnO modified membrane surface turned to hydrophilic state with an 85.6° contact angle. As for the blank membrane, no significant changes of contact angle were observed indicating no self-cleaning ability, since there were no ZnO nanorods on the membrane surface. This result suggests that ZnO modified membrane is capable of performing self-cleaning under UV irradiation due to the presence of ZnO nanorods which enhances the specific surface and photo-catalytic efficiency.

Figure 6-11 Water contact angle change with the duration of UV irradiation.

Moreover, the self-cleaning property was also test by repeating 5 cycles. Similar to procedure described in the previous paragraph, the membrane was first immersed into the olive oil/acetone solution for 10 min to contaminate it and measured the contact angle. Thereafter, the membranes were placed under UV irradiation for 4 hr and tested the contact angle again. This process was regarded as one cycle and one piece of membrane was tested for 5 cycles. Figure 6-12 illustrates the water contact angle change of 5 cycles. ZnO nanorods modified displayed the capability to be reused for

self-cleaning even after 5 cycles, as the water CA remained at around 90° . Therefore, it can be concluded that ZnO nanorods can be reused without drastic decrease in their performance, and thus, have displayed potential application for self-cleaning purposes.

Figure 6-12 Transformation of water contact angle for 5 cycles under UV irradiation.

6.6 Conclusion

In conclusion, inspired from the light-responsive water transportation of the stomata, we successfully fabricated a photo-responsive ZnO nanorod modified PSF membrane, which possesses the photo responsive wetting property. After UV irradiation, the membrane surface becomes hydrophilic, which is capable of the efficient oil-water separation. Moreover, by evaluating the recyclability of the prepared membrane, it displays the capability of self-cleaning ability, which exhibits the potential for numerous oil-water separation application like controllable filtration and self-cleaning material.

Chapter 7 Manta ray gill inspired radially distributed nanofibrous membrane

7.1 Introduction

Manta rays are large sea creatures which feed on suspended food particles in the ocean by filtering water rapidly and continuously (Paig-Tran and Summers 2014). Manta rays have never suffered from the clogging of food particles, even although they have to filter large amount of water all the time, and this phenomenon is owing to their special structured gill rakers (Stewart, Beale et al. 2016). As illustrated in Figure 7-1(a), manta rays separate the food particles from seawater via a crossflow filtration instead of dead-end filtration which prevents the clogging of their gill rakers (Brainerd 2001, Sanderson, Cheer et al. 2001, Paig-Tran, Kleinteich et al. 2013). As seawater and the suspended food particles enter its mouth, the stream travels across gill rakers. These rakers allow seawater to pass through but retains the suspended food particles. These suspended food particles are washed off the gill rakers to avoid clogging. Thereafter, the stream of seawater becomes more concentrated with suspended food particles and travels into the esophagus of manta rays. This crossflow filtration is beneficial as the particles and contaminants are less likely to be attached to the gill rakers of manta rays, compared with the dead-end filtration (Dou, Tian et al. 2017). This unique filtering structure from nature is inspiring for water treatment, especially in oil-water separation.

As we discussed in the Chapter 2, natural special wetting behavior inspired researchers to fabricate super-wetting materials by manipulating the micro-/nano-structure or surface composition with the development of colloid and interface science (Darmanin and Guittard 2014, Lu, Sathasivam et al. 2015, Savage 2015, Wang, Liang et al. 2015, Wang, Liu et al. 2015). Among them, super-hydrophilic and underwater super-oleophobic membranes have been widely investigated and effectively employed for the gravity-driven dead-end oil-water separation (Field 2012, Kota, Kwon et al. 2012, Zhang, Zhang et al. 2013, Zhang, Zhu et al. 2014). However, this method has intrinsic limitations, these membranes can be easily clogged by oil and the water flux will decrease significantly. Furthermore, the

accumulation of oil on the membrane surface renders the separation process cannot be conducted continuously.

Figure 7-1 Crossflow filtration in manta ray gills and bioinspired silk fibroin membrane. (a) Illustration of crossflow filtration in fish gills. (b) Gill structure of the manta rays. (c) Bioinspired electrospun silk fibroin membrane. (d) Illustration of bioinspired crossflow oil-water separation.

Inspired by the crossflow filtration of manta rays, we can solve this problem by combining membrane technology and the structure of manta ray gill rakers. By mimicking manta ray gills, a membrane based oil-water separation set-up was created. The membrane with aligned nanofiber was fabricated by electrospinning on a

specially designed collector, as shown in Figure 7-1(c-d). During the oil-water separation process, water permeates through the membrane rapidly, while oil is repelled and collected in the inner iron pipe. Silk fibroin was chosen as the raw material to fabricate the nano-fibrous membrane due to its naturally super-hydrophilicity and underwater super-oleophobicity.

The laboratory scale experiments have verified that the membrane exhibits the ability to separate oil and water continuously and efficiently. Moreover, silk fibroin is a natural material which exhibits no hazard to the environment. This work provides a new perspective to achieve efficient and continuous oil-water separation. Additionally, silk fibroin has exhibited great potential as a novel material for water treatment.

7.2 Fabrication of the radially distributed nanofibrous membrane

According to the results discussed in Chapter 4, low concentration of silk fibroin (<10%) led to the “beads-on-string” structure of electrospun nanofibers, which influenced the quality of membrane. When the concentration reached 10%, uniform no-bead nanofibers were obtained successfully, and therefore 10% was chosen for the fabrication our membrane in this research. 10% silk fibroin solution was produced by adding 1.0 g of solid silk fibroin into 7.54 mL of formic acid and was stirred for 6 hours until the solid silk fibroin was fully dissolved. The electrospinning was carried out at room temperature in a closed chamber. A 5mm iron pipe was used as the electrically conducted collector which was connecting to earth. A plastic pipe was surrounding the iron pipe for the silk fibroin fibers to attach itself (as shown in Figure 7-1(b)).

The silk fibroin nanofibers were then electrospun. The tip collector distance was kept at 20 cm and a voltage of 24 kV was supplied. The silk fibroin solution was placed in a syringe with a blunt-tip needle (nozzle diameter of 0.7 mm). Using a micro-syringe pump, the spinning solution was pushed through the needle at a feeding rate of 0.2 mL/h, 6 hours were required to produce the membrane by electrospinning.

Thereafter, the electrospun membrane was dipped in ethanol for 1 h to ensure that the fibers do not clump together when it come in contact with water.

7.3 Characterizations of the membrane

By specially designing the collector of electrospinning as illustrated above, the nano-fibrous membrane setup could be obtained easily. The microstructures of prepared silk fibroin membrane were characterized by field emission scanning microscopy (FESEM). The radiate distribution of nano-fibers was proved by the FESEM image as shown in Figure 7-2(a). This fiber-radiate membrane was designed to mimic the manta ray gills for continuous oil-water separation. Figure 7-2(b) is the enlarged image of the nanofibers. It is clearly observed that the diameter of the fibers was around 100 nm. The average diameter of the fibers was 106 nm. The largest was 198 nm, while the smallest was 40.3 nm. The fiber diameter distribution shown in Figure 7-3 was calculated by measuring 71 fibers at random using image J program. Therefore, a manta ray gills inspired nano-fibrous membrane was obtained by silk fibroin electrospinning.

Figure 7-2 FESEM images of nano-fibrous silk fibroin membrane.

Figure 7-3 Fiber diameter distribution (Number of fibers = 71).

7.4 Wetting behaviour

Wetting Behavior of the membrane plays an important role in oil-water separation. As shown in Figure 7-4(a), during the contact angle testing process, when a water droplet contacted with the membrane surface, it quickly spread, and the water contact angle in air was 0° , which illustrated the super-hydrophilicity of the membrane. When the membrane was underwater, as shown in Figure 7-4(b), the oil contact angle was 154° , which illustrated the underwater super-oleophobicity of the membrane.

Figure 7-4 Contact angle of nano-fibrous silk fibroin membrane. (a) Water contact angle in air. (b) Oil contact angle in water.

This wettability of the membrane is naturally from the abundant hydroxyl and amino groups on the surface of silk fibroin fiber. According to Wenzel model and Cassie-Baxter model, a hydrophilic surface can become more hydrophilic or super-hydrophilic with the increase of roughness (Gao and Jiang 2004, Feng and Jiang 2006). Due to the micro-/nano-structure of electrospun nano-fibers, this membrane possesses great roughness and thus super-hydrophilicity. Meanwhile, with the accordance of the wetting theories, the in-air-hydrophilic surface always shows oleophobicity underwater (Cassie and Baxter 1944, Jung and Bhushan 2009), which is the same as the result of our test. With super-hydrophilicity in air and super-oleophobicity underwater, this membrane exhibits great potential in oil-water separation.

7.5 Oil-water separation

Continuous oil-water separation was conducted to test the efficiency of the membrane. The separation efficiency was evaluated using six types of oil including vegetable oil, olive oil, silicon oil, hexane, diesel and engine oil. The oil concentration was measured based on the total organic carbon. The separation efficiency was calculated using Equation 3.1.

A certain volume of oil-water mixture was discharged into the set-up continuously. Water passed through the membrane quickly by gravity and was collected by the plastic tube, while rejected oil was collected through the inner pipe by a beaker as shown in Figure 7-5(b). Digital images of raw oil-water mixture and the permeated water are shown in Figure 7-5(c) and (d). Figure 7-6 illustrated that the separation efficiency for six types of oil was at least 99.9%, showing efficient separation behavior (99.96% for olive oil-water mixture, 99.92% for silicone oil-water mixture, 99.96% for hexane-water mixture, 99.97% for vegetable oil-water mixture, 99.91% for diesel-water mixture and 99.91% for engine oil-water mixture).

Figure 7-5 Oil-water separation test of nano-fibrous silk fibroin membrane. (a) Schematic illustration of the radially arrayed nanofibers for oil droplet self-transportation. (b) Separation setup. (c) Feed oil-water mixture. (d) Permeate water.

Due to the super-hydrophilicity and underwater super-oleophobicity of the membrane, there will be a water film on the membrane surface, which is a stable underwater Cassie-Baxter wetting mode and can help achieve a robust water cushion between oil droplets and the membrane to prevent oil from permeating through (Cassie and Baxter 1944, Xue, Wang et al. 2011, Chu, Feng et al. 2015, Yong, Chen et al. 2016). Meanwhile, the radial arrays of nanofibers and the crossflow of oil-water mixture creates a continuously decreasing oil-water contact friction (Bliznyuk, Seddon et al. 2012, Du, Zhao et al. 2016, Li, Qin et al. 2016). As a result, when an oil droplet is deposited on the surface, it will be driven to the center by both the wettability gradient and gravity as shown in Figure 7-5(a), rather than attaching on the membrane surface and blocking the pores. At the same time, when oil droplets are accumulated to the center, small droplets will converge to form big ones and finally be collected in the central pipe, just like the feeding process of manta rays. Therefore, this membrane setup is able to achieve efficient and continuous oil-water separation.

Figure 7-6 Separation efficiency of six types of oil (99.96% for olive oil-water mixture, 99.92% for silicone oil-water mixture, 99.96% for hexane-water mixture, 99.97% for vegetable oil-water mixture, 99.91% for diesel-water mixture and 99.91% for engine oil-water mixture).

7.6 Long term filtration tests

In order to quantify the suitability of the membrane for long term filtration, separation tests were also conducted over time and permeate volume.

Firstly, to test the effectiveness of the membrane performance over a long period of time, the electrospun silk fibroin membrane subjected to constant filtration of a 1:9 olive oil-water mixture by volume. Samples are taken every hour over a period of 8 hours. These samples are then tested for its TOC concentration to calculate its separation efficiency over 8 hours. As seen from Figure 7-7, the membrane rejection performance remains high over a period of eight hours. This showed the effectiveness of the crossflow filtration that was adopted in the membrane setup. This ensures the membrane performance for oil water separation can be maintained at a high level after extended periods of time.

Figure 7-7 Olive oil water mixture separation efficiency over time.

Secondly, the membrane was tested for its permeate quality after producing certain amounts of permeate water. Samples are taken from 50 mL to 700 mL of permeate water produced. As shown in Figure 7-8, the permeate quality remains high even after producing 700 mL of permeate. This demonstrated the effectiveness of the crossflow filtration that was utilized in the membrane setup. This ensures that permeate quality from oil water separation can be maintained at a high level after producing a substantial amount of permeate.

Figure 7-8 Olive oil water mixture separation efficiency over permeate volume.

7.7 Conclusion

Inspired by the manta ray gill rakers, a novel silk fibroin membrane was successfully fabricated for the efficient oil-water separation. By specially designing the collector of electrospinning, the crossflow nano-fibrous membrane setup could be obtained easily, which was able to achieve efficient and continuous oil-water separation. Water was collected in the outer cylinder, while oil was collected via the middle iron pipe. The membrane possessed super-hydrophilicity and underwater super-oleophobicity, which enabled the efficient oil-water separation, and the cross-flow design of the membrane also allowed continuous separation process. This investigation of bio-mimic designing and fabricating of nano-fibrous membrane for continuous and efficient oil-water separation provided great insights for water purification and water collection in different areas.

Chapter 8 Nano-structured multi-dimensional super-hydrophilic material for directional water transportation

8.1 Introduction

Development of water technologies had been widely studied in the past years, while most of them, including seawater desalination and wastewater purification, are severely hindered by huge energy consumption (Elimelech and Phillip 2011, Logan and Elimelech 2012, Werber, Osuji et al. 2016). Water transportation across micro-/nano-channels is of great importance for designing energy-efficient water purification technology (Zhu, Xie et al. 2016, Qin, Liu et al. 2018). Conventionally, it is believed that the directional movement of water requires osmotic or hydraulic pressure gradient (Chua, Ji et al. 2015, Karpitschka, Das et al. 2015). Therefore, mechanical pumps and osmotic pressure are widely used. However, these technologies are energy-intensive to overcome the hydro-dynamics barrier. As a result, it is a key factor to find out a novel approach to achieve efficient water transportation with little energy consumption.

Nature continues to inspire researchers in many fields. Trees developed many fantastic structures for natural processes from the billions of years of evolution, especially their water transportation process which has drawn much attention for its efficient delivery of water from root to the upper crown through its trunks (Cochard 2006, Ledford 2008). The cellulose-dominated hydrophilic xylem with its multi-channel structure forms the “vessels” for the transportation of water and nutrients; the water and nutrients are then utilized by the transpiration of the trees; this water loss through trans-evaporation from the pores on the leave surfaces results in negative pressure within the “vessels” and this drives the water up as the fluid is subjected to the tension caused by the metastable state (Wheeler and Stroock 2008). This is explained by the venerable cohesion-tension theory.

Recently, some studies have been focusing on such tree-inspired designs (Chen, Kuang et al. 2019). However, most of them are focusing on the evaporation of water and thermal insulation of the evaporator, and the distance of water movement is short (Li, Gao et al. 2017, Li, Gao et al. 2017, Zhu, Li et al. 2017). Although they are well-

designed for mimicking the transpiration of trees, the transportation of water is neglected. Either polymer based or natural wood based water pathways are unable to work as the trunk to lift water to several meters high. Is it possible that we are able to lift the water to several meters or even dozens of meters high just like trees?

From the material point of view, the transportation of water is based on hydrophilic materials with small pores to carry the water upwards via capillary forces (Chaudhury 1992). However, these materials are often in micron range, and in our opinion, they are not small enough. The size does matter, which is the major obstacle to transport water in long distance. Hence, to overcome this limitation, we fabricated a novel nano-fibrous matrix that possesses remarkable advantages like small pore size, high porosity with 3D-connected pores, high specific area and high surface charge density. This unique structure of the nanofiber matrix will increase its surface energy which will maintain the hydration and drive the movement of the polar molecular H_2O , which could provide a good solution for the long-distance low-energy water transportation.

8.2 Characterization of the super-hydrophilic nanofibers

We fabricated the TiO_2 -PVDF nanofiber (TPNF) matrix utilizing a home-designed rotating-drum setup on an aluminum foil. 15 wt.% PVDF was dissolved in a DMAC/Acetone (weight ratio 8:2) solution as the precursor solution for electrospinning. In order to increase the hydrophilicity of the nanofibers, we added 3 wt.% hydrophilic TiO_2 nano-particles (P25) in the precursor solution to modify its surface property (Zhou, Bahi et al. 2013, Li, Kang et al. 2016). After 8hr stir by the magnetic stirrer at 100 rpm and 70°C, a well-mixed P25-PVDF precursor was obtained. Thereafter the electrospinning was conducted in a closed chamber with 45% humidity. The voltage was 20 kV, which the pumping rate was 1.5 mL/hr.

Figure 8-1 shows the morphology of the as prepared nanofibers observed by the field emission scanning electron microscopy (FESEM). Before the FESEM observation, platinum coating was conducted at 20mA for 30s. The FESEM images showed that the diameter of nanofibers was around 100 nm. Image J program was utilized to

measure the fiber size distribution of the membrane as shown in Figure 8-2. The average fiber diameter was 93.6nm, while the standard error is 32.7nm. The cross-section FESEM image (Figure 8-3) of the nanofiber layer shows a unique, scaffold-like, porous structure with the interconnected pores between individual nanofiber.

Figure 8-1 FESEM images of TPNF (a) Low magnification image, (b) High magnification image.

Figure 8-2 Fiber diameter distribution (number of fibers = 106).

Figure 8-3 Cross-section FESEM image of TPNF

EDX was conducted to determine the chemical composition of the TPNF. In the EDX spectrum observed from Figure 8-4(b), the peaks of titanium and oxygen were prominent. Carbon and fluoride peaks were from PVDF, while platinum was from the platinum coating before FESEM and aluminum was from the aluminum foil as electrospinning collector. The elemental mapping images as shown in Figure 8-4(c) and (d) illustrated the well-dispersion of Ti and O, which indicated that TiO_2 nanoparticles were well mixed in the precursor solution by the magnetic stirrer.

Figure 8-4 EDX result of TPNF. (a) FESEM image of TPNF, (b) EDX spectrum, (c) Elemental mapping image of oxygen; (d) Elemental mapping image of titanium.

8.3 Wetting behavior of TPNF

At the same time, the electrospun nano-fibrous structure will increase the surface area of the material and further render it super-hydrophilic (contact angle $\theta = 0^\circ$). As we discussed above, hydrophilic material is preferable in this study. As shown in Figure 8-5, when a water droplet (2 μm) contacted with the nanofibers, it quickly spread within 0.8s, which suggests the super-hydrophilicity of the nanofibers. This property

insures the water can be fully filled in the micro-/nano-structure of the nanofibrous matrix.

Figure 8-5 VCA snapshots illustrating the process of the spreading of a water droplet on TPNF in air. (a)0s, water just contacted with the nanofibers; (b)0.37s, water quickly spread out; (c)0.77s, water droplet spread out demonstrating the 0° water contact angle.

8.4 Water lifting of the TPNF

During the past decades, many water directional transportation phenomena have been extensively studied, and *capillary surface* are used to describe the interface (Chen, Zhang et al. 2016). Actually, it is believed that the gradients in surface energy influence the water movement in hierarchical structural features at microscale and nanoscale (Li, Li et al. 2016, Park, Kim et al. 2016). As discussed in Section 2.8, the rising height of liquid in small channels can be calculated by the equation

$$h = \frac{L}{S} \cdot \frac{\gamma \cos \theta}{\rho_w g} \text{ (Equation 8.1).}$$

As γ , ρ_w and g are the surface tension, the density of water and the gravitational constant, which are constant, in order to make the longer distance water transportation (higher h), it is the necessary to have larger L/S (the wetting perimeter / surface area of the tube) and larger $\cos \theta$. Thus porous matrix with larger L/S and super-hydrophilic material with $\cos \theta = 1$ are preferred. According to the Wenzel model and Cassie-Baxter model, a hydrophilic surface can become more hydrophilic or even super-hydrophilic with the increase of the interface area (Wang, Liu et al. 2015, Wang, Elimelech et al. 2016). Therefore, the hydrophilic material with nano-sized hierarchical structure fabricated demonstrated great potential in transportation without any mechanical pumping.

As the hypothesis, the as-prepared TPNF matrix with very thin nanofiber and super-hydrophilicity should be able to transport water due to its interconnected nano-pores and special wetting behavior. So we will compare the water lifting property of TPNF with hydrophilic fibrous material with thicker fiber and hydrophobic nano-fibrous material, and TPNF should have better performance than them.

To study the relationship between fiber size and their performance, a commercial hydrophilic PET substrate and TPNF matrix were compared in this study. The water lifting results are shown as Figure 8-6. We can easily observe the nano-fibrous matrix able to lift water to a higher level compared to fibrous structure in the micron range after 1hr. Hydrophobic PVDF nanofibers were also test as comparison as shown in Figure 8-7. It is observable that water could not move upward via the hydrophobic nano-fibrous matrix.

Figure 8-6 Water lifting by TPNF and PET substrate

Figure 8-7 Water lifting by TPNF and hydrophobic PVDF nanofibers

Actually, some researches have been conducted and proves that the liquid rise in small pore less than $1\text{ }\mu\text{m}$ exceeds the prediction of Jurin's Law (Moldover and Gammon 1984). Since water is an ionic liquid, a charge double layer will be created at the solid-liquid interface. This will induce the celebrated “disjoining pressure” and further reduces the effective value of L/S (De Gennes 1985). It is believed that at nano range, water dissociation and hydrogen bonds between water molecules help to drive the movement (Manzano, Moeini et al. 2012).

8.5 Pure water flux test and filtration test

In order to determine the water permeability of the nanofibers, a dead-end filtration set-up was adopted to test the pure water flux as shown in Figure 3-3. The testing process and calculation equation were the same as the description in Section 3.6. A commercial $0.45\text{ }\mu\text{m}$ nylon membrane was also tested at the same condition for comparison. Figure 8-8 shows the pure water flux of TPNF and $0.45\text{ }\mu\text{m}$ nylon membrane. The pure water flux of TPNF was $16792.8\text{ L/m}^2\text{-hr}$, while the flux of $0.45\text{ }\mu\text{m}$ nylon membrane was $8153.2\text{ L/m}^2\text{-hr}$, which is only half of TPNF. This result indicated that the TPNF possessed much better water permeability. This could be explained because of the low tortuosity and high porosity of the electrospun nanofibrous matrix (Song, Liu et al. 2011).

At the same time, due to the small pore size of the nano-fibrous matrix, we are able to draw clean water and remove some pollutants. Dead-end filtration tests were also conducted to determine the TPNF's rejection rate of polystyrene beads with different diameters (0.19 μm , 0.51 μm and 0.99 μm). Also, 0.45 μm nylon membrane was also test for comparison. As shown in Figure 8-9, TPNF had excellent rejection rate of 0.51 μm and 0.99 μm polybeads (98.68% and 98.06%), which was similar to that of 0.45 μm nylon membrane (98.70% and 98.95%). As for 0.19 μm polybeads, 0.45 μm nylon membrane had better rejection rate (45.95%) than TPNF (16.19%), but actually both rejection rates were low.

In summary, this nano-fibrous matrix exhibited great water permeability and high rejection rate of solids with diameter $> 0.51 \mu\text{m}$. Therefore, it is a promising candidate for directional water movement as well as separation some pollutants from water. A simple gravity-driven water directional movement test was adopted to determine the property of TPNF to transport water as well as remove small particles in water. After the test began, the TPNF was quickly wetted by water (Figure 8-10(a)) and fully wetted within 30s (Figure 8-10(b)). After 10 mins, it could be observed that water was directly transported from the upper petri dish to the lower one (Figure 8-10(c)). After 5hr, the water permeation from left to right was observable from the water level change in the petri dish (Figure 8-10(d)).

Figure 8-8 Pure water flux of TPNF and 0.45 μm nylon membrane

Figure 8-9 Rejection rate of polybeads with different diameters

Figure 8-10 Water permeation test. (a) TPNF was quickly wetted by water in the beginning; (b) TPNF was fully wetted within 30s; (c) 10 mins after the test started; (d) 5hr after the test started.

8.6 Continuous directional water transportation

Actually trees do not transport water freely. Neither does the super-hydrophilic nanofibrous matrix. This lift of water is increased by the reduction of surface energy. Although the porous nano-structure is able to move the water upward, we need to utilize the water and overcome the surface energy to draw the water out of the matrix. In Figure 8-10, we used gravity to achieve water transportation, but in this way we cannot lift water uphill. Trees once more give us the inspiration. According to plant scientists, transpiration motivates the water transportation through the tree (Scholander, Bradstreet et al. 1965, Wheeler and Stroock 2008). Water loss by evaporation on the leaf surface pulls the liquid water out of soil, up to the xylem, and finally to the leaves. The schematic illustration of the water transportation of trees is shown in Figure 8-11.

Figure 8-11 Schematic illustration of the continuous water transportation by tree. (a) water transportation through the trunk to leaves; (b)(c)(d) water evaporation; (e) continuous water stream along the nanofiber.

Generally, super-hydrophilic material cannot achieve continuous directional water movement after lifting the water uphill and reaches the equilibrium, unless there is a chemical gradient or pressure gradient (Du, Zhao et al. 2016, Zhao, Wang et al. 2017). However, if we are able to interfere this equilibrium like trees provide the chemical gradient for water, we are able to achieve constant water directional movement. Therefore, in this research, a cost-effective evaporation process was utilized to consume the lifted water and remove the pollutants and ions in water at the same time. Figure 8-12 illustrated the customized water directional movement setup inspired by tree. Evaporation of water vapor maintained the directional water transportation via the nano-fibrous matrix from the small beaker to atmosphere just like leaves. Humidity meter was adopted to measure the continuous water evaporation. In order to avoid the influence of the evaporation directly from the water in beaker, the beaker was well-seal to make sure water could only evaporate from the leaf-like nano-fibrous matrix. A blank test without TPNF was also conducted for comparison.

Figure 8-13 shows the humidity change in the closed chamber with time. It is observable that with the presence of TPNF, the humidity increased significantly in the initial stage and kept increasing with a slower rate, while the humidity didn't change much with normal hydrophobic PVDF or without any nanofibers (blank), which indicated the continuous water evaporation as well as the continuous water transportation via the super-hydrophilic nano-fibrous matrix from the small beaker to atmosphere.

Figure 8-12 Schematic illustration of the home-made water movement setup

Figure 8-13 Humidity change with time

8.7 Conclusion

Inspired by the water transportation process of tree, we fabricated a facile super-hydrophilic nano-fibrous matrix which was capable of transport water to a long distance as well as separate the particle pollutant from water, without hydraulic pressure. Evaporation process was utilized to draw the transported water from the matrix and provide continuous water movement and reclamation. The energy source of this process is eventually solar energy.

This process could be an affordable water transportation method in water industry. The only energy spent in the whole process is solar energy for evaporation. Therefore, it is an eco-sustainable solution to help solve water and energy problems throughout the world. In addition, the in-depth understanding of this phenomenon offer us an alternative method to reduce the energy required for water purification. We envision that this understanding will provides more energy-free innovation for the conveyance of water. Nanotechnology can not only remove the pollutants in water but also help the transportation of water.

Chapter 9 Conclusion and recommendation

9.1 Conclusion

From the inspiration of natural surfaces with special wetting behavior, super-hydrophilic materials are believed to obtain many fantastic properties to overcome the existing problems of current water technology, especially oil-water separation and directional water transportation. Possessing hierarchical micro-/nano-structure and high surface energy, super-hydrophilic materials have excellent affinity for water, which allows them to create “water gap” on their surface and exhibit great potential in rejecting oil droplets and anti-oil fouling. At the same time, these “water gaps” are able to fulfill these micro-/nano-structures to form the continuous “water channels” for long-distance low energy water transportation.

In this study, electrospun nano-fibrous membranes are employed to fabricate the hierarchical micro-/nano-structure materials with special wettability and multi-functional purposes. At first, we successfully fabricated the super-hydrophilic membranes made from natural hydrophilic silk fibroin via electrospinning. Due to the low chemical and heat resistance of silk fibroin, we subsequently fabricated polymeric nano-fibrous membrane with CuO, ZnO and TiO₂ modification. CuO, ZnO and TiO₂ were chosen because of their ideal property of wetting and facile synthesis processes. Electrospinning and hydrothermal process were adopted for the in-situ growth of CuO and ZnO nanoparticles on the fiber surfaces to obtain the flexible membrane with small pore size and high oil-removal efficiency. CuO modification rendered the hydrophobic membrane to hydrophilic. ZnO modified membrane exhibited UV-responsive wetting behavior. Due to the high-temperature and high-pressure condition of TiO₂ hydrothermal growth, it was difficult to obtain the TiO₂ modified membrane by hydrothermal process, so the membrane was fabricated by the blending of TiO₂ nanoparticles with PVDF electrospinning precursor, which was more hydrophilic compared with CuO and ZnO. The attained experimental results have demonstrated tremendous potential in providing new solutions and opportunities of water technology.

Silk fibroin nano-fibrous membrane was successfully fabricated via electrospinning an innovative precursor solution and post-treatment by ethanol. This membrane was well characterized by FESEM, TGA, FTIR and water contact angle tests. Above all, a nano-fibrous membrane possessing optimized surface structure, super-hydrophilicity ($WCA = 0^\circ$) and underwater super-oleophobicity ($OCA = 154^\circ$) were synthesized. The oil-water separation testing further illustrated that the silk fibroin membrane was able to separate oil-water mixture efficiently ($\sim 99.9\%$).

Traditional polymers, like PVDF and PSF, possessing good thermal and chemical resistance, can be another option to fabricate nano-fibrous membrane. However, due to the hydrophobicity of the polymers, hydrothermal growth of nanosized metal oxide was initiated to modify their surface property. CuO nanosheets modified PVDF membrane was first fabricated in this study. Copper acetate was added in the precursor solution of electrospinning as Cu seed. After the electrospinning and post-treatment process, hydrothermal growth of CuO nanosheets was adopted to modify the surface structure of the membrane. FESEM and EDX showed the morphology the CuO modified nano-fibrous membrane and its chemical composition. Due to the hydrophilicity of CuO and its hierarchical micro-/nano-structure, the as-prepared membrane exhibited super-hydrophilicity and underwater oleophobicity. This property rendered the membrane a promising material for oil-water separation. The following test results indicated that the membrane displayed excellent oil removal rate and water permeation flux. It is anticipated that this type of membrane will have numerous applications in water treatment particularly oil-water separation, and this synthesis method can also be adopted to fabricated different materials with their unique properties in distinct applications.

Thereafter, mimicking light-responsive water transportation of leaf stomata, a photo-responsive ZnO-nanorods modified PSF nano-fibrous membrane was developed via the similar strategy combining electrospinning and hydrothermal process. FESEM and EDX were utilized to characterize the surface morphology and chemical composition of the membrane. The UV-responsive property of ZnO allows the membrane to exhibit switchable wetting behavior. After UV irradiation, the

hydrophobic membrane was rendered hydrophilic. Thus, the membrane was capable for the efficient UV-responsive oil-water separation, which was proven by the oil-water separation test. Moreover, by evaluating the photocatalytic oxidation and recyclability of the prepared membrane, it demonstrates the capability of self-cleaning ability, which exhibits the potential for reusable oil-water separation application like controllable filtration and self-cleaning material.

To overcome the limitation of traditional gravity driven dead-end oil-water separation, a novel crossflow silk fibroin membrane setup was successfully fabricated, inspired by the manta ray gill rakers. A specially designed collector of electrospinning was adopted to fabricate the well-aligned radially distributed nano-fibrous membrane. The membrane possessed super-hydrophilicity and underwater super-oleophobicity, which enabled the efficient oil-water separation, and the cross-flow design of the membrane also allowed continuous separation process. With this crossflow membrane setup, efficient and continuous oil-water separation was achieved. This investigation of bio-mimic design and fabrication of nano-fibrous membrane for continuous and efficient oil-water separation provided great insights for water purification and water collection in different areas.

Super-hydrophilic material also presents great potential in the directional water movement due to their high surface energy. A novel super-hydrophilic nano-fibrous matrix was successfully fabricated from the inspiration of water transportation of trees, which was capable of transport water to a long distance as well as separate the particle pollutant from water, without hydraulic pressure. Evaporation process was utilized to draw the transported water from the matrix and provide continuous water movement and reclamation. This process could be an affordable water transportation method in water industry. The only energy spent in the whole process is solar energy for evaporation. Therefore, it is an eco-sustainable solution to help solve water and energy problems throughout the world. In addition, the in-depth understanding of this phenomenon offer us an alternative method to reduce the energy required for water purification. We envision that this understanding will provides more energy-free

innovation for the conveyance of water. Nanotechnology can not only remove the pollutants in water but also play a role in the transportation of water.

9.2 Future works

This thesis has demonstrated the fabrication of different kinds of hydrophilic materials and the application for oil-water separation as well as the directional water transportation. In order to bolster the environmental prospect of the novel biomimic nano-fibrous membranes developed in the first part of this study, future works are required and have been outlined. Moreover, building up the empirical data to justify more fundamental theories to their separation mechanism is also necessary. It is crucial to foster a deep understanding and firm foundation which will pave the way for its functional enhancement (through preparation methods and modification) and practical application in future. The future works are as follows:

9.2.1 Synthesis

Although we have successfully fabricated two kinds of nano-sized metal oxide modified membrane, this method combining electrospinning and hydrothermal growth still have ample room for further research and development.

Different operation conditions of electrospinning including temperature, humidity, flowrate of precursor solution and voltage of the power supply can be pursued to obtain optimization of the nanofibers. In addition, the reaction temperature, solution concentration and reaction duration of hydrothermal process can be further investigated to gain more insights of the reaction mechanism to optimize the morphology and the properties of the membrane.

Moreover, this combination method is versatile and facile which can be utilized for the synthesis of different materials with distinct properties. Although copper oxide and zinc oxide have notable properties and can be easily grown on the surface of nanofibers, they are also suffering from low chemical resistance. Therefore, titanium dioxide and silica, which are hydrophilic and possess good chemical resistance, can be suitable substitutes for ZnO (Liu, Cao et al. 2014, Tian, Su et al. 2014). At the same time, since the melting polymers are relatively low ($<200^{\circ}\text{C}$), the conditions of hydrothermal reaction are restricted. Hence, more functionalized additives and

materials can be encapsulated in the electrospinning precursor to fabricate multifunctional membranes.

9.2.2 Process and mechanism

Effect of different operating condition on oil-water separation can be investigated to enable process optimization in laboratory scale, which includes the pH, size of oil droplets, oil concentration and temperature. Furthermore, the oil-water separation mechanism and kinetics can be studied as a function of pH, size of oil droplets, oil concentration and temperature. Since membrane separation process is conducted underwater, water will play an important role in the separation process. In addition, the underwater properties of oil droplets and membrane surface will be different compared to those in the air. Upon completion, the overall oil-water separation mechanism and fundamentals by the novel super-hydrophilic membranes will be deduced based on the empirical findings from the above-mentioned tasks.

More importantly, the in-depth understanding of the water transportation via super-hydrophilic materials is crucial. Different conditions like pH, wastewater concentration, temperature, and UV light / visible light need to be investigated to build on fundamental data. Based on them, the mechanism and kinetics of the water directional movement will be more clear and guide the further understanding and application.

At the same time, it is of great importance to understand the interaction between water droplets and hierarchical micro-/nano-structural surface. At nanoscale, long-range forces like Van de Waals forces are highly relevant to the behavior of water molecules. Since water is the polar liquid, double layer can be formed at the solid surface. The double layer force can also play a part influencing the water movement behavior in a larger extent. The study of the nanoscale interactions will be crucial for the further optimization of the super-hydrophilic materials and the application in the industry.

9.2.3 Application

Photo-responsive materials possess the potential to combine with nano-fibrous matrix for the water directional transportation and create a light-driven “water ladder”. Just like trees, water transportation via this photo-responsive nano-fibrous matrix can be controlled by light. With the light irradiation, water is able to move upwards via the hierarchical micro-/nano-structures, while in the dark, these “water channels” will be closed. This process achieves the switchable energy-efficient water transportation, and traditional pumps with intensive energy consumption are no longer necessary.

In order to utilize the super-hydrophilic materials at industrial scale, it is important to scale up of the synthesis process as well as reduce the cost of fabrication. Therefore, industrial-scale production method can be investigated to fabricate the super-hydrophilic material with the consideration of the production consistency, capacity and efficiency. As discussed in 9.2.1, the operation condition can be further optimized to meet the industrial requirements. Meanwhile, the equipment and setup innovation are also required in real application.

Furthermore, it is essential to evaluate the treatment or transportation of real wastewater with more complicated contaminants which differs much from the synthetic wastewater. This will also provide us with more fundamental data to encourage the further study of the material and the process, which favors the extend from lab scale application to industrial application and leads to more innovation in water technology.

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