Electrospun carbon-silica composite nanofibers for selective removal of oil and water

Tai, Ming Hang

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NANYANG
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**ELECTROSPUN CARBON-SILICA COMPOSITE
NANOFIBERS FOR
SELECTIVE REMOVAL OF OIL AND WATER**

TAI MING HANG

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2015

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TAI MING HANG

School of Civil and Environmental Engineering

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Abstract

There is an increasing demand for cost-effective and efficient oil spill remediation and purification technologies due to the rising public concern over the corresponding environmental impact and the increasingly stringent environmental regulations. This thesis explores the feasibility of carbon-based nanofibers and its derivatives as separation medium for mixture of oil and water.

The pristine carbon nanofibers (CNFs) were prepared by a combination of electrospinning and thermal treatment. The electrospun nanofibers have average fiber diameter of 200-300 nm with carbon content up to ~ 80%. The microstructure of CNF is turbostratic with the carbon atomic sheets stacked together randomly. Despite non-crystalline structure, the CNFs could withstand a temperature as high as 500°C. With respect to its wettability property, CNF is hydrophobic and oleophilic. This makes it suitable for selective removal of oils and organic solvents from water. However, CNF suffers from low strain or toughness which restricts its applications.

To reinforce CNFs, a flexible carbon-silica composite nanofibers were electrospun. The characterization results suggested that the electrospun composite nanofibers were constructed by carbon chains interpenetrated through a linear network of 3-dimensional SiO₂. Thermogravimetric analysis indicated that the presence of insulating silica further improved the thermal resistance of the membrane. Additionally, the mechanical strength test showed that the membrane's toughness and flexibility could be enhanced if the concentration of SiO₂ was maintained below 2.7 wt%. Thermal and chemical stability test showed that the membrane's wettability properties could be sustained at an elevated temperature up to 300 °C and no discernible change in wettability was observed under highly acidic and basic conditions. After surface-coating with silicone oil for 30 min, the composite membrane exhibited ultra-hydrophobic and superoleophilic properties with water and oil contact angles being $144.2 \pm 1.2^\circ$ and 0° , respectively. The enhanced flexibility and selective wetting property enable the membrane to serve as an effective substrate for separating free oil from water. Lab-scale oil-water separation test indicated that the membrane possessed excellent oil-water separation efficiency. In addition, its

inherent property of high porosity allows oil-water separation to be performed in a gravity-driven process at high-flux.

The advancement of compacting the material into a sponge using the same technology showed that the carbon-silica nanofibers were capable of adsorbing oil up to 140 times its own weight with sorption rate being solution viscosity dependent. The electrospun sponge has high porosity (99%) and is ultrahydrophobic and superoleophilic which are the essential characteristics for an efficient oil sorbent. Furthermore, it is lightweight and compressible. This makes the sponge regeneration and oil recovery feasible by using cyclic distillation and mechanical squeezing.

The selective wetting property of carbon-silica nanofibers can be reversed by anchoring titanium dioxide (TiO₂) nanosheets via solvothermal reaction. The hierarchical TiO₂ micro/nanostructure that grows on the surface of CNFs renders the membrane superhydrophilic and underwater superoleophobic. Coupled with the characteristic of high porosity and micron-scale pore size, the membrane is capable of separating oil from water by gravity. Thermal analysis shows that the oil-water separation efficiency was greater than 99 %. Furthermore, the membrane has an oil breakthrough pressure up to 3.63 m. Stability test indicates that the membrane was stable in ultrasonic, thermal and extreme pH conditions. Without compromising the separation efficiency, a permeate flux of 400-700 L/m²-hr was achieved.

The separation performance of carbon-silica nanofiber membrane was further evaluated by using a large amount of water-in-oil emulsion and under the condition of low pressure cross-flow microfiltration. Results show that the oil permeability of membrane is high without sacrificing its selectivity at low pressure. However, the membrane performance including emulsion rejection efficiency and flux decline is substantially influenced by the tangential flow rate and the applied pressure. The total resistance analysis revealed that the membrane might be fouled internally, externally or a combination of these under different operating condition. The contour plot suggests that the membrane performance is optimum when operated at high cross-flow velocity and relatively low applied pressure.

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Chapter 1 Introduction

1.1 Background

Oil is a hydrophobic liquid that is rich with hydrogen and carbon. It serves as an important energy resource and raw materials for various synthetic polymers and chemicals. There is a wide variety of oils that can be categorized based on the viscosity, volatility, toxicity and etc. For commercial use, oil needs to be processed to meet certain requirements such as high purity. This involves selective removal of unwanted components while concentrating the desired substances. One of the contaminants likely found in oil is water. Water can exist in oil in three states, namely free water, emulsified water and dissolved water. In some industries such as oil refinery and recovery industries, the existence of water in oil poses adverse effect to the oil performance and even to the machine component longevity. Therefore, purification of oil is important prior to further processing.

In the event of an oil spill that poses serious environmental impact, cost effective and time-efficient removal of oil from water is essential. In any case when oils are spilled to marine environment, their physical and chemical properties are substantially altered by various weathering processes such as evaporation, photolysis, biodegradation, spreading and formation of oil-water emulsions. These will collectively lead to the changes in oil viscosity, density and interfacial tension which complicating the cleaning up recovery processes (Daling and Strøm 1999). Hence, efficient techniques employed for the disposal of oil into the marine water should be carefully adopted. Several remediation technologies have been developed for the oil spill response. It includes mechanical recovery, use of dispersants and solidifiers, in-situ burning and bioremediation (Dave 2011).

Sorption is deemed as an effective approach to clean up the remnant oil after skimming operation (Dave 2011). It transfers the oil (liquid phase) from the spilled area to some transportable forms of storage (semisolid phase) without changing its physical and chemical properties (Adebajo, Frost et al. 2003). A promising sorbent

should be hydrophobic and oleophilic with high sorption capacity and sorption rate. A surface is hydrophobic if the contact angle formed between the water phase and solid surface is greater than 90° . If the angle exceeds 150° , the surface is known as superhydrophobic. For an oleophilic surface, the contact angle formed between oil and solid phase is smaller than 90° . The surface becomes superoleophilic when zero contact angle is achieved. Both hydrophobicity and oleophilicity are very important properties because they facilitate the affinity between oil and the sorbent surface. They also promote the wicking that eases the oil transport along the sorbent surface. The reverse phenomenon for oleophilicity is oleophobic. Basically, the material of adsorbent can be natural organics, natural inorganic and synthetic materials. With the rapid development of nanotechnology, sorbents using advanced nanomaterials have been extensively studied. Some examples are nonwoven polymeric nanofibers (Zhu, Qiu et al. 2011; Wu, Wang et al. 2012), nanostructured carbon (Gui, Wei et al. 2010; Gui, Zeng et al. 2013), cryptomelane nanowires (Yuan, Liu et al. 2008), nanocellulose (Korhonen, Kettunen et al. 2011) and nanoclays (Sharafimasoleh, Bazgir et al. 2011). To maximize the sorption capacity, sorbents with highly porous structure are made. With high porosity, a sorption capacity with a few order of magnitude higher than the sorbent's weight can be readily achieved. To fabricate porous sorbent, several methods have been reported. It includes freeze casting (Nishihara, Mukai et al. 2005; Xie, Zhou et al. 2013; Zhang, Sèbe et al. 2014), chemical vapour deposition (Gui, Cao et al. 2010; Hashim, Narayanan et al. 2012), hydrothermal reaction (Xu, Sheng et al. 2010; Zhao, Ren et al. 2012), polymerization (Li, Li et al. 2014) and electrospinning (Sun, Long et al. 2012). However, sorbent prepared from electrospinning is only limited to polymers. An electrospun sponge that is made of carbonaceous materials is still lacking. Carbonaceous sponge is of interest because it is mechanically tough, chemically and thermally stable (Gui, Wei et al. 2010). These are essential properties especially when oil spill cleanup are to be carried out under harsh conditions, for example in a polar zone (Wu, Li et al. 2014).

Sorption is a general term that embraces the process of both adsorption and absorption. Adsorption refers to the surface deposition of solutes from a gas, liquid

or dissolved solid to a surface whereas absorption is the penetration of fluid into the bulk phase of gas, liquid or solid surface. The adsorption process can be further classified into physisorption and chemisorption depending on the interaction types between the solutes and the surface (Rouquerol, Rouquerol et al. 2013). One major difference between adsorption and absorption lies on that adsorption takes place on the surface while absorption involves the entire volume of the material. Aside from adsorption and absorption, capillary action could also be the controlling mechanism of oil sorption by porous sorbents (Choi and Moreau 1993). Capillary action or so-called wicking can be understood as the ability of liquid flowing through narrow spaces or permeable substances without the presence of external force. Such behaviour can be attributed to the adhesive and cohesive force between the liquid and the surface. In other words, the capillary action is the consequence of adhesion force and surface tension of liquid. The capillary action can be mathematically expressed as $h = (2\gamma\cos\theta)/(\rho gr)$ where h is the height of liquid lifted, γ the liquid-air surface tension, θ the water contact angle, ρ the liquid density, g the acceleration due to gravity force and r the radius of the pore. As seen in the equation, low contact angle at the solid-liquid interface and small pore are needed to exert strong capillary force on the sorbates. This implies that the characteristics of porous structure of sorbent play an important role in determining the sorption capacity. It should be stressed that the oil sorption mechanism is complex and is not solely governed by a single mechanism. It is the joint effect of adsorption, absorption and capillary action that make sorption possible.

The sorption behaviour of mesoporous (pore size between 2-50nm) or microporous (pore size <2nm) sorbents have been studied by using various sorption isotherms. Isotherms that are frequently used in carbonaceous sorbents include Langmuir, Freundlich and Polanyi-based theory (Yang and Xing 2010; Zhang, Shao et al. 2010). These models consider the characteristics of sorbent, molecular properties of sorbates as well as the operating conditions. However, when sorbents are structured into nonwoven fabrics, it is presumed that they exhibit totally different sorption pattern and capacity (Choi, Kwon et al. 1993). Many literatures have reported that the sorption capacity of nonwoven carbon sorbents for various oils strongly depends

on the bulk pore volume or porosity (Inagaki, Kawahara et al. 2002; Rengasamy, Das et al. 2011). In nonwoven fibrous sorbents, the pore volume refers to the total void volume created by the entangled fibers. The sorption capacity increases with increasing pore volume. This is easy to understand because a porous structure is capable of offering more free space for oil to be sorbed. Hence, under an ideal condition, the maximum capacity of oil that can be achieved equals to the total pore volume of the sorbent. It is interesting to point out that sorbents with high surface area such as granular activated carbon did not exhibit high oil sorption capacity compared to those carbonaceous sorbents with high porosity (Inagaki, Kawahara et al. 2002). In other words, the surface area is not the determining factor for efficient oil sorption.

When a hydrophobic nonwoven sorbent assembled by fibers is in contact with oil, oil is entrapped inside the pores formed between fibers. The retention of oil within the pores are dominated by the complex interaction of Van der Waals force and hydrophobic interaction in conjunction with the available void fraction and the oleophilicity of fibers. For sorbent with high packing density, it is the capillary pressure that induced by the open pore structure of sorbent holds up the oil. The entrapped oil are further stabilized by the liquid-liquid bridge formed between the entrapped oil and the hydrophobic fiber surface while they move towards the internal structure through diffusion (Abdullah, Rahmah et al. 2010; Wang, Zheng et al. 2014).

The sorption kinetics of carbonaceous sorbents have been largely studied by fitting into pseudo second-order model from which the equilibrium amount of sorbate sorbed or saturated sorption capacity and the rate constant of sorption can be determined. For nonwoven fibrous sorbent with open-pore structure, a faster sorption kinetic is expected due to reduced external mass transfer resistance. However, the sorption rate is largely dependent on the extent of packing density of the sorbent as well as the viscosity of the sorbates (Abdullah, Rahmah et al. 2010). Generally, the sorption rate is inversely proportionally to the sorbate's viscosity and the sorbent's packing density.

Depending on the diameter (d) of dispersed phase, the mixture of water and oil can be classified as free oil and water ($d > 150\mu\text{m}$), dispersion ($20\mu\text{m} \leq d \leq 150\mu\text{m}$) or emulsion ($d < 20\mu\text{m}$) (Kota, Kwon et al. 2012) among which emulsion can be further split into three major group, namely water-in oil, oil-in-water and multiple emulsions. Emulsion is a mixture of two or more immiscible liquids wherein droplets of dispersed phase are dispersed or encapsulated within in the continuous phase. Hence, water-in-oil emulsion refers to that water droplets are dispersed within in oil whereas oil is dispersed in water for oil-in-water emulsion. The emulsion can be prepared through several methods, such as agitation, ultrasonication and use of emulsifiers. To efficiently separate oil/water emulsions, it is of importance to characterize and evaluate the stability of emulsion. There are several factors that govern the stability of such emulsion, including dosage of emulsifier, ratio of oil and water, temperature, mixing time and etc (Chen and Tao 2005). Especially for emulsifiers such as surfactants, they helps to reduce the interfacial tension between liquid-liquid phases and therefore inhibit the liquid coalescence. This leads to the formation of an emulsion with higher stability. The oil recovery from water/oil mixture or water-oil separation becomes more difficult for a relatively stable emulsion and thereby decreases the oil-water separation efficiency. One needs to consider the effect of interfacial tension when coping with the mixture in the form of emulsion.

In oil refinery industries, water-in-oil emulsions are more common. The conventional method employed to separate water from oil involves chemical demulsification followed by gravity settling or skimming. However, the use of chemicals during the treatment incurs higher cost. Apart from that, the water produced may need further purification. There have been several novel and effective demulsification methods (Zouboulis and Avranas 2000; Eow and Ghadiri 2002; Chen and He 2003; Mostefa and Tir 2004) reported. Among these methods, membrane-based separation is attractive owing to its cost-effectiveness and energy-efficiency. A membrane is a selective medium that permits passage of favourable constituents (e.g. water) while retaining the other constituents on the surface. After

the membrane surface is modified to become hydrophobic, oil can easily permeate through whereas water droplets or emulsified water will be retained, thus separating water from oil. Till far, only a few literatures have reported the use of traditional membrane for purification of oil (Scott, Jachuck et al. 2001; Solomon, Hyder et al. 2014). The major challenges encountered in oil purification using traditional membranes are achieving high flux without compromising the selectivity. When a higher pressure is applied to achieve higher flux, dispersed droplets can deform and squeeze through the membrane even though the size of pore is smaller than the droplets. In this context, the use of electrospun membrane could be a potential solution to this limitation. By virtue of its high porosity and unique interconnected structure, the electrospun membrane permits high flux at relatively low pressure. However, oil purification using electrospun membrane is currently an unexplored area. This is because the complex oil mixtures can be corrosive to the membrane (especially for polymeric membrane) and thus deteriorate the functionality of membrane. Therefore, in this study, a flexible electrospun carbon-based composite nanofibrous membrane was used for oil purification because carbon-based membrane is intrinsically hydrophobic and resistant to chemical corrosion. Moreover, compared to the polymeric membrane, carbon-based membrane is more amenable to chemical treatment under harsh conditions such as chemical vapour deposition at high temperature. In other words, this will make the surface modification of carbon nanofibers more feasible and therefore enhance its functionalities.

1.2 Research Objectives

Overall objective is to fabricate and examine electrospun carbon-based composite nanofibers for efficient separation of oil and water. The explicit objectives are to:

- i. electrospin hydrophobic carbon-silica composite nanofibers that is flexible, tough and stable against elevated temperature and harsh chemicals.
- ii. examine the removal efficiency of oil by carbon-silica composite nanofibers in the form of sponge.

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- iii. assess the oil sorption performance of carbon-silica nanofibers using hierarchical structure.
 - iv. study the performance of cross-flow microfiltration using flat-sheet electrospun carbon-silica nanofiber membrane for separation of water from water-in-oil emulsion.

1.3 Thesis Overview

This thesis contains 9 chapters and 2 appendices. **Chapter 1,2 and 3** include brief introduction of the project, literature review as well as methodology, respectively.

Chapter 4 involves the preliminary characterization of electrospun CNF membrane. Apart from the basic physical characterization, the membrane's mechanical strength, surface wetting property and thermal stability are included. This chapter also reports the feasibility of the membrane as sorbent of oils and organic solvents.

Chapter 5 reports the mechanical reinforcement made to the brittle pristine CNFs by addition of silica into the precursor solution. This followed by the applicability study of the carbon-silica membrane for gravity-driven separation of water and oil.

Chapter 6 introduces an electrospinning-derived, highly porous carbon-silica nanofiber sponge as an alternative to membrane-based separation of water and oil. The oil sorption performance of the sponge is assessed with particular emphasis on the sorption capacity and rate, sponge regeneration and oil recovery.

Chapter 7 studies the effectiveness of carbon-silica nanofiber membrane on water-oil separation after incorporated with titanium dioxide nanosheets to form hierarchical structure. The influence of ultra-sonication, temperature and pH on the membrane's stability and separation efficiency are also studied.

Chapter 8 investigates the cross-flow microfiltration of water-in-oil emulsion using the flat-sheet carbon-silica nanofiber membrane under various operating conditions including tangential flow rate and operating pressure. Several membrane fouling

models derived from Darcy's law are employed to elucidate the membrane fouling mechanism. Also, the optimum operating conditions are proposed.

Chapter 9 concludes the obtained experimental results and investigation. Recommendations and suggestion are given to the future works.

Appendix A shows the methods of calculating the porosity of carbon-silica nanofiber sponge whereas **Appendix B** tabulates the sorption capacity of various oil sorbents for comparisons.

Chapter 2 Literature Review

2.1 Introduction to Oil Spill Cleanup Technologies

Oil spills have received increased attention during recent years due to the rise in number of oil spills. Such accidents usually occurred through accidental episodes of oil tankers, oil rig drilling, war and natural events (Bayat, Aghamiri et al. 2005). The spilled oil often posed detrimental impacts to the fresh water and marine environments, harming the wildlife through physical damage (e.g. coating birds with a layer of oil) and poison the exposed organisms due to its toxicity. One of the well known examples was the oil spill disaster which occurred in Gulf of Mexico in 2010. Up to 4.4 million barrels or 700000 m³ of crude oil was spilled into the ocean (Crone and Tolstoy 2010). The spill has not only caused severe damage to the marine and wildlife habitats but also impacted the Gulf's fishing and tourism industries.

Apart from the environmental impact, the rising oil spill cleanup cost urges the need to control the releases of oils. In practice, the estimation of cleanup cost is difficult and complex. Due to the involvement of several factors such as type of product spilled, location and timing of spill, sensitive area affected, local and national laws, cleanup techniques employed and etc. Since 1990, a greater public demand for environmental responsibility and the increasingly litigious climate in many countries have engendered the rise in cleanup cost by as much as 4 to 5 times. As a consequence, a small oil spill can be exceedingly expensive as polluters were forced to comply with public opinion and local and national laws in mounting a responsible cleanup operation (Etkin 2000). In this context, the development of efficient and cost effective technology for oil spill remediation is imperative.

Oil spill remediation can be performed in physical, chemical and biological ways. Physical method employs sorbents, booms and skimmers. For booms and skimmers, the oils are physically corralled for collection whereas sorbents collect the oil and

separate it from the water by sorption (Adebajo, Frost et al. 2003). However, the efficiency of booms and skimmers is unsatisfactory because much of recovered oil is mixed with water. Secondary treatment that incurs additional recovery cost is then required (Bayat, Aghamiri et al. 2005). Chemical method involves the use of dispersants, solidifiers and in-situ burning. The reaction of solidifiers with oil forms cohesive, floatable, solidified mass that is easily removed (Adebajo, Frost et al. 2003). For in-situ burning, although the amount of oil in water can be reduced through controlled thermal oxidation, secondary pollution is inevitable. Chemical method is costly due to the use of chemicals. Furthermore, the chemicals used are hazardous to environment. On the other hand, the biological removal of spilled oil is possible by adding microorganisms which degrade a wide range of hydrocarbons existed in the oil. However, the performance of bioremediation is limited by the nutrient and oxygen supply and the process takes a longer time for biodegradation than the physical and chemical methods. The following table summarizes the pros and cons of some conventional technologies commonly used in oil spill cleanup (Dave 2011).

Table 2.1 Pros and Cons of Some Conventional Remediation Technologies for Oil Spill (Dave 2011).

Technologies	Pros	Cons
Booms	<ul style="list-style-type: none"> - Applicable for all kind of oils - Recovery of oil is possible 	<ul style="list-style-type: none"> - Expensive - Labor intensive - Efficient under selected weather conditions
Skimmers	<ul style="list-style-type: none"> - Applicable for all kind of oil except inflammable oil - Recovery of oil is possible 	<ul style="list-style-type: none"> - Expensive - Labor intensive - Collected oil needs further treatment - Subject to clogging with floating debris - Efficient under selected weather conditions - Maintenance is required
Dispersants	<ul style="list-style-type: none"> - Short cleanup time - Hastened natural degradation of oil - Effective on wide spectrum of oil 	<ul style="list-style-type: none"> - Oil recovery is not possible - Ineffective for viscous, non-spreading and waxy oil

	<ul style="list-style-type: none"> - Less labor intensive - Applicable under all weather conditions 	
Solidifiers	<ul style="list-style-type: none"> - Short cleanup time - Applicable under all weather conditions 	<ul style="list-style-type: none"> - Oil recovery is not possible - Low efficiency - Substantial amount of solidifiers are required - Cleanup is possible to limited type of oil
In-situ burning	<ul style="list-style-type: none"> - High efficiency - Cost effective - Short cleanup time - Less labor intensive 	<ul style="list-style-type: none"> - Oil recovery is not possible - Induce secondary pollution due to emission of gases and particulates during burning
Bioremediation	<ul style="list-style-type: none"> - Applicable under all weather conditions - Cost effective - Mineralized products are CO₂ and H₂O - Less man power is needed 	<ul style="list-style-type: none"> - Oil recovery is not possible - Applicable to limited type of oil - Remediation efficiency greatly affected by indigenous microorganisms and nutrient availability on site

2.2 Sorbents

Of the oil spill remediation technologies, physical sorption has emerged as an interesting alternative to the traditional techniques due to its simplicity and high effectiveness. Sorption facilitates the change of spilled oil from liquid to semi-solid phase, thus making the removal of oil straightforward and easier. Ideally, a promising sorbent should possess the following features: (1) superhydrophobicity and superoleophilicity (Cong, Ren et al. 2012; Zhou, Zhang et al. 2013) (2) mechanical stability under deformation (Deschamps, Caruel et al. 2003; Lim and Huang 2007; Choi, Kwon et al. 2011) (3) high porosity (Li, Sun et al. 2011; Yue, Li et al. 2011; Cervin, Aulin et al. 2012) and (4) high oil uptake amount (Wu, Wang et al. 2012; Li, Liu et al. 2013) in order to meet the practical demand for selectivity, recyclability, uptake rate and sorption capacity.

A wide variety of porous sorbent materials have been studied and can be classified into 3 categories namely inorganic mineral products (e.g. silica, zeolites, activated

carbon and clay), organic synthetic products (e.g. polypropylene and polyurethane) and natural sorbents (e.g. rice straw, kapok fiber and kenaf) (Adebajo, Frost et al. 2003) and the advantages and disadvantages varies among the sorbent. For example, high specific surface area, hydrophobic zeolites can be regenerated with steam or by calcinations but it is low in adsorption capacity (Adebajo, Frost et al. 2003). Hydrophobic, oleophilic polypropylene and polyurethane which are commonly used commercial sorbents are not biodegradable. The acetylated rice straws has poor in buoyancy despite having the advantages such as low cost, high sorption capacity, high uptake rate and ease of desorption (Sun, Sun et al. 2002). To overcome these constraints, blending different types of sorbents has been proposed (Choi and Cloud 1992).

Over the past years, particular attention has been paid to the use of high surface area nanomaterials as novel approach to the oil spill cleanup. Magnetic nanoparticles (Gomes de Souza, Marins et al. 2010; Zhu, Tao et al. 2010), aerogels (Nguyen, Feng et al. 2013; Yang, Tong et al. 2014), meshes (Crick, Gibbins et al. 2013; Wang and Guo 2013), micro and nano-titanium dioxide (Kwon, Fan et al. 2008; Narayan 2010), carbon nanostructures (Moura and Lago 2009) and nano-structured organoclays (Sharafimasooleh, Bazgir et al. 2011) are some examples of sorbent material. Amongst these methods, hydrophobic sponge-like sorbents were found to be efficient for oil clean up as well as separation of oil and water due to their excellent sorption capacity and high selectivity. For instance, the superhydrophobic silanized melamine sponge prepared by Pham and Dickerson was able to sorb 82-163 times its own weight in organic solvents and oils (Pham and Dickerson 2014). A general and straightforward route to prepare sponge-like sorbent was using commercial polymeric sponge as skeleton followed by manipulation of surface wettability (Zhu, Pan et al. 2011; Calcagnile, Fragouli et al. 2012; Sun, Li et al. 2013; Zhou, Zhang et al. 2013; Zhu, Chu et al. 2013). Other preparation methods include freeze casting (Nishihara, Mukai et al. 2005; Xie, Zhou et al. 2013; Zhang, Sèbe et al. 2014), chemical vapour deposition (Gui, Cao et al. 2010; Hashim, Narayanan et al. 2012), hydrothermal reaction (Xu, Sheng et al. 2010; Zhao, Ren et al. 2012), and polymerization (Li, Li et al. 2014).

Making use of the inherent property of hydrophobicity and oleophilicity of carbon, a lightweight and highly porous carbonaceous sponge (Hanzawa, Kaneko et al. 1996; Gui, Wei et al. 2010; Liang, Guan et al. 2012; Bi, Yin et al. 2013; Wu, Li et al. 2013; Gao, Zhou et al. 2014) was designed as oil adsorbent. The high porosity of the carbonaceous sponge exhibited superior sorption capacity. Moreover, the excellent flexibility, mechanical and thermal stability ease the sponge regeneration and oil recovery after use. However, the large-scale use of carbonaceous sponge is restricted by the complex fabrication process as well as the utilization of costly technologies. Therefore, a cost-effective approach to fabricating such spongy sorbent with similar performance is in high demand.

Figure 2.1 Digital photograph showing the selective removal of oil and water by graphene/ α -FeOOH aerogel and its regeneration after use (Cong, Ren et al. 2012).

2.3 Membrane-based Separation of Oil and Water

Aside from direct adsorption, separation of oil and water can also be achieved by using a filtration membrane. A membrane is a selective barrier that allows the passage of certain constituents while rejecting other constituent. In the field of industrial oily water and wastewater treatment and oil refinery, apart from the factor of low cost, it is important for an oil-water separation membrane to possess certain favorable properties such as selective wetting behavior, high-throughput production of clean water, easy regeneration and reusability.

In general, the fabrication of membrane with selective wetting property can be achieved via modification of its surface geometry (e.g. design of hierarchical roughness at two different length scales) (Ji, Fu et al. 2006; Lee and Baik 2010; Zhang and Seeger 2011; Hejazi, Nyong et al. 2012; Kota, Li et al. 2012) and surface chemical composition (e.g. fluorine-based coating) (Ding, Li et al. 2006; Zimmermann, Rabe et al. 2008; Wang, Yao et al. 2009; Shang, Si et al. 2012; Zhang, Zhang et al. 2012). For instance, Ma et al. (Ma, Gupta et al. 2007) reported the superhydrophobic function of an electrospun nonwoven fibrous mat prepared by decorating micrometer-scale fibers with nanometer sized particles. Apart from that, by employing in-situ polymerization of fluorinated monomer, Tang et al. (Tang, Si et al. 2013) have endowed a hydrophilic electrospun nanofibrous membrane with superhydrophobic and superoleophilic property. Other than the selective wettability, it is equally important for the separation substrate to be highly porous to achieve a high throughput. A highly porous structure will greatly affect the permeation rate across the membrane.

Membrane-based separation of oil-water (Hlavacek 1995; Cheryan and Rajagopalan 1998; Chen, Su et al. 2009) under pressurized condition is a widely used techniques in industries due to high quality permeate produced, simple modular design and lower chemical consumption compared to other treatments (Maphutha, Moothi et al. 2013). However, the pressure-driven membrane separation has a major drawback – fouling (Arnot, Field et al. 2000; Mohammadi, Kazemimoghadam et al. 2003; Pan, Wang et al. 2007). Under a high trans-membrane pressure difference, liquid droplets depositing on the membrane surface are deformed and forced to enter the pores. This results in the pores being blocked and the permeate flow rate is consequentially decreased. Therefore, it is expected that an oil-water separation at low pressure is largely preferred as the more sustainable approach. To carry out a low pressure operation, the membrane should have large pore size and low tortuosity according to Hagen Poiseuille equation. In this regard, electrospinning offers a promising way to fabricate nonwoven fibrous mats with high porosity and controllable thickness.

2.4 Electrospinning

Electrospinning is a versatile, inexpensive technique to produce continuous fibers at micrometer and even nanometer scale. The production of fiber is a consequence of the substantial elongation of viscoelastic polymer solution jet in high electric field. Theoretically, when the applied electric force is sufficient to overcome the surface tension of the polymer liquid, a thin polymer jet is ejected from spinneret and undergoes uniaxial stretching. The stretching causes the jet to elongate, slimming down the diameter of the jet to a scale of submicron and even nanometer. Meanwhile, the jet thinning is accelerated by the evaporation of the solvent in the polymer liquid. The jet deposited on a substrate forms a random, nonwoven fiber mat (Teo and Ramakrishna 2006). A schematic diagram showing the basic principle of electrospinning is shown in Figure 2.2. One of the major advantages of electrospinning is that it enables manipulation of nanofiber components. This makes the fabrication of membrane with desirable functionalities possible.

Figure 2.2 Basic Principle of Electrospinning (Ramakrishna, Fujihara et al. 2006).

A number of processing parameters governs the final morphology of the resultant fibers. These include intrinsic properties of the electrospinning dope solution or solvent/solute system such as the type of polymer, the conformation of the polymer chain, the viscoelasticity, conductivity, polarity and the surface tension of the

solvent, operating conditions such as applied electric field strength (the electrical force over spinneret-collector distance), feeding rate of solution, temperature and humidity (Doshi and Reneker 1993; Li and Xia 2004). Tan and his co-workers carried out a systematic study to investigate the effect of solution properties to the morphology of the resultant fibers. They found that the polymer concentration, viscosity and electrical conductivity of the solvent play a decisive role (Tan, Inai et al. 2005). At too low polymer concentration, the uniformity of the fibers cannot be sustained and fibers with beads, which is unfavorable, is resulted. However, the fiber uniformity can still be preserved at low polymer concentration provided that the solution viscosity is kept sufficient. This concept can be fundamentally linked to the understanding and the influence of the surface tension. Surface tension always tends to shape liquid into spherical droplet in order to minimize the surface area to volume ratio. Therefore, to produce uniform fiber during the process of electrospinning, sufficient viscoelastic forces are required to hamper the rapid shape change. Alternatively, a solvent with lower surface tension can be applied to facilitate the electrospinning of continuous bead-free fibers. On the other hand, the increase of solution conductivity through the use of salt was observed to produce finer fibers. The underlying logic is based on the charge density of the jet. Under the same applied field strength, a higher degree of elongation can be triggered if the net electrical charge of the jet is higher. Field strength is defined as the voltage applied per unit length. In the case of electrospinning, field strength refers to the voltage applied between distance from a spinneret to a grounded collector. The correlation between the morphology of fiber with the field strength is very weak but it could affect the stability of the electrospinning process by altering the conical shape of the pendant drop from which the liquid jet is initiated (Deitzel, Kleinmeyer et al. 2001). As the jet spinning rate exceeds the solution feeding rate, the conical shape is unable to sustain and gradually shrinks in volume. In this case, the electrospinning is not stable. The ideal circumstance is a good liquid mass balance between the feeding rate and spinning rate. This can be achieved by adjusting the applied voltage or electrical field strength. With a decreased instability of liquid jet, the bead density of the resultant fibers can be lessened. Nevertheless, the field strength was observed to have no influence on the fiber diameter (Gu, Ren et al.

2005). There are also a few studies investigating the effects of factors such as temperature and humidity towards the electrospinning process. Demir et al reported that, at higher solution temperature, the diameter of the electrospun fibers was uniform. Simultaneously, the fibers deposition rate was significantly enhanced (Demir, Yilgor et al. 2002). Furthermore, the fiber diameter decreased with increasing the solution temperature due to the decline in viscosity. On the other hand, the humidity has been attributed to the formation of circular pores on the fiber surface (Pham, Sharma et al. 2006). The resultant fiber diameter could be computed by mean of modeling. A theoretical modeling suggests that the fibers diameter was dictated by balance between normal stresses due to surface tension and surface charge repulsion (Fridrikh, Jian et al. 2003).

Electrospinning technique, as a top-down manufacturing process, is advantageous due to its relatively low cost (Dzenis 2004) and the easiness of continuous nanofiber production (Reneker and Chun 1996) compared to that of most bottom-up methods. More importantly, the one-dimensional electrospun membrane has shown enormous potential in various applications because it displays excellent structural mechanical strength, large specific surface area coupled with remarkable porosity due to the interconnected pore structure. Due to the open pore structure, the membrane allows water transport at low tortuosity (short water path length). As a result, the membrane has a high water flux.

Electrospun membrane has been well exploited in the environmental and energy fields (Thavasi, Singh et al. 2008). The environmental application can be exemplified by the electrospun inorganic TiO_2 nanofiber that serves as a NO_2 gas sensor. It displays an exceptional sensitivity to the gas at concentration lower than 1 ppb. This was ascribed to the 1-D sensing architecture that facilitates the mass transfer of gaseous molecules to and from the interaction region and the molecular recognition interactions taking place at the nanofibers surface (Kim, Rothschild et al. 2006). The sensitivity is not only applicable to the gases but also to the liquid (Aussawasathien, Dong et al. 2005). The functionality of TiO_2 nanofiber can even be extended to biotechnology. For instance, a biosensor can be simply made via

encapsulation of various appropriate enzymes into the porous electrospun nanofiber (Patel, Li et al. 2006).

The electrospun membrane has enormous potential in the field of water purification. For example, electrospun polyvinylidene fluoride nanofiber membrane was able to separate polystyrene microparticles at a separation efficiency up to 90%. This implies that an electrospun nanofibrous membrane could serve as a separation medium for efficient pre-treatment of feed water during the process of water and wastewater treatment (Gopal, Kaur et al. 2006). Researchers also studied the potential of the electrospun nanofiber membrane as a new replacement for asymmetric ultrafiltration membrane obtained from phase inversion in order to achieve high permeate flux yet low fouling tendency. (Barhate and Ramakrishna 2007) High flux performance of electrospun membrane in the applications of forward osmosis, (Song, Liu et al. 2011) ultrafiltration and nanofiltration (Yoon, Kim et al. 2006) has been recently reported.

Figure 2.3 The SEM Micrograph of (a) clean nanofiber membrane before filtration and (b) nanofiber membrane after filtration with 1 µm polystyrene particles (Thavasi, Singh et al. 2008).

With respect to the energy applications, much attention has been given to the use of electrospun nanofiber webs as supercapacitor, solar cell, fuel cell as well as hydrogen storage material. Electrospun CNFs which show excellent electrical conductivity were largely studied and were observed to be suitable to be applied as an electrode for supercapacitor due to high value of specific capacitance observed. This high specific surface area in addition to the high density of mesopores in the conductive nanofibers were accounted for the remarkable performance (Kim and

Yang 2003; Kim, Ngoc et al. 2007). Additionally, by using light-harvesting nanofibers such as TiO₂ nanofibers as electrode in dye-sensitized solar cells (DSSC), the power conversion efficiency was greatly improved (Song, Kim et al. 2004; Chuangchote, Sagawa et al. 2008). All of the above examples indicated the versatility of the electrospun nanofibers as well as the advantageous properties of the electrospun nanofibers. Other significant aspect of electrospun nanofibers apart from the energy and environment applications is the implementation in the niches of healthcare, biotechnology, and defense and security (Ramakrishna, Fujihara et al. 2006).

2.5 Carbonaceous Nanomaterials

Polymeric membrane commonly used in industrial oily water and wastewater treatment poses issues due to its thermal and chemical stability. Although inorganic membrane is relatively stable, it is brittle and vulnerable to high pressure. Therefore, the search for thermally, structurally and chemically stable membrane becomes imperative to overall such problems.

Carbonaceous nanomaterials such as carbon nanotube (CNT), CNF and graphene oxide (GO) are well known for its excellent thermal stability (Pang, Saxby et al. 1993; Muramatsu, Hayashi et al. 2005) and chemical inertness (Zhai, Dou et al. 2011). The structure of a CNT can be visualized as a sheet of graphite that is rolled into a tube with end caps containing pentagonal rings (Chatterjee and Deopura 2002). Essentially, CNT can be categorized into single-walled carbon nanotube (SWCNT), which consists of only a layer of carbon atoms with pores in the microporous range, and multiwalled carbon nanotube (MWCNT) which consists of more than a layer and has pores in mesopore range shown in Figure 2.4. The reported methods for manufacturing CNTs include direct current arc discharge, laser ablation, thermal and plasma enhanced chemical vapor deposition (CVD) (Schlittler, Seo et al. 2001).

Figure 2.4 Schematic Structure of SWCNT and MWCNT (Zhang, Shao et al. 2010).

The characteristics of carbonaceous nanomaterials have been extensively studied by researchers. The mass transport through CNT was simulated by Hummer's group based on the molecular dynamic theory. The result indicated fast molecular transport of water molecules through SWCNTs despite the hydrophobicity of the 1-2 nm pore (Hummer, Rasaiah et al. 2001). This suggests that a membrane comprised of CNT arrays could offer high selectivity and high flux which are essential properties for filtration. Srivastava et al fabricated a filter from aligned MWCNTs via spray pyrolysis inside a temperature-controlled furnace and tested its filtering behavior. One of the major advantage of such filter was its reusability because the filtration efficiency can be fully recovered simply by purging, ultrasonication or autoclaving (Srivastava, Srivastava et al. 2004).

Close attention was also made to the sophisticated graphite and its derivatives, in particular the graphene oxide paper which could be prepared easily through simple vacuum filtration. During the process, many layers of GO nanosheets were stacked up in an ordered manner to form a free-standing substrate. This process resulted in a paper-like material, or so called GO paper which has shown marked mechanical properties in terms of tensile strength, fracture strength and stiffness. Such layered geometry enable individual GO nanosheet effectively interlocked with the adjacent one in a near-parallel fashion, thus facilitating the load distribution across the entire macroscopic assembly. The collective properties allowed for the proposed fabrication of large-area GO paper for use in membrane with controlled permeability (Dikin, Stankovich et al. 2007).

Apart from the use of vacuum filtration free-standing membrane, electrospinning is an economic option to fabricate similar free-standing three-dimensional (3D) macroscopic assembly such as CNF membrane. The CNF membrane can be derived from polymer precursors after undergoing thermal treatment in an inert atmosphere. Various polymers have been electrospun to obtain CNFs, among which polyacrylonitrile (PAN) is the most favor because of relatively higher carbon yield and the resulting CNFs possess better mechanical strength (Liu, Yue et al. 2009). To produce good quality CNFs, pretreatment of electrospun PAN nanofibers is crucial. Generally, two thermal processes are required to transform electrospun PAN nanofibers into CNFs - stabilization and carbonization. Stabilization is performed at relatively lower temperature between 200°C and 300°C in the presence of oxygen with the aim of cross-linking the PAN chains at a intermolecular level. The cross-linked polymeric chains ensures the preservation of molecular and fibrillar orientation during the subsequent thermal treatment. When CNF is stabilized at a higher temperature, the sudden evolution of heat would cause a scission of PAN macromolecular chains. This would result in mechanically weak CNFs. Both cyclization and dehydrogenation take place during the stabilization process and are responsible for the fibers shrinkage (Gupta and Harrison 1996; Edie 1998). Hence, tension is required to reduce the shrinkage during the process. After stabilization, the PAN-based nanofibers are carbonized at higher temperature in an inert atmosphere. During the carbonization process, the stabilized PAN nanofibers are transformed into CNFs by evolving other noncarbon elements in the form of methane, hydrogen, hydrogen cyanide, water, carbon monoxide and various other gases (Edie 1998). It was reported by Zhou et al that at a temperature lower than 1000°C, the microstructure of the CNFs displays turbostratic whereas increasing the temperature up to 2200°C produces graphitic CNFs. In turbostratic carbon, the sheets of carbon atoms are extensively folded. Graphitic carbon means that its graphene sheet are stacked together to form ribbon-shaped structure. The finding showed that, in contrast to turbostratic CNFs, the graphitic CNFs show improved higher tensile strength and increased electrical conductivity (Zhou, Lai et al. 2009).

Due to its inherent property of hydrophobicity and oleophilicity, carbonaceous materials have been deemed as a promising candidate for oil sorption and oil-water separation (Lee, Johnson et al. 2011; Shi, Zhang et al. 2013). A great advantage that carbonaceous nanomaterials offer in selective removal of oil-water is the easy regeneration after use and oil recovery due to its high thermal and chemical stability. A notable example was the carbonaceous sponge prepared from chemical vapor deposition. Gui and his co-workers synthesized the interconnected CNTs that were self-assembled into a lightweight, highly porous and compressible sponge-like bulk material. This hydrophobic CNT sponge showed exceptional adsorption capacity for a wide range of oils and organic solvent with highest value reaching 180 times heavier than its own weight (Gui, Wei et al. 2010). However, carbonaceous materials often suffer from low rigidity when they are assembled into macrostructure. This largely restricts its performance in the real-life applications. For this reason, the carbonaceous materials must be reinforced to withstand the possible physical impact during the applications such as oil sorption or oil-water separation. While majority of studies works on carbon nanotubes and its 3D assemblies for oil-water separation, the study of using continuous CNFs in the form of nonwoven mat or membrane for oil-water separation is still absent.

2.6 Membrane Fouling Theory and Models

In a cross-flow microfiltration process, the permeate flow declines with time as a result of membrane blocking by the retained constituents. The membrane blocking mechanism was first studied by Hermans and Bredée (Hermans and Bredée 1935). Hermia (Hermia 1982) studied the intermediate blocking mechanism. The mechanism was further revised by collating all the proposed blocking mechanisms and reformulated them into the frame of power-law non-newtonian fluids. The revised clogging of the membrane was classified into four mechanisms, namely standard blocking, complete blocking, intermediate blocking and cake filtration.

The four membrane blocking mechanisms describe the fate and behavior of depositing particles when arriving to the membrane (Bowen, Calvo et al. 1995). For standard blocking, it is assumed that each particles deposited onto the internal pore

walls, causing the restriction of pores and the eventual flux decline. When the depositing particles block pores without superposition, the mechanism is called complete blocking. It is also possible for particles to settle onto the particles which is already blocking the pores of the membrane surface. In this scenario, the membrane is clogged through intermediate blocking. As all the membrane pores are blocked, further deposition of particles will cause the deposited particle layer to increase, forming a gel form so called cake layer. The presence of the cake layer creates an additional hydraulic resistance to the permeate flow and this resistance increases with increasing cake layer thickness. Figure 2.5 shows the schematic drawing of different blocking mechanisms. It is reasonable to assume that the permeate flow decline in a filtration experiment can result from a combination of different blocking processes that take place successively, for instance flux decline due to standard pore blocking followed by the cake layer formation.

The consequence of pore blockage is the formation of dynamic membrane. The degree of pore blockage is dependent on the shape and relative size of particle and pore. On this basis, Tanny (Tanny 1978) has split the dynamic membrane into three types. Type I dynamic membrane is formed when the solute size is greater than the average membrane pore size. This phenomenon is also known as concentration polarization. The instantaneously built up of concentration on the retentate side of membrane and reduces when the pressure diminishes. The formation of Type II dynamic membrane occurs when the solute size is smaller than the pore size. Under such condition, the internal pore clogging mechanism prevails. As the size of solute and pore is comparable, the pore blockage will prone to complete blocking which cause an exponential decrease in permeate flux. Type III dynamic membrane is resulted in this case.

Figure 2.5 Schematic diagram of membrane blocking mechanisms. a) Complete blocking b) Standard blocking c) Intermediate blocking and d) Cake filtration.

To identify the fouling mechanism, the resistance model derived from Darcy's law has been developed. The resistance model is expressed as

$$J = \frac{\Delta P}{\mu_o(R_t)} = \frac{\Delta P}{\mu_o(R_m + R_c)} \quad (1)$$

which can be rearranged into

$$R_t = \frac{\Delta P}{\mu_o J} \quad (2)$$

where J is the permeate flux, ΔP transmembrane pressure, μ_o the solution viscosity, R_t total resistance to flow, R_m the inherent membrane resistance and R_c the cake fouling resistance and R_t is the summation of R_m and R_c . The increase in R_m over time is due to the internal fouling that occurs in the internal pore structure of the

membrane whereas the formation of the cake layer is denoted with increase in R_c . Both standard blocking and complete blocking account for the internal fouling. On the other hand, external fouling is due to the formation of cake layer on membrane surface.

For standard blocking model, it is assumed that the foulants deposited evenly along the pore wall such that the pore diameter is reduced due to constriction in pore diameter while the number of pores is remained constant (Tracey and Davis 1994). These assumptions yield the following expressions

$$\frac{t}{V} = K_1 t + \frac{1}{Q_0} \quad (3)$$

where t is operation time, V the accumulated permeate volume, K_1 the standard blocking constant, Q_0 the initial permeate flow rate. The value of initial flow rate and the constant, K_1 can be determined by plotting t/V versus t using experimental data. The standard blocking model can also be written in terms of membrane resistance as a function of time:

$$R_m = R_{m0}(1 + K_1 Q_0 t)^2 \quad (4)$$

where R_{m0} is initial membrane resistance. From equation (4), one can see that the resistance increases over time with an increasing slope and the curve produced from plotting the resistance versus time is concave up.

Assuming that the pore diameter is constant and the number of clogged pores increases with the permeation volume, the flow rate described by pore blocking model can be estimated using the following equation (Tracey and Davis 1994):

$$Q = Q_0 - K_2 V \quad (5)$$

where K_2 is the pore blocking constant. The value of Q_o and K_2 can be determined by plotting Q versus V . The expression in term of membrane resistance for pore blocking model is as follow:

$$R_m = R_{mo}e^{(K_3t)} \quad (6)$$

The membrane resistance increases exponentially over time with an increasing slope. The plot of resistance against time produces a curve that is concave up.

The resistance to flow can also be contributed by the formation of cake due to the accumulation of rejected foulants on membrane surface. The membrane is fouled externally in this case. For external fouling, the membrane resistance is constant whereas the cake resistance increases with the time due to the accumulation of rejected foulants. This yields the following equation (Tracey and Davis 1994):

$$\frac{t}{V} = K_3V + \frac{1}{Q_o} \quad (7)$$

where K_3 is cake filtration constant. In terms of total resistance, the cake filtration model can be expressed as

$$R_{tot} = R_{mo}(1 + 4tK_3Q_o^2)^{0.5} \quad (8)$$

Like internal fouling model, the resistance increases with time. However, the changing pattern is a decreasing slope and the curve is concave down. In short, internal fouling model is characterized by an increasing slope while external fouling model has a decreasing slope. Therefore, by looking at the characteristic slope (concave up and down, increasing or decreasing slope) in a total resistance curve, one can readily identify the fouling mechanism.

Chapter 3 Methodology

3.1 Chemicals

All chemicals are reagent grade unless otherwise stated. PAN (molecular weight $M_w = 150,000\text{g/mol}$), N,N-dimethyl formamide (DMF) was purchased from Sigma-Aldrich. Tetrabutyl orthotitanate (TBOT), isopropyl alcohol (IPA) and acetyl acetone iron (AAI) were supplied by Merck. Acetic acid (glacial grade) and hexadecane are from Fischer Scientific. All of the chemicals were used without further purification. Deionized (D.I.) water produced from Millipore Milli-Q water purification system was used for cleaning, rinsing purposes throughout the experimental processes.

3.2 Characterization and Instrumentation

3.2.1 Field Emission Scanning Electron Microscopy (FESEM)

The morphology of samples was observed by using FESEM (JEOL JSM-7600F) operated at 5kV. To prevent electron charging, prior to analysis, all samples were glued onto a carbon tape and sputter-coated with platinum for 20 seconds. An Integrated FESEM analyzer was used for fiber diameter measurement.

3.2.2 Transmission Electron Microscopy (TEM)

TEM investigations were carried out using a JEOL JEM-2010 microscope which was operated at 200kV accelerating voltage. The sample was diluted and made homogenously suspended via ultra-sonication in ultrasonic bath for at least 30mins. Subsequently, the diluted sample was dried overnight in an oven before deposited onto a copper grids for TEM observation.

3.2.3 Thermogravimetric (TG) Analysis

The thermal properties of as-prepared samples and permeate purity were analyzed by using TG analyzer (Perkin Elmer Pyris 7). Before loaded with sample, the

silicone pan was heated in air atmosphere from 30°C to 900°C at a ramping rate of 10°C/min for cleaning purpose.

3.2.4 CHNS Elemental Analysis

The carbon content of the fabricated CNFs was determined by using CHNS elemental analyzer (Perkin Elmer Series II CHNS/O analyzer). Note that data gives the percentage of only carbon, hydrogen, nitrogen and sulphur. Due to the instrument limitation, the percentage of oxygen is unavailable. The samples were measured thrice to get average values. Prior to analysis, samples were grinded into powders for more accurate measurement.

3.2.5 N₂ Adsorption-Desorption

Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the samples were determined by using a micropore system (Quantachrom Autosorb-1 supplied by ITS Science & Medical PTE LTD, nitrogen ranges from 0.05 m²/g to no known upper limit, pore diameter range 3.5 to 5000Å with nitrogen) at liquid nitrogen temperature of 77K. Before the analysis, samples were degassed overnight to remove the moisture .

3.2.6 X-ray Diffraction

X-ray diffractometer (XRD, Shimadzu XRD-6000) with monochromated high-intensity Cu K ($\lambda = 1.5418 \text{ \AA}$) operated at 40kV and 30mA was used to analyze crystal phase of the samples. The scanning speed was 0.05°/s.

3.2.7 Contact Angle Measurement

All the measurements (in air and water) were conducted by using a video contact angle (VCA) instrument (AST products inc, Optima series). The measurements were repeated three times at different locations on the sample surface and the results were averaged. For a solid-oil-water system, the measurements were conducted by using dichloromethane (DCM) as oil. DCM is heavier than water so it sinks in water. Hence, underwater oleophobicity of the membrane could be easily

determined by measuring the oil contact angle under water ($CA_{o/w}$) formed between the three-phases (i.e. water, solid and oil).

3.2.8 Mechanical Strength Analysis

The Young's modulus of a single SiO_2 -carbon composite nanofiber and CNF was evaluated by carrying out atomic force microscopy (AFM, Park Systems XE-100) based on the method of Kracke and Damaschke (Kracke and Damaschke 2000; Ko, Gogotsi et al. 2003; Mack, Viculis et al. 2005). In this work, a PPP-NCHR silicon cantilever with 169 GPa modulus and force constant of 42 N/m was employed. The cantilever has a pyramidal tip with contact radius < 10 nm. During the experiment, the samples were placed on a stainless steel spherical holder. The force mapping on the fiber surface was done from a randomly selected area of $5 \times 5 \mu m^2$. To derive the Young's modulus, the relationship between the fiber nanoindentation and the force applied was utilized which is given by

$$\frac{dF}{d\delta} = (2/\pi^{0.5})E^*A^{0.5} \quad (9)$$

where A is the contact area and E^* the effective Young's modulus, defined as

$$\frac{1}{E^*} = \frac{1-\nu_{tip}^2}{E_{tip}} + \frac{1-\nu_{sample}^2}{E_{sample}} \quad (10)$$

where ν is the Poisson ratio.

To measure bulk mechanical strength, tensile strength test was conducted by using Instron 5567 computerized universal testing machine. Throughout the test, 1×5 cm samples with grip length of 2 cm were clamped and pulled at a rate of 0.2 mm/min. For each sample, a stress-strain curve could be obtained and used for toughness measurement (by integrating the area under the stress-strain curve).

3.3 Sample Preparation

3.3.1 Fabrication of Electrospun SiO₂-Carbon Composite Nanofibers

The spin dope for SiO₂-carbon composite nanofibers was prepared by mixing PAN (M.W.=150000 g/mol, 7 wt%) and TEOS (0.5-5 wt%) in a mixture solvent of DMF/acetic acid (volume ratio of 15/1). TEOS was used as an alkoxide precursor of SiO₂ while PAN serves as both a carrying polymer for TEOS and a precursor of CNF. Glacial grade acetic acid was added to acidify the mixture while ensuring low water/TEOS ratio. The mixture was then heated at 90 °C until a crystal clear solution was obtained. Following this, the prepared spin dope was electrospun in a closed chamber where the electric field strength was kept at approximately 0.6-0.8 kV/cm. The solution feeding rate was 9-10 µl/min. The SiO₂-PAN nanofibrous mat was collected by using a rotating drum and the as-spun mat was left in air overnight for further hydrolysis despite that the moisture in air could engender the hydrolysis to some extent during the electrospinning. To prevent the nozzle blockage by the rapidly hydrolyzed spin dope, a solvent vapor jacket is designed and used to cover the spinneret as shown in Figure 3.1.

Figure 3.1 a) Diagram of electrospinning setup. b) Schematic design of electrospinning spinneret equipped with home-made plastic jacket to prevent pendant droplet from solidification during the electrospinning process.

The collected sheets of SiO₂-PAN fibrils were then oxidized (stabilized) at 280 °C in air for 2 hours in a programmable furnace ((Nabertherm, temperature range 30-3000°C) and carbonized at 900 °C in nitrogen for 2 hours in a programmable tube furnace (Lenton furnaces, 40mm in tube diameter supplied by Lenton Thermal

Designs LTD, maximum allowable temperature of 1200°C). In both processes, the ramping rate was kept at 3 °C/min. The pure SiO₂ nanofibers can be obtained by heating at 550 °C in air for 2 hours at a ramping rate of 8 °C /min to remove the carbon framework. For comparison, pure carbonaceous nanofibers were also fabricated. Throughout the experiments, the PAN content in the spin dopes was fixed at 7 wt%.

3.3.2 Fabrication of TiO₂ nanosheet-anchored carbon nanofibrous membrane

DMF was first mixed with IPA for 30 min. Subsequently, TBOT was added into the mixture and stirred for another 20 min. The volume ratio of DMF:IPA:TBOT was 1:1:0.067. The final mixture was then transferred into a Teflon-lined autoclave containing the carbon fibrous substrate and heated in an oven at 180 °C for 20 hrs. The final product was collected and washed thoroughly with ethanol to remove remnant TiO₂. Lastly, the product was dried overnight at 60 °C.

3.3.3 Fabrication of Electrospun Silica-CNF Sponge

The spin dope was prepared according to section 3.3.1. However, to obtain 3D self-assembled PAN nanofiber sponge, the electrospun nanofibers were deposited on a static collector instead of a rotating collector. Similarly, during the electrospinning process, nitrogen gas was purged to avoid nozzle blockage by the rapidly hydrolyzed spin dope. In order to derive carbon-silica sponge, the collected PAN sponge was then stabilized in air at 280°C for 2 hours followed by carbonization in nitrogen at 900°C for 2 hours.

3.3.4 Preparation of Magnetic Silica-CNF Sponge

To impart the carbon-silica sponge with magnetism property, AAI (5wt%) was added into the as-prepared spin dope. The electrospun product was collected and went through the steps as described in section 3.3.3. It was reported that, at elevated temperature, AAI was converted into iron (II,III) oxide (Fe₃O₄) nanoparticles (Jeanne, Jinwoo et al. 2008).

3.4 Experiments

3.4.1 Qualitative Analysis of Oil-Water Separation Efficiency

Silicone oil-coated SiO₂-carbon composite membrane was used as separation medium and a mixture of petroleum spirit and 0.2 M hydrochloric acid (HCl) aqueous solution (dyed with methyl violet) was prepared. Prior to the separation test, the flexible membrane was folded to fit in the opening of a vial containing 0.2 M silver nitrate (AgNO₃) aqueous solution which is dyed with methyl violet. The addition of methyl violet to the HCl and AgNO₃ aqueous solution could result in different colors due to the difference in pH. In an acidic solution (pH <1.6), methyl violet appears to be yellowish and it is turned into blue-violet when the pH value rises above 1.6. Hence, the as-prepared HCl and AgNO₃ aqueous solution gave rise to yellowish and blue-violet, respectively. The as-prepared oil-water mixture was then poured into the vial through the coated composite membrane. Due to its high sensitivity to Cl⁻ ions, the AgNO₃ aqueous solution in the vial can serve as an indicator in a sense that it reacts with HCl to immediately form whitish AgCl precipitate (solubility product, $K_{sp} = 1.8 \times 10^{-10}$). Hence, even a minuscule amount of HCl aqueous solution penetrating through the membrane will be detected. By observing the formation of AgCl precipitates, the membrane's separation efficiency can be qualitatively determined. The separation performance was conducted under two pouring conditions, i.e. water was added immediately followed by oil and vice versa. The membrane used in the experiment was initially dry.

3.4.2 Quantitative Analysis of Oil-Water Separation Efficiency

The purity of filtrate after oil-water separation was estimated by measuring the thermal loss in weight of water. Typically, a known mass of the filtrate was heated in oil bath from room temperature to 105°C and the temperature was held constant for 1 hr. Note that all oils used in the experiment have boiling points higher than water. To further confirm the results, TG analysis was conducted. The sample was heated from 30°C to 100°C at a rate of 10°C/min and was held constant for 30 mins. Density measurement was also carried out to estimate the degree of separation. The density of the filtrate was compared with the density calibration curves which were

plotted by using the density of oil-water mixtures containing different oil compositions (0 – 2 wt%).

3.4.3 Procedure for Oil Sorption Test

To characterize the oil sorption capacity, the as-prepared sorbents with known mass was immersed in the oils or organics solution until it was fully wetted. Note that the sorption rate for carbon-silica sponge is so fast that the wetting process was complete within a minute. After that, the sorbent was drained and allows the surface residual liquid to drip away before it was weighed on a digital balance. The oil sorption capacity was determined using the equation given by

$$Q = \frac{(m_f - m_i)}{m_i} \quad (11)$$

where Q (g/g) is sorption capacity of the carbon-silica sponge, m_f (g) the weight of sponge after sorption and m_i (g) the initial weight of sponge. The same procedure was applied to pristine CNFs.

3.4.4 Gravity-Driven Oil-Water Separation Experiment

The as-prepared TiO_2 nanosheet-anchored CNF membrane with effective surface area of $1.018 \times 10^{-3} \text{ m}^2$ was sandwiched between a funnel and a volumetric flask. The oil-water mixtures were added onto the membrane and the separation was conducted by gravity only i.e. no external power was applied. The time taken to filter the mixture of known volume was recorded to determine the permeate flux of the membrane.

3.4.5 pH and thermal stability Test

The pH of deionized water solutions were adjusted to pH 1, 7 and 14 by using 5M sodium hydroxide or 1M hydrochloric acid. Three pieces of TiO_2 nanosheet-anchored CNF membranes were then separately immersed into the solutions for 7 days before the subsequent analyses. The membranes' thermal resistance was determined by performing TG analysis. The sample was heated from 30°C to 900°C

at a rate of 10°C/min and was immediately cooled down after reaching the pre-determined temperature.

3.4.6 Carbon-Silica Sponge's Porosity Measurement

The sponge porosity was calculated as $(V_V / V_T) \times 100\%$, in which V_V is the pore volume and V_T the bulk volume. The bulk density is simply the sponge mass over its volume. To determine pore volume, both direct method and fluid saturation method were employed. In the direct method, the sponge volume was determined by subtracting CNF volume from the bulk volume. In fluid saturation method, the sponge was saturated with hexadecane and the volume of adsorbed hexadecane was determined from (mass of saturated sample - mass of dry sample)/density of hexadecane. A detailed calculation is shown in Appendix A.

3.4.7 Membrane Pore Size Determination

The pore size of the as-fabricated membrane was determined by a capillary flow porometer (CFP 1500A, Porous Material. Inc. (PMI), Singapore). The method used is bubble point analysis which is based on the fact that the pressure required to force an air bubble through the pore is inversely proportionally to the pore size. Hence, under wetting condition, the pore size can be determined from the pressure necessary to push water out of the pore.

Prior to analysis, the membrane was pre-wetted with Galwick fluid (surface tension = 15.9 dynes/cm). The measurement was performed in a dead-end cell where the wetted membrane was placed onto a filter holder that was connected to a source of regulated pressure. The pressure on the membrane was then increased stepwise while giving a 10 min stabilization time after each 14 kPa increment. 3 identical membrane samples were analyzed and the average values were obtained.

3.4.8 Cross-flow Microfiltration of Water-in-Oil Emulsion

Electrospun carbon-silica composite nanofiber membranes after pre-treated with silicone coating via chemical vapor deposition were employed in this experiment. Prior to introduction into the membrane module, the membrane were cut into a

shape that fits the membrane module. It is noteworthy that a pristine CNF membrane is very vulnerable to cutting and readily causes cracks. The cracks should be avoided because it adversely affects the filtration performance by lowering down the membrane rejection efficiency and giving inaccurate permeate flux. On the contrary, a carbon-silica nanofiber membrane is flexible and is more tolerable to some physical processing. Furthermore, the carbon-silica nanofiber membrane with enhanced toughness is capable of withstanding higher pressure.

Water-in-hexadecane emulsion was used as feed solution. A specified amount of deionized water was added into hexadecane (density = 0.77g/ml) to make 1% water-emulsified hexadecane. No surfactant was added in the preparation. The mixture then went through low-intensity ultrasonication in a water bath for 5 mins under mild mechanical mixing to form milky emulsion. The water-in-oil droplet sizes were observed under optical microscope.

Figure 3.2 Schematic diagram of experimental setup for cross-flow microfiltration experiment.

The apparatus constructed for the cross-flow filtration experiment is shown schematically in Figure 3.2. A gear recirculation pump (Cole-Parmer) was used to circulate the feed emulsion from a feed tank into a membrane module unit. A

pressure reading gauge was fitted at the outlet (retentate side) of the module unit to monitor the transmembrane pressure. The transmembrane pressure was adjusted through the throttling valve. By doing so, a back-pressure could be generated to the outlet of the membrane unit. The cross-flow velocity was determined by taking the feed flowing rate at the applied pressure over the cross-sectional area of the feed channel spacer. Both the permeate and retentate were pumped back to the feed tank. For permeate flux measurement, the permeate was collected in a beaker and weighed on a digital balance every 5 mins. The permeate collection time ranged between 20s and 60s. After that, the permeate was immediately transferred to the feed tank for recirculation. To avoid gradual depletion of water concentration due to the coalescence and deposition on the side of tank, the feed solution was replenished with stable emulsion every 5 mins.

Figure 3.3 Schematic diagram of a membrane module unit for cross-flow filtration.

The membrane module unit is constructed by two pieces of machined rectangular plastic constructions, each has a dimension of 14 x 12 x 2.5 cm. The upper section includes a rectangular feed flow channel where filtration process was performed. The lower section is used to hold the membrane. A hole with 0.5 cm diameter is drilled at the lower section so that the filtrate that permeate through the membrane can flow to the collecting outlet. To assembly, the membrane is first wetted before it is mounted and sealed with O ring gaskets. A permeate spacer (polymeric mesh) of

the same size is placed underneath the membrane. The upper and lower sections is secured by 6 tie bolts. During the operation, the membrane has an effective filtration area of 23.76 cm² or 0.002376 m². The design of the membrane module unit is illustrated in Figure 3.3.

Before each experiment, the membrane was pre-coated with silicone oil via chemical vapor deposition. The coating was performed in oil bath at 140°C for an hour. Prior to permeate flux measurement, the membrane was pre-filtered with pure hexadecane for 60 mins to complete membrane compaction which may affect the membrane performance. This followed by filtration of water-in-hexadecane emulsion for another 150 mins. For each run, the transmembrane pressure and cross-flow velocity were varied to study their effect to the membrane performance, respectively. The operating conditions are listed in Table 3.1. The permeate was collected at a time interval of 5 mins and the mass of the collected permeate was measured on a digital balance (Shimadzu, UX4200H). All the experiments were conducted at temperature of 21-22°C.

Table 3.1 Operating conditions used in the cross-flow filtration experiments.

Experiment No.	Applied Pressure (bar)	Cross-flow Velocity (m/s)
1	0.07	0.5421
2	0.138	0.5421
3	0.138	0.7690
4	0.138	0.8387
5	0.206	0.5421
6	0.275	0.5421

Chapter 4 Preliminary Study of Electrospun Carbon Nanofibers

4.1 Electrospinning of PAN Nanofibers

Spin dopes with different concentration of PAN (2, 3, 4 and 7 wt%) were prepared to investigate the effect of PAN concentration on the electrospun fibers' morphology. As seen in Figure 4.1, fibers with beads were formed when the PAN concentration is below 4 wt%. This is because the solution viscosity is so low that the corresponding viscoelastic forces are insufficient to resist the rapid solution shape change incurred by electrical force during electrospinning. As a result, the spin dope solution was shaped into spherical droplets by surface tension rather than into fibers. Above 4 wt%, uniform nanofibers were formed and the average diameter of nanofibers was increased with increasing concentration. A similar observation has also been reported previously (Subbiah, Bhat et al. 2005). For the ease of electrospinning, the PAN content in the spin dope was fixed at 7 wt% and used throughout the project.

Figure 4.1 Electrospun nanofibers with various PAN concentrations. a) 2% b) 3% c) 4% and d) 7%.

4.2 Preparation and Characterization of Electrospun CNFs

To obtain CNFs, electrospun PAN nanofibers have to undergo two thermal treatment steps, namely oxidative stabilization and carbonization. During the stabilization at 280°C, the colour of the nonwoven fibrous mat or membrane was changed into brown from white. The subsequent carbonization at 900°C in N₂ atmosphere turned the membrane into black. This can be clearly seen in Figure 4.2. It is noted that overheated PAN membrane appears dark brown which might give rise to CNF with inferior mechanical property.

Figure 4.2 Left: pristine electrospun PAN nanofiber membrane was white before heat treatment. Centre: membrane turned brownish after oxidative stabilization at 280°C for 2 hours. Right: membrane became black after carbonization at 900°C for 2 hour in N₂ atmosphere.

Aside from colour change, it was observed that the membrane also experienced chemical and physical changes, resulting in weight loss and fiber size shrinkage. During the heating treatment at elevated temperature, some small molecules in the polymer chain were broken down into volatile gases such as hydrogen and carbon dioxide which led to weight loss and shrinkage. To mitigate the shrinkage problem in the meantime increase its mechanical strength, the membrane was hot-stretched during the stabilization by applying weight at the four edges of the membrane.

However, no hot-stretching was performed during the carbonization due to the technical limitation.

Figure 4.3 FESEM images of PAN nanofiber membrane after carbonized at a) 600°C b) 700°C c) 800°C d) 900°C. (Image Magnification 1000x)

The as-fabricated PAN nanofiber membranes were carbonized at four different temperatures, i.e. 600, 700, 800 and 900°C in order to elucidate the temperature effect to the structural morphology. The results are shown in Figure 4.3. As seen, the membranes' structural continuity was retained after the thermal treatment at all four temperatures. The average fiber diameter and the fiber diameter distribution were statistically estimated based on 100 random fiber measurements by using FESEM image analyzer. It was found that the mean fiber diameters for membranes carbonized at 600, 700, 800 and 900°C were 312.4 ± 31.8 nm, 229.7 ± 20.8 nm, 224.0 ± 22.9 nm and 252.8 ± 26.2 nm, respectively. Except the 600°C treated membrane, all other membranes have mean fiber diameters below 300 nm. The fiber diameter distribution is shown in Figure 4.4. It is noteworthy that the fiber diameter can be manipulated by varying the mass ratio of the components in the

binary PAN/DMF mixture. For instance, the PAN/DMF ratio can be decreased to reduce the fiber diameter and vice versa (Inagaki, Yang et al. 2012).

Figure 4.4 The fiber diameter distribution obtained from 100 measurement of random PAN nanofibers after carbonized at a) 600°C b) 700°C c) 800°C and d) 900°C.

On the other hand, N_2 adsorption-desorption analysis showed that the CNF membrane heated at 800°C has a BET surface area of 348 m^2/g . This high specific surface area could be attributed to the formation of the mesopores in the nanofibers as well as the diameter at nanoscale. The pore size distribution analysis showed that the nanofibers have pores with majority being around 3 nm (see Figure 4.5).

Figure 4.5 Pore size distribution of an electrospun CNF prepared from carbonization at 800°C. It shows that the dominant pore size of CNF is 3 nm as indicated by the peak value of dV/dD .

The effect of heating to the morphology of the sample was examined. Carbonization temperatures of 600°C, 700°C, 800°C and 900°C in N_2 atmosphere were selected. The morphology of the resultant samples were analyzed in FESEM. The results are shown in Figure 4.6. At all four temperatures, rough surfaces comprised of two-dimensional granular polycrystals were observed. This is in good agreement with the observation reported by Zussman (Zussman, Chen et al. 2005). Furthermore, the cross-section of the broken fibers seen in Figure 4.6b and d shows that these polycrystals are orientated randomly yet firmly across the entire tubular structure, indicating their structural homogeneity. Figure 4.6b reveals the inner surface nanotexture after the first layer of crystalline sheet is, by chance, peeled off from the surface. It shows that the nanotexture of the layer beneath is identical to the first layer. Therefore, it is postulated that the CNF may be constituted by layers of crystalline sheets with each sheet wrapping along the fiber axis.

Figure 4.6 FESEM images showing cross-sectional CNFs heated at temperature of a) 600°C b) 700°C c) 800°C and d) 900°C.

To confirm the postulation, TEM analysis was performed to the CNF heated at 800°C. It is clearly seen in Figure 4.7 that the nanofiber is formed by sheets of carbon with varying degree of ordering. Such layer-by-layer crystalline sheet configuration may be the reason for the formation of mesopores which gives rise to high BET surface area. In overall, the results indicate that the heating temperature from 600°C to 900°C has no discernible influence to the structure of CNFs at microscopic level. This observation is in good agreement with the results of Zhou et al who reported that the microstructure of the CNFs are remained turbostratic and the carbon atomic sheets are extensively folded at temperature lower than 1000°C (Zhou, Lai et al. 2009). At above 1000°C, the carbon will change from turbostratic into graphitic, a desirable crystallite structure where the carbon atomic sheets are orderly stacked together.

Figure 4.7 Representative TEM image of a CNF carbonized at 800°C (left) and the corresponding layered structure showing the crystalline sheets of carbon crystals growing in a disorientated direction(right). This confirms that the as-prepared CNF is made of turbostratic carbon instead of graphitic one.

The oxidation resistance or thermal stability of electrospun CNFs carbonized at 800°C was studied by TG analysis. The result is shown in Figure 4.8. It was found that the CNF is highly resistant to oxygen because it remains stable even at elevated temperature. CNF was burnt off and oxidized into carbon dioxide at temperature above 500°C. At approximately 750°C, CNF was completely burnt off. This is evidenced from the substantial drop in weight (red curve). To determine its maximum oxidation rate, the first derivative of the red curve was taken and presented in blue curve. It shows that the highest oxidation rate occurs at 715°C, thus further confirming that the fabricated CNFs are highly resistant to oxygen. Note that the first weight drop was due to the evaporation of water moisture within the sample.

The thermal stability of CNFs treated at different carbonization temperatures (600-900°C) were also performed. Interestingly, all the samples displayed similar thermal stability and were degraded at temperature above 500°C. At the end of the analysis, there was almost no residues left. The TG analysis also implies that the as-prepared CNF may contain high carbon content. To justify, CHNS test was performed and the result is shown in Figure 4.9. Clearly, the carbonaceous samples have carbon content above 60% with the highest value being 79.3% for CNF

carbonized at 900°C. The results are within the expectation because more gases containing non-carbon elements were evolved at higher carbonization temperature, leaving carbon remained in the fibers. Based on this logic, it makes sense that the CNF heated at 600°C has the lowest carbon content (65.3%).

Figure 4.8 Thermogravimetric analysis of CNFs carbonized at 800°C showing its weight loss and oxidation rate at a heating rate of 10°C/min in air.

Figure 4.9 a) Thermal stability of electrospun CNF membranes and b) Carbon content of electrospun CNF after carbonized at various temperatures (600-900°C).

The carbonaceous nanomaterials are well known for their high mechanical strength (Lin 2001). Therefore, mechanical test was performed to measure the tensile strength of the fabricated CNF membrane. The results showed that the highest bulk tensile strength of CNF membrane carbonized at 700°C was 1.4 MPa with strain being 1.1% as shown in Figure 4.10. This value is, however, much lower than that of carbon fibers (Landmarks). One plausible explanation could be insufficient hot-stretching which is crucial to produce CNFs with superior mechanical strength. Hot-stretch is usually applied before and during the stabilization (Edie 1998). However, in the experiment, hot-stretch was only applied during the stabilization. Another reason could be due to the diminished mechanical strength when CNFs are assembled into macroscopic structure. CNF with low mechanical strength can make the subsequent material processing and handling uneasy. To improve the fiber strength, CNFs were mixed with silica to make a composite nanofibers which will be discussed in details in the next chapter.

Figure 4.10 Stress-strain curve of an electrospun CNF membrane carbonized at 700°C.

4.3 Oil Sorption Performance of Electrospun Carbon Nanofibers

Carbonaceous materials are hydrophobic and oleophilic. This makes them a potential candidate for oil sorption or selective removal of oil from water during oil spill remediation. To justify the wetting property of CNF membrane carbonized at 900°C, water contact angle in air was performed. Surprisingly, the water contact angle for the membrane was measured to be close to 0°C. It is suspected that this phenomenon is due to the strong capillary action resulted from the high porosity of membrane. The capillary effect is a phenomenon that is often found in porous materials. To improve membrane hydrophobicity and to facilitate the selective removal of oil and water, the membrane was coated with silicone oil in an oil bath through chemical vapour deposition. After the coating, the membrane becomes ultra-hydrophobic with water contact angle being 147°C (Figure 4.11).

Figure 4.11 Water contact angle in air before (left) and after (right) coating of the CNF membrane (carbonized at 900°C) with silicone oil. After coating, the CNF membrane becomes ultra-hydrophobic with water contact angle being 147°.

To optimize the silicone oil content, the CNF membrane was coated with silicone oil for different duration and tested its vegetable oil sorption performance based on the method described in section 3.4.3. The result is shown in Figure 4.12. Clearly, a coating time beyond an hour will diminish the sorption capacity. Therefore, it can be concluded that the optimum coating time for CNF membrane is an hour.

Figure 4.12 The effect of coating time to the vegetable oil sorption capacity of an electrospun CNF membrane (carbonized at 900°C). The sorption test refers to the method as described in section 3.4.3.

Carbonaceous materials such as granular and powdered activated carbon are commonly used adsorbents in water purification to remove organic pollutants, taste and odour (McCreary and Snoeyink 1977; Lambert, Holmes et al. 1996; Le Cloirec, Brasquet et al. 1997). They are also used in oil spill cleanup (Inagaki, Kawahara et al. 2002; Inagaki, Kawahara et al. 2002; Hussein, Amer et al. 2008). To evaluate the sorption performance of CNF membrane carbonized at 900°C, various oils (vegetable oil, pump oil, kerosene) and organic pollutants (ethylene glycol, DMF) were selected. For comparison, commercial granular activated carbon (GAC) was used.

Generally, the samples with known mass were immersed in the solutions. At certain time interval, the samples were taken out for weighing. For oil sorption, the CNF membranes were taken out from solution and hang in the air for 30 seconds until all the surface residual oils were dripped away before they were weighed. For organic pollutant sorption test, the vials containing the organic reagents were weighted before immersing and after removing the CNF membrane. The sorption capacity was calculated by using $Q = (T_{\text{initial}} - T_{\text{final}})/m$ where T_{initial} and T_{final} are the weight of vial (g) before immersing and after removing the membrane of known mass, m (g).

Figure 4.13 The saturated sorption capacity of selected pollutants by GAC and CNF membrane (carbonized at 900°C). Sorption experiment was repeated 3 times to obtain the standard deviation.

The saturated sorption capacity for both GAC and CNF membrane is plotted in Figure 4.13. Compared to GAC, the sorption capacity of CNF membrane is significantly higher. The highest sorption capacity for CNF membrane was found to be 21.28 g/g whereas it was only 1.05 g/g for GAC. In overall, the average sorption capacity of CNF membrane is about 10 times higher than that of GAC.

To evaluate the sorption kinetics, the pseudo second-order model was employed. This is a model frequently used to fit the sorption kinetics of carbonaceous sorbents (Ho and McKay 1999; Malik 2004; Jumasiyah, Chuah et al. 2005; Hameed, Din et al. 2007). The model can be written as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + Kt \quad (12)$$

where q_e is the amount of sorbate sorbed at equilibrium (g/g) or saturated sorption capacity, q_t the amount of sorbate sorbed at any time t (g/g), K the rate constant of sorption (g/g-min) and t the sorption time (min). Eq. (12) can be rearranged to obtain linearized form as follow:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{Kq_e} \quad (13)$$

The constants, K and q_e can then be determined from the intercept and slope of plots of t/q_t against t . The constant K is governed by the viscosity, surface tension of the tested pollutants as well as the pore structure of the pollutants. In addition to sorption kinetic, the efficiency of the carbonaceous sorbents can also be characterized by the "half-time", t_h , which is defined as the time taken to reach the half of the equilibrium sorption capacity. All the sorption parameters (q_e , K , t_h) are computed in Table 4.1. The r^2 refers to the correlation coefficient which relates to the curve fitting. The higher the coefficient is, the better the curve fits the selected model. On the other side, Figure 4.14 shows the sorption kinetics model for both GAC and CNF membrane.

Table 4.1 Sorption characteristics of different pollutants adsorbed by GAC and CNF membrane (carbonized at 900°C).

Pollutants	GAC				CNF			
	q_e (g/g)	K (min ⁻¹)	t_h (min)	r^2	q_e (g/g)	K (min ⁻¹)	t_h (min)	r^2
Vegetable Oil	0.61	0.24	6.68	0.999	15.08	0.04	1.75	0.999
Pump Oil	0.62	0.17	9.70	0.999	16.16	0.02	3.20	0.999
Kerosene	0.92	0.11	9.52	0.996	13.21	0.01	12.08	0.991
Ethylene Glycol	1.01	0.29	3.44	0.997	21.28	0.01	6.12	0.998
DMF	1.05	1.35	0.71	0.999	10.22	0.02	5.29	0.997

Figure 4.14 Pseudo second order sorption kinetics of different pollutants for a) CNF membrane, b) GAC, c) plots of sorption capacity versus time for different pollutants onto CNF membrane and GAC.

As seen in Figure 4.14, the fitting results show good agreement with the experimental data. For all the sorption tests, the r^2 is greater than 0.99. This indicates that the sorption kinetic obey the pseudo second-order model. The smallest t_h values for GAC and CNF are 0.71 min and 1.74 mins, respectively. However, after taking average of each t_h , one can find that GAC and CNF have similar values (5.832 vs 6.01 mins). This implies that CNF can perform as effectively as GAC with respect to the adsorption rate.

The high sorption capacity of CNF membrane can be ascribed to the highly porous structure and low packing density. The electrospinning process results in non-

woven membrane with lower packing density compared to GAC ($0.12 - 0.95 \text{ g/cm}^3$). Lower packing density means that the pore volume in the membrane is increased. Also, as observed in Figure 4.3, the membrane is made of continuous CNFs that are entangled to each other. Such fiber entanglement forms a unique structure where the pores are interconnected. As a result, the pore volume is increased and can offer more space for adsorption. Hence, the sorption capacity is improved. Moreover, the flat-sheet geometry of the membrane facilitates the sorption process because the surface contact area with the sorbates is larger than GAC. The open interconnected network of CNFs forms a system of capillaries that builds up a capillary pressure. It induces capillary force that facilitates the adsorption. Both the adsorption rate and efficiency are enhanced considerably when coupled with the capillary action. It is noteworthy that the sorption capacity turns to be higher for high density liquids. This is due to the fact that high density liquid is heavier. Hence, the sorption capacity of ethylene glycol (density= 1.11 g/cm^3) turns out to be the highest among all sorbates.

In contrast to the flat-sheet CNF membrane, sorption onto GAC relies more on the diffusion due to smaller pore size. It was observed that air bubbles were rising out rapidly from the GAC during the sorption test. A similar phenomenon was also observed with structured fiber assemblies which are highly packed (Rengasamy, Das et al. 2011). These air bubbles exerted a resistance due to the back pressure and hindered the pollutants from filling into the pores within GAC. As a result, a lower sorption capacity was obtained.

4.4 Conclusions

A nonwoven membrane made of CNFs is derived from electrospinning PAN nanofibers. The fabricated CNFs have an average fiber diameter ranging between 200 nm and 300 nm. The TEM observation reveals that the CNF is turbostratic and constituted by layers of polycrystalline sheet which grows along the fiber axis. The thermal testing indicates that CNFs were remained structurally stable at elevated temperature (up to 500°C). However, CNFs is very brittle and vulnerable to folding.

Hence, the bulk mechanical strength of CNF needs to be improved in order to facilitate its processing and handling.

The as-prepared CNF membrane exhibits weak hydrophobicity due to the capillary effect. To improve its surface wettability, the membrane is coated. The adsorption performance of CNF membrane was studied by using a variety of oils and organic solvents. It was found that the average adsorption capacity for CNF membrane was more than 10 g/g which is 10 times more than the commercial GAC. Moreover, the adsorption rate of CNF membrane follows the pseudo second-order model. The adsorption behaviour of CNF membrane is dominated by its packing density, porous structure and capillary pressure. However, for practical use, the oil removal efficiency of CNFs still requires improvement. More advanced and tough carbon-based materials should be designed.

Chapter 5 Highly Efficient and Flexible Electrospun Carbon-Silica Nanofibrous Membrane for Ultrafast Gravity-driven Oil-Water Separation

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Figure 5.1a shows the FESEM images of as-spun SiO₂-carbon composite nanofibers prepared from 5 wt% TEOS. It can be seen that the membrane is composed of entangled nanofibers with an average diameter of 481 ± 57 nm based on 150 fiber measurement. This highly dense fiber entanglement leads to the formation of 3D macroporous network which could facilitate the liquid permeation rate across the membrane due to the decreased mass transfer resistance. The enlarge image in Figure 5.1b reveals that the nanofiber has a rough surface with wrinkles. The formation of wrinkles is probably due to the competition between the phase

5.1 Characterization of Electrospun Carbon-Silica Nanofibrous Membrane

Figure 5.1 Characterization of electrospun composite nanofibers. a) top view of electrospun composite nanofibrous mat. b) surface morphology of a single composite nanofiber.

separation and the fast evaporation rate of the DMF solvent in solution jet during the electrospinning process. It is interesting to note that, the fiber-like morphology of the composite is still preserved even after the carbon is removed by calcination at 550 °C as seen in Figure 5.2. The calcination also turns the nanofibers from black into white. This suggests that the SiO₂ present in the composite forms a linear network.

Figure 5.2 FESEM images of pure SiO₂ nanofibers (left) and its magnified image (right) after carbon removal by calcination at 550°C.

XRD pattern of both pristine CNFs and SiO₂-carbon composite nanofibers, as seen in Figure 5.3, show broad diffraction peaks at approximately 25°, suggesting that the phase of carbon and SiO₂ is amorphous. It is noteworthy that the characteristic peak for both amorphous carbon and SiO₂ are close to each other (~23-25°) (Choi, Lee et al. 2003; Liu, Sagi et al. 2008; Woo, Dokko et al. 2008) and the diffraction peak of carbon overlaps that of SiO₂ in this case. This explains why the XRD spectrum of SiO₂-carbon composite nanofibers shows only one diffraction peak which appeared to be similar with the pristine CNFs. TEM examination further confirms the amorphous phase of SiO₂ in the composite nanofibers (see Figure 5.3b). Figure 5.3d demonstrates that the composite nanofibrous membrane can be bent to a radius curvature of 1.5 mm without any cracks. The membrane can be even severely folded. Due to its excellent flexibility, the membrane can be readily cut into desired shape as shown in the inset of Figure 5.3d. The membrane flexibility and its corresponding mechanical properties will be further discussed in a later section.

Figure 5.3 a) XRD pattern showing amorphous carbon and silica in pristine CNFs and the composite nanofibers. b) TEM image of a pure SiO₂ nanofiber and c) its amorphous phase, as evidenced from the SAED pattern shown in the inset. d) flexibility of the composite nanofibrous mat which can be easily cut into desirable shape, as shown in the inset.

Figure 5.4 shows the FTIR spectra of pristine CNFs and SiO₂-carbon composite nanofibers. For CNFs, the spectrum shows the characteristic peaks at ca. 1222 and 1601 cm⁻¹ which correspond to the C=C stretching and bending vibrations of the carbon backbone, respectively. The broad peak at 3100-3700 cm⁻¹ can be assigned to the N-H bonds (Yan, Tai et al. 2011). However, the peak at 3440 cm⁻¹ belongs to the asymmetrical stretching vibration of O-H groups due to the water adsorbed on

the surfaces (Wang, Du et al. 2014). After the addition of TEOS, the resultant composite nanofibers show new peaks of Si-O stretching and bending vibrations at ca. 1082 and 1053 cm^{-1} , respectively. The peak at 885 cm^{-1} is ascribed to the silanol (Si-OH) vibration (Patel, Li et al. 2007). The detection of Si-O indicates the formation of SiO_2 in the fibers. No Si-C bond is observed, suggesting that there is lack of intermolecular interaction between the silica and the carbon species in the composite system and they form interpenetrating structure separately during their transformation (Si, Feng et al. 2013). It is noted that, although most of Si-OH groups can be removed by dehydroxylation at elevated temperature during the carbonization process, the detected Si-OH can be attributed to the isolated single silanols remained on the silica surface (Zhuravlev 2000).

Figure 5.4 FTIR spectra of the as-prepared CNFs and SiO_2 -carbon composite nanofibers.

To verify the presence of silica in the fibers, the composition of CNF sample containing 5 wt% Si precursor was further characterized by EDX as shown in Figure 5.5a-e. The results from the EDX analysis confirms that the composite nanofibers are mainly composed of Si, O and C. These are indicated by the strong peaks in the EDX spectrum. In addition, it can be seen that the Si element is evenly distributed across the surface of the nanofibers as shown in Figure 5.5e.

Figure 5.5 a) FESEM image of SiO₂-carbon composite nanofibers. b) EDX spectrum and c) carbon d) oxygen and e) silicon maps of SiO₂-carbon composite nanofibers taken in a).

On the basis of the experimental results, the formation mechanism of SiO₂-carbon composite nanofibers is proposed and illustrated in Figure 5.6. Prior to electrospinning, the sol-gel precursor is prepared by mixing PAN, TEOS, DMF, acetic acid. During the process where the precursor sol is spun into fibers under appropriate electrical strength, phase separation takes place. The DMF solvent in the precursor evaporates quickly from the fiber in the meantime the TEOS undergoes hydrolysis. The surface morphology of the electrospun fibers is the result of the competition between phase separation dynamics and evaporation rate of DMF solvent in solution jet during electrospinning. During the hydrolysis, TEOS is polycondensed to form SiO₂ linear framework instead of SiO₂ colloidal particles

Figure 5.6 Schematic of fabricating silica-PAN composite membrane, silica-carbon composite membrane and pure silica nanofibrous membrane by employing electrospinning technique.

owing to the fact that the rate of condensation is slow relative to the rate of hydrolysis under the acidic catalysis (Sakka and Kamiya 1982; Novak 1993). Consequently, the resultant composite nanofibers is a continuous PAN phase with homogenously dispersed, phase separated SiO₂ domains. Upon carbonization at elevated temperature under inert atmosphere, the PAN phase is converted into carbon phase. The process also leads to complete condensation of hydrolyzed TEOS to SiO₂ (Patel, Li et al. 2007). The final state of SiO₂ in the composite is remained as evidenced from the broad band diffraction peak at 2θ values of approximately 25° in the XRD spectra in Figure 5.3a. It is noted that the morphology and integrity of the composite nanofibers is well-retained after carbonization despite that carbon and silica have different shrinkage rates. This is owing to the interpenetration framework of carbon and SiO₂ which allows the shrinkage to be engendered in a homogenous manner (Si, Feng et al. 2013). After removing carbon framework through calcination, pure whitish SiO₂ nanofibers can be obtained. However, the resultant SiO₂ nanofibers are very fragile because predominant volumetric fraction

of the composite is occupied by carbon and its removal renders the nanofibers mechanically weak.

The percentage of the silica component in the composite nanofibers can be derived from TG analysis. The TG curves shown in Figure 5.7 indicate that the addition of 0.5, 1, 3 and 5 wt% TEOS resulted in SiO₂ loading of 2.7, 3.2, 8.5 and 15.8 wt%, respectively, in the composite fibers. With increasing SiO₂ loading, the thermal stability of the composite nanofibers is remarkably enhanced. It is observed that the maximum temperature at which the composite fibers are oxidized shifted toward higher temperature region. Apart from that, the weight loss rate is decreased. Compared to the pure CNFs, the composite nanofibers exhibits less steep weight loss and stabilized at higher temperature. Among the samples, 15.8 % SiO₂-carbon composite nanofibers have the lowest weight loss rate and stabilize at the highest temperature. The inset of Figure 5.7 shows the maximum oxidation rate derived by taking the first derivative of the TG curves. As seen, the onset of maximum oxidation rate (the highest peak in the differential curve) is delayed with increasing SiO₂. The maximum oxidation rate for 15.8 wt% SiO₂-carbon composite nanofibers occurs at 720 °C. This enhancement in thermal stability could be attributed to the thermal insulation effect of silica in the composite fibers (Liu, Wei et al. 2004).

Figure 5.7 TG analysis result showing the enhanced thermal stability with increasing SiO₂ content.

The mechanical property of a single CNF and 15.8 wt% SiO₂-carbon composite nanofibers was studied by using AFM in contact mode. The force applied after the tip contacts with the sample and the force required to pull off from the sample surface can provide a measurement of stiffness. 17 force-distance (F-D) curves for each samples were collected from a randomly selected area of the sample which was placed on a stainless steel substrate. Figure 5.8 shows the representative F-D curves of the electrospun CNF, the SiO₂-carbon composite nanofibers and stainless steel (as standard). The relative difference in Young's modulus of CNF and SiO₂-carbon composite nanofiber can be estimated from the slope of the force-indentation curve by using the approach as described in the experimental section. The calculation shows that SiO₂-carbon composite nanofiber has an average Young's modulus about 3 times lower than that of CNF, suggesting that SiO₂-carbon composite nanofiber is more flexible than CNF. It is observed that the membrane flexibility can be manipulated by tuning the SiO₂ content in the composite nanofibers. This enhanced flexibility can be confirmed by manually twisting the membrane. As seen in the inset of Figure 5.8, the membrane could be severely twisted without breaking. After twisting, the membrane could recover very quickly to its initial state without causing structural deformation. On the contrary, the pure CNF membrane was brittle and quickly broke into pieces after folding.

Figure 5.8 Relative difference in flexibility between a single CNF and SiO₂-carbon composite nanofiber. Inset shows the excellent flexibility of the composite membrane.

To further study the effect of silica, tensile test was conducted on the fabricated membranes with different SiO₂ loading. As seen in Figure 5.9, the Young's modulus is decreased with increasing SiO₂ concentration. At 15.8 wt% SiO₂ concentration, the Young's modulus of the membrane is dropped from 317.6 to 56.3 MPa or by 82.3 %. However, the membrane toughness is increased followed by a steep drop which occurs after a threshold concentration (2.7 wt%) is reached. The drop in membrane toughness suggests that the strengthening effect of silica is only effective when its concentration is maintained below 2.7 wt% or 0.5 wt% TEOS loading. Since there are weak interactions between the carbon matrix and the silica as evidenced from FTIR analysis, silica, in this case, acts as a nonreactive and nonreinforcing filler. When an external stress is applied to the composite nanofiber, it is transferred from the carbon matrix to the embedded SiO₂ which deflects the crack propagation on the carbon matrix and consequently the stress concentration at the crack tips is reduced, thus preventing the structural failure (Chen and Iroh 1999). However, as the SiO₂ content increased to a concentration above 2.7 wt%, the membrane toughness decreased substantially. This can be attributed to the agglomeration of SiO₂ which becomes a flaw to the composite nanofibers rather than a crack deflector.

Figure 5.9 Plots of a) Young's modulus and b) normalized toughness as a function of SiO₂ loading.

The membrane flexibility was further examined under harsh condition. To do so, the membrane was immersed in liquid nitrogen (-196°C) for seconds before it was

taken out and folded. For comparison, a similar test was conducted to commercial cellulose acetate (CA) membrane. It is found that the CA membrane was very brittle and could be easily break apart a few seconds after it was taken out from the liquid nitrogen. On the contrary, the SiO₂-carbon composite nanofibrous membrane remained highly flexible even after several time of immersion and folding, thus implying its high durability at super low temperature. This excellent flexibility under harsh conditions helps to maintain the structural integrity of the composite membrane during the oil-water separation process as will be discussed in the later section. Moreover, the approach to preparing flexible carbon-based membrane through silica addition provides a solution to the carbon brittleness which is normally alleviated through optimizing the precursors and preparation method.

5.2 Wetting Behavior of Carbon-Silica Nanofibrous Membrane

To examine the wetting behavior, water contact angle (WCA) and oil contact angle (OCA) were measured by dropping 3 μl water (72.1 mNm^{-1}) and oil (dichloromethane, 35.4 mNm^{-1}) onto the fabricated composite membrane. As shown in Figure 5.10, the membrane displays a WCA of $138.6 \pm 1.6^\circ$ and OCA close to 0° , indicating its ultrahigh hydrophobic and superoleophilic character. This is under expectation because carbonaceous materials are intrinsically hydrophobic.

Figure 5.10 The hydrophobicity and oleophilicity property of the composite membrane before and after silicone oil coating.

However, it was observed at some locations of the membrane that the water droplet was shape-unstable and rapidly absorbed by the membrane within several seconds. The absorption process is illustrated in Figure 5.11. In other words, at these particular locations, the surfaces are superamphiphilic. This nonhomogeneity in surface wettability is probably a consequence of the competition between the natural hydrophobic effect and the porosity-driven hydrophilicity. It has been reported that porous materials such as silica thin film and methyltriethoxysilane sol-gel foam is more likely to display hydrophobic-to-hydrophilic switching (Shirtcliffe, McHale et al. 2005; Cebeci, Wu et al. 2006). Therefore, it is speculated that the observed wetting transition is engendered by the high porosity of the composite membrane that drives water infiltrate into the 3D fibrous network.

Figure 5.11 The sequential absorption process of a 3 μ l water droplet by the electrospun SiO₂-carbon composite membrane. The absorption process is complete within a few seconds.

To improve its hydrophobicity property and ensure homogeneous hydrophobic–oleophilic surface pattern, the membrane was coated with silicone oil at 125 °C for 0.5 hour by mean of vapor deposition. Upon heat treatment, silicone oil is thermally degraded and the vaporized molecules deposit homogeneously on the nanofiber surface. After coating, the membrane exhibits WCA of $144.2 \pm 1.2^\circ$ which is slightly higher than the untreated one while the membrane superoleophilicity is sustained at an OCA close to 0° (Figure 5.10).

5.3 Stability Test of Carbon-Silica Membrane Wettability

Chemical stability test was performed to evaluate the effect of pH to the membrane's wettability. As seen in Figure 5.12, the membrane could maintain

ultrahigh hydrophobicity towards a broad range of pH (2-14), suggesting its excellent stability against extreme pH condition. This implies that the membrane is superior over those polymeric membranes.

Figure 5.12 WCAs when exposed to aqueous solutions with different pHs. Inset shows the ultrahigh hydrophobicity at different pHs and superoleophilicity of the membrane.

The membrane's hydrophobicity after calcination for 2 hours at various temperatures (100-400 °C, ramping rate of 5 °C /min) was also studied. As shown in Figure 5.13, the hydrophobicity is maintained after annealing treatment up to 350 °C. At 400 °C, the membrane was reduced to its initial state and lost its constancy of hydrophobicity which can be manifested by the substantial drop in WCA close to 0°. Several implications can be drawn from the chemical and thermal stability test. Firstly, the membrane wettability is switchable between hydrophobic and hydrophilic states by coating the surface with hydrophobic/hydrophilic materials that can be removed at elevated calcination temperature. Secondly, with stable hydrophobicity at high temperature (300 °C), the membrane should be able to serve effectively as a separation medium under high temperature condition such as oil spill incidents accompanied by a great fire due to burning of oil spill. Thirdly,

the oil-fouled membrane can be easily regenerated and reused by means of calcination and chemical cleaning.

Figure 5.13 Variation of WCAs after calcination at various temperatures for 2 hours. Inset figures show water shape at different temperatures.

5.4 Gravity-driven Oil-Water Separation Performance

The characteristic of high porosity coupled with selective wettability makes the SiO₂-carbon composite membrane a promising material for oil-water separation. As a proof of concept, the gravity-driven oil-water separation experiment was conducted and the separation performance was evaluated qualitatively. A mixture of petroleum spirit (colorless) and 0.2 M HCl aqueous solution (yellowish) was prepared and poured slowly onto the coated membrane which is flexible enough to be fitted into the opening of a vial as shown in Figure 5.14a and c. The vial was pre-filled with 0.2 M AgNO₃ aqueous solution (violet) which was used to detect the HCl that penetrated through the membrane. Owing to the fact that Ag⁺ is highly sensitive to Cl⁻ ions, even a tiny amount of HCl will react with AgNO₃ to form whitish precipitate. As seen in Figure 5.14b, whitish precipitate was immediately formed after a 5 μ l droplet of HCl was added into AgNO₃ solution. However, when petroleum spirit was added onto the membrane immediately followed by HCl

solution, the solution in the vial remained as clear as before after the oil-water separation, as seen in Figure 5.14c. Only HCl aqueous solution was retained on the membrane. The separation performance was remained unaltered even when HCl solution was first poured followed by petroleum spirit. These indicate that the coated membrane can separate oil from water efficiently regardless the pouring conditions.

Figure 5.14 Ultrafast gravity-driven oil-water separation. a) Mixture of petroleum spirit and HCl aqueous solution as feed. b) Whitish AgCl precipitate formed after HCl reacts with AgNO₃ solution (violet). c) Demonstration of gravity-driven oil-water separation. Enlarged pictures show that water is completely retained on the membrane surface and no AgCl precipitate is formed during the separation.

Apart from the excellent separation performance, the membrane also allows ultrafast oil-water separation by solely gravity. The fluxes of various oils permeating through a membrane are measured and the flux test was repeated 3 times to obtain average values. The average permeate flux for petroleum spirit, iso-octane and hexane was found to be 3032.4 ± 234.6 , 1719.1 ± 36.2 and 2648.8 ± 89.7 L/m²-hr, respectively when a 213.3 ± 21.8 μ m thick membrane (effective membrane area is 0.000962 m²) was used (Figure 5.15). These values are comparable to or even higher than other advanced filtration membranes such as mineral-coated polypropylene microfiltration membrane (>2000 L/m²-hr) (Chen and

Xu 2013), superhydrophobic polyvinylidene fluoride membrane (700-3500 L/m²-hr) (Zhang, Shi et al. 2013) and crosslinked polyethylene glycol diacrylate-coated membrane (<100 L/m²-hr) (Ju, McCloskey et al. 2008). The variations in flux for different oils are due to the viscosity difference. According to the Hagen-Poiseuille equation, flux is inversely proportional to liquid viscosity. The viscosity for petroleum spirit, isooctane and hexane is 0.3, 0.5 and 0.3 mPa.s, respectively. Such fast mass transport could be attributed to both the superoleophilic surface as well as the open, interconnected pore structure of the membrane which substantially decrease the mass transfer resistance. When compared to the conventional pressure-driven filtration membranes such as polymeric flat-sheet (Chakrabarty, Ghoshal et al. 2008), hollow fiber membrane (Hlavacek 1995) and ceramic membrane (Mueller, Cen et al. 1997), the use of electrospun carbon-silica membrane for oil-water separation is advantageous because (1) it is energy efficient (separation by gravity). (2) significantly high permeate fluxes of 1500-3000 L/m²-hr can be achieved (i.e. high throughput production). (3) it is able to work effectively under harsh conditions such as oil spill in a polar zone and leakage of high temperature oils due to its high thermal and chemical resistance.

Figure 5.15 Permeate flux for different types of oils. Inset shows the cross-sectional view of the membrane thickness.

5.5 Conclusions

In summary, a free-standing and flexible SiO₂-carbon composite nanofibrous membrane was fabricated by using electrospinning technique followed by thermal treatment. The bulk mechanical properties i.e. Young's modulus and toughness of the as-prepared membrane can be easily tuned by manipulating the SiO₂ loading. It is found that the composite membrane is tougher than the pristine CNF membrane when the embedded SiO₂ concentration is kept at 2.7 wt%, beyond which the membrane toughness is reduced. After coated with silicone oil, the composite membrane becomes ultra-hydrophobic and superoleophilic. The chemical and thermal stability tests suggest that the wettability of the coated composite membrane is resistant to elevated temperature (up to 350 °C) and stable towards a wide range of pH values (2-14). Such wetting behavior allows the membrane to be applied as a substrate for separation of free water and oil. The quality test of oil-water separation shows that the membrane is highly effective in separating free oil and water. More importantly, the separation process is ultrafast and driven solely by gravity. This study opens up a new avenue for fabrication of free-standing carbonaceous composite membrane with tunable flexibility for energy-efficient, high throughput production of purified water. With improved toughness and flexibility, the membrane is now mechanically strong to be used for other environmental applications such as oil-water separation and selective sorption. These are discussed in the subsequent sections.

Chapter 6 Self-assembled Superhydrophobic Electrospun Carbon-Silica Nanofiber Sponge for Selective Removal and Recovery of Oils and Organic Solvents

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Tai, M. H., B. Y. L. Tan, et al. (2015). "A Self-Assembled Superhydrophobic Electrospun Carbon-Silica Nanofiber Sponge for Selective Removal and Recovery of Oils and Organic Solvents." *Chemistry – A European Journal*, Vol. 21, No. 14, pp. 5395-5402.)

6.1 Characterization of Carbon-Silica Nanofiber Sponge

Figures 6.1a-c shows the macroscopic PAN-SiO₂ sponge prepared by electrospinning. The sponge is a highly fluffy, loosely packed web which is resulted from vertical accumulation of PAN-SiO₂ nanofibers. The fluffiness of the web can be attributed to the electrostatic repulsion between nanofibers as a result of the charges on them (Yousefzadeh, Latifi et al. 2012). The FESEM characterization reveals that the sponge is made of continuous PAN-SiO₂ nanofibers with fiber diameter ranging between 300 and 500 nm. These nanofibers are self-assembled into an interconnected, porous and 3D structure. It was observed that the resultant PAN nanofiber sponge is very soft and fluffy that it can readily disintegrate during the deformation by mechanical compression and stretching. Also, the presence of residual charge on the nanofibers causes the resultant sponge "sticky", thus making the handling difficult. More importantly, the sponge does not exhibit selective wettability which is important for oil removal from water.

Figure 6.1 Digital photograph a) and FESEM images b)-c) of the porous structure of PAN-SiO₂ sponge.

Therefore, heat treatment was performed to the resultant polymeric sponge. The oxidative stabilization was conducted followed by carbonization. Carbonization was performed at 900°C in nitrogen atmosphere to convert PAN-SiO₂ sponge into carbon-silica sponge. The resulting product is a black sponge made of continuous, curly carbon-silica nanofibers with diameter in the range of 200 and 300 nm (Figure 6.2a-c). This shrinkage in fiber diameter is due to the evolution of gas species during the carbonization process. The heat treatment improved the sponge compactness which alleviate the over-fluffiness problem as observed for PAN-SiO₂ sponge. The sponge after carbonization also exhibited enhanced toughness and elasticity which makes it more resistant to irreversible deformation under frequent compression.

Figure 6.2 Digital photograph a) and b)-c) FESEM images of electrospun carbon-silica sponge.

Based on the fact that electrospinning is a bottom-up process during which multiple layers of nanofibers are built up to form macroscopic non-woven mat, it is postulated that the sponge is a macroscopic structure that is loosely packed with multi layers of carbon-silica nanofibers. To confirm the postulation, the sponge formation process was observed. As shown in Figure 6.3, the formation of sponge could be divided into 3 stages, namely deposition, compaction and thickening. In the stage of deposition, the electrospun nanofibers settled loosely on the substrate to form a nonwoven layer. The deposited nanofiber layer was immediately compressed by the next pool of electrospun nanofibers that would subsequently form the second layer. Due to the electrostatic repulsion between nanofibers, the degree of layer compaction is not significant such that the low density of sponge

was attained. Through the repetitive process of deposition and compaction, the volume of the nanofiber layers was gradually increased and a nanofibrous sponge was resulted. The number of layers or the volumetric size of sponge can be easily manipulated by controlling the volume of precursor solution used for electrospinning. This also implies that the sponge production is scalable.

Figure 6.3 Digital photograph of the self-assembly process of electrospun silica-carbon sponge. The insets illustrate the formation mechanism of deposition, compaction and thickening. The electrospun fibers first deposited loosely on the substrate to form nonwoven fibrous layer (1st and 2nd figure from left). As the fibers were deposited, they were slightly compacted (3rd figure from left). The layer was thickened as more and more fibers deposited (last figure from left). It was obvious that the sponge in the last figure was thicker than in the 1st figure.

The bulk density of electrospun carbon-silica sponge is measured to be 9.6 mgcm^{-3} . This is comparable to the various carbon-based sponges derived from other strategies, such as carbon nanotube sponge ($5\text{-}10 \text{ mgcm}^{-3}$) (Gui, Wei et al. 2010), hydrothermally-derived CNF sponge (10 mgcm^{-3}) (Wu, Li et al. 2014) and graphene sponge ($12 \pm 5 \text{ mgcm}^{-3}$) (Bi, Xie et al. 2012). When compared to the conventional carbon-based sponge ($100\text{-}800 \text{ mgcm}^{-3}$) (Fu, Zheng et al. 2003; Wu, Fu et al. 2004), its bulk density is two orders of magnitude lower. The sponge's low bulk density stems from its macroporous structure. To measure the bulk porosity of the as-prepared sponge, we based the calculation on two methods, namely direct method and fluid saturation method. The former measures porosity by subtracting volume occupied by carbon-silica nanofibers from total sponge volume whereas the latter determines the pore volume occupied by adsorbed liquid such as hexadecane

used in this experiment. In direct method, by using a density of $1.95\text{--}2.17\text{ gcm}^{-3}$ for CNF (Vamvakaki, Tsagaraki et al. 2006), the bulk porosity of the as-fabricated sponge is estimated to be $>99\%$. On the other hand, the fluid saturation method resulted in a porosity of $\sim 97\%$ (The detailed calculation can be found in Appendix A). Such high porosity can be evidenced from FESEM examination on cross-section of a carbon-silica sponge shown in Figure 6.2a-c.

Despite high porosity, the as-fabricated sponge displays excellent structural flexibility and instantaneous shape recovery. After subjecting to a compressive strength equivalent to 48 grams, the sponge at dry state can be instantaneously recovered to its original volume without deforming permanently, indicating a highly elastic property. During the experiment, the sponge can reduce to its original shape even after undergoing $> 90\%$ volume reduction in the compression test (Figure 6.4a-c). Such mechanical property of sponge can be attributed to the flexible carbon-silica nanofibers that are entangled with each other in a 3D configuration. On the other hand, it was found that the structure of the electrospun sponge did not disintegrate after 15 min ultrasonication. This structural robustness is contributed by the highly interconnected structure that prevents the misalignment of the nanofibers. Hence, no further structural reinforcement is required.

Figure 6.4 Macroscopic visualization showing reversible shape deformation of the sponge after compression.

6.2 Surface Wetting Property of Carbon-Silica Sponge

The carbon-silica sponge is intrinsically hydrophobic and oleophilic with water and oil contact angle being $145.6 \pm 4.3^\circ$ and 0° , respectively (Figure 6.5a-b). To improve its hydrophobicity, the sponge was coated with silicone oil in an oil bath at

140°C for an hour. After coating, the sponge exhibits superhydrophobicity with average water contact angle being $155.4^\circ \pm 1.3^\circ$ (Figure 6.5c). With its superhydrophobicity and low packing density (approximately 1% of the water density), the coated sponge could float steadily on the water surface. In contrast, a commercial polyurethane sponge sank below water surface owing to its hydrophilicity, as shown in Figure 6.5d. When the sponge was immersed into water, a mirror reflection could be observed on the sponge surface (Figure 6.5e). This phenomenon is caused by the formation of interface between the surrounding water and the air entrapped in the sponge. Thus, the superhydrophobicity property of the sponge is manifested.

Figure 6.5 a) Macroscopic demonstration showing the intrinsic hydrophobicity and oleophilicity of an electrospun carbon-silica sponge. b) The water contact angle for a pristine electrospun carbon-silica sponge. c) Photograph of water droplets on an sponge surface. Inset shows the water contact angle measurement. d) Comparison of wetting property between silicone-oil coated carbon-silica sponge and

polyurethane sponge. e) Mirror-reflection phenomenon observed when immersed carbon-silica sponge in water, manifesting its hydrophobicity.

Not beyond our expectation, the sponge also shows superoleophilicity. As seen in Figure 6.6a, the sponge quickly sorbed iso-octane (colorless) from water (blue-dyed) at the moment they came into contact. The entire sorption process is almost instantaneous and completed within 0.15 second, demonstrating the ultrafast sorption rate of the sponge. The fast sorption rate is mainly contributed by the highly oleophilic surface of carbon-silica nanofibers and amplified by the capillary force. The irregular pores and microroughness of nanofiber surface present in the sponge also promoted the sorption (Gui, Li et al. 2011). The sorption is also applied to pump oil of higher viscosity but with slower uptake rate or longer sorption time.

Figure 6.6 Video snapshot showing the sorption of a) isooctane (colorless) and b) pump oil by sponge.

6.3 Sorption Removal Efficiency of Carbon-Silica Sponge

The high porosity and selective wettability of carbon-silica sponge make it a favorable sorbent material for uptake of spilled oils and other organic solvents. To

characterize the sorption performance of the sponge, the sorption capacities for various kinds of commercial petroleum products (e.g. pump oil), fats (e.g. olive oil) and organic solvents (e.g. DMF) were studied. The results showed that electrospun carbon-silica sponge exhibits high sorption capacities of 65 to 140 times their own weight with larger sorption capacities for liquids of higher density (e.g. benzyl alcohol) (Figure 6.7a-b). However, there is no apparent relationship between sorption capacity and viscosity observed (Figure 6.8). The observed high sorption capacity can be ascribed to high porosity and low density of the sponge.

Figure 6.7 a) Sorption capacity of the sponge for a range of oils and organic solvents. b) The proportional relationship between sorption capacity and liquid density.

Figure 6.8 The variation of sorption capacity of carbon-silica sponge over the liquids with different viscosities.

Compared to other advanced carbon-based adsorbents, the sorption capacity of the electrospun sponge is outstanding. It is higher than spongy graphene (20-86 times) (Bi, Xie et al. 2012), hydrothermal-derived carbonaceous nanofiber (CNF) sponge (40-139 times) (Liang, Guan et al. 2012; Wu, Li et al. 2014) and comparable to that of graphene/carbon nanotube (CNT) hybrid foam (80-130 times) (Dong, Chen et al. 2012) and CNT sponges (80-180 times) (Gui, Wei et al. 2010). However, it is still considerably lower than those of bacterial cellulose-derived CNF sponge (106-312 times) (Wu, Li et al. 2013), ultralight graphene framework (200-600 times) (Zhao, Hu et al. 2012) and the synergistically assembled carbon sponges (215-743 times) (Sun, Xu et al. 2013) which are lower in density. More sorption capacity comparison between various kind of sorbents can be found in Appendix B. Nevertheless, owing to the simplicity and versatility of the technique, sponge fabricated in this work is expected to be easily scaled-up for industrial applications at relatively low cost.

Table 6.1 Sorption Capacity Comparisons between Different Carbonaceous Materials Using DMF as Sorbate

Materials	Sorption Capacity(g/g)
CNF membrane	10.2
Carbon-silica nanofiber membrane	11.6
Carbon-silica nanofiber sponge	64.9

To elucidate the effect of silica, specific surface area as well as total pore volume to the sorption capacity, flat-sheet carbon-silica nanofiber membrane, pure CNF membrane and carbon-silica sponge were fabricated and used to compare their sorption capacities of dimethylformamide. The result shows that the sponge exhibited the highest sorption capacity whereas both carbon-silica nanofiber membrane and pure CNF membrane have similar sorption capacities (Table 6.1). Compared to the sponge, the flat-sheet membranes are denser and have lower pore volume. Thus, lower sorption capacities were resulted. Furthermore, BET analysis reveals that the carbon-silica nanofibers and pure CNFs have similar dominant pore size with specific surface area being 41.8 and 125.2 m²/g, respectively. The carbon-silica nanofibers have lower surface area because they have larger fiber diameter (481±57 nm vs 252.8±26.2 nm)(Tai, Gao et al. 2014). However, the CNFs with larger surface area did not exhibit higher sorption capacity. This suggests that neither specific surface area nor addition of silica have predominant effect to the sorption capacity. As previously reported (Tai, Gao et al. 2014), silica only serves as a "softener" that improves the flexibility and toughness of CNFs. Therefore, it can be concluded that that the excellent sorption capacity of sponge does not stem from the micropores of the nanofibers but from the macroporous structure of the sponge.

The sorption kinetics process of the carbon-silica sponge can be described by the second-order model which is expressed as $1/(Q_m - Q) = 1/Q_m + Kt$, where Q is the sorption capacity at time t, Q_m the maximum sorption capacity, t the sorption time and K the sorption constant that is dependent of sorbate viscosity. Based on the

model, the fitting results are plotted in Figure 6.9 and the fitted parameters are provided in Table 6.2. The results show good agreement with the experimental data. For dimethylformamide (0.92 cP), the maximum sorption capacity can be achieved within 20s with a sorption constant being $1.1 \times 10^{-2} \text{ s}^{-1}$. However, it takes about a minute for highly viscous pump oil (125 cP) to reach the maximum sorption capacity. This is because the viscous pump oil penetrates relatively slower through the sponge. The discrepancy in time taken to reach saturation sorption capacity indicates the viscosity-dependent property of the sponge. Notwithstanding, the sorption rate is still comparable to or even faster than many other reported sponge-like sorbents such as CNF aerogel (Wu, Li et al. 2014), CNT sponge (Gui, Li et al. 2011) and ultra-flyweight carbon aerogel (Sun, Xu et al. 2013).

Figure 6.9. Sorption kinetics of different pollutants adsorbed by the carbon-silica sponge: a) dimethylformamide and b) pump oil.

Table 6.2 Fitting Parameter for Sorption Kinetic of Carbon-Silica Sponge

Sorbates	Q_e (g/g)	K (s^{-1})	r^2
Dimethylformamide	70.92	0.011	0.99
Pump Oil	67.11	0.003	0.99

6.4 Recyclability of Carbon-Silica Sponge

Recyclability of the carbon-silica sponge and recovery of the sorbed oils and organic solvents, which are important requirements for cost-effective spilled oil cleanup, were evaluated. Effectively, the sorbed oils can be harvested simply by compressing the sponge. As seen in Figure 6.10, the acetone (red-dyed) adsorbed by the sponge can be easily squeezed out under compression.

Figure 6.10 Digital photograph of the carbon-silica sponge regeneration by mechanical compression. Acetone was used and dyed with red for clear presentation.

After the compression, the sponge was densified and its volume was substantially reduced. To recover the sponge, solvents or oils can be introduced. Figure 6.11 demonstrates that a sponge that was used to adsorb isooctane was densified by compression in order to squeeze out the sorbed isooctane. The densified sponge was swelled immediately upon addition of isooctane droplets. After drying out, the sponge can be reused for next few rounds of sorption. The squeezing-swelling process can be repeated many times, hence making the sponge highly recyclable.

Figure 6.11 Photograph showing densification of the sponge and the subsequent recovery upon isooctane sorption and/or after drying.

The reversible structural deformation of the sponge is engendered by the randomly distributed carbon-silica nanofibers. As a result, the formation of van der Waals interaction between them is prohibited. Therefore, as the liquid is re-adsorbed into the macropores within the sponge, the nanofibers are readily pushed away (Gui, Wei et al. 2010), resulting in a swelling process. It is noteworthy that the shape recovery is not 100% if the volume compression exceeds 90%.

Cyclic distillation was also employed as an alternative approach to concurrent recycling of pollutants and sponge regeneration. For demonstration, isopropyl alcohol (IPA) with a boiling point of 82.5° was sorbed by the sponge and subsequently boiled off at 85° for 10-15min in oil bath to vaporize IPA. This sorption-distillation process was repeated for 10-11 times and the results were shown in Figure 6.12. As seen, more than 98% of IPA can be removed or recovered after each cycles while sustaining a constant sorption capacity of approximately 37 g/g. It is noteworthy that no significant structural damage of sponge was observed throughout the recovery process.

Figure 6.12 The recyclability and recovery studies of carbon-silica sponge over 10-11 cycles of distillation by using isopropyl alcohol as sorbate.

Additionally, a sorption-squeezing test was also performed for comparison. It was observed that the sponge could adsorb IPA up to 734 mg in the first cycle. However, there were 178 mg IPA remained in the sponge after squeezing because not all IPA can be reclaimed by mechanical extrusion due to the interactions between IPA and the sponge (Figure 6.13). As a result, only a partial bulk volume is available for the subsequent sorption process. The reduced sorption volume can be reflected in the substantial reduction of the sorbed mass and recovered mass in the second cycle of sorption. It was observed that the sorbed mass and recovered mass were dropped 28% and 34%, respectively. Nevertheless, from second cycle onwards, the mass obtained from the sorption and recovery procedures became stable and were maintained at approximately 560 mg and 400 mg, respectively.

Figure 6.13 The recyclability and recovery studies of carbon-silica sponge over 10-11 cycles of squeezing by using isopropyl alcohol as sorbate.

In regard of the sponge's structural stability, it was found that the sponge slightly disintegrated via delamination after 6 times of mechanical squeezing. However, the

fiber morphology of the sponge is very well preserved (Figure 6.14a-b). In overall, the as-prepared sponge has displayed excellent sorption performance and recyclability. For the purpose of practical applications, both squeezing and distillation are good ways to be used for recycling the sorbed pollutants and sponge regeneration. Specifically, squeezing is more effective for recovering oils or pollutants with high boiling point (although extra care has to be taken when performing squeezing) whereas distillation is promising when working with volatile pollutants.

Figure 6.14 FESEM image of electrospun carbon-silica nanofibers after 6 cycles of a) distillation and b) squeezing.

6.5 Practical Implications on Oil Spill Cleanup

As shown, the self-assembled electrospun carbon-silica sponge is lightweight and highly compressible. During transport, the sponge can be compressed to minimize its volume so that more sponges can be carried in a trip whereas the lightweight property ensures lower fuel consumption of vehicle. Therefore, it permits easy and cost-effective transportation. Additionally, since the oil-saturated sponge can be regenerated quickly and readily, the material cost is reduced. The low density sponge may be difficult to collect after they are spread on the water as it can readily disperse by wind. However, this problem can be avoided simply by packing them in an appropriate material (Figure 6.15).

On the other hand, to work effectively under harsh conditions such as oil spill occurred in a polar zone or a high temperature oil leakage, the sorbent must be

resistant to elevated temperature or chemically inert. In this regard, the as-prepared sponge could meet the requirement because it has been reported that the wettability and flexibility of the carbon-silica nanofibers are largely unaffected under high temperature and super low temperature, respectively (Tai, Gao et al. 2014). To confirm, the sponge was repeatedly immersed in liquid nitrogen (-196°C) for seconds and bended. It was observed that the shape and volume of the sponge was remained unchanged. Besides that, the sponge flexibility was not deteriorated.

Figure 6.15 Digital photograph showing the selective removal of oil from water by carbon-silica sponges packed in a tea bag. Sponges were packed to facilitate its collection after use. Water was contaminated with red-dyed vegetable oil.

Figure 6.16 FESEM image of electrospun magnetic carbon-silica-magnetic particle nanofibers. Inset shows the magnetic property of the resulting sponge.

The electrospinning is a versatile technique that allows manipulation of chemical composition within the nanofibers. This implies that carbon-based nanofibrous sponge with favorable functions can be designed to tackle with the selective removal of oil under various conditions. To exemplify, a magnetic sponge composed of carbon-silica-magnetic particle nanofibers has been fabricated by adding acetyl acetone iron (AAI) into the electrospinning precursor solution (Figure 6.16). The sponge with magnetic responsivity could ease the selective removal of oils from water in a manner that the sponge can be driven towards the area of contamination with minimal energy consumption. With this technique's versatility, it is expected that other interesting and advanced functionalities can also be imparted to the sponge and hence promote the ease of selective removal of oil from water.

6.6 Conclusions

Sponge composed of interconnected 3D structure of carbon-silica nanofibers has been fabricated by using a versatile, economical and easily scalable electrospinning technique. The sponge exhibits some unique features including high porosity, ultra-light weight, low density, hydrophobicity and oleophilicity and high compressibility. These inherent properties make the sponge a promising material as adsorbent for efficient oil spill cleanup. The sorption tests indicate that the sponge displays a high sorption capacity and fast uptake rate for various kinds of petroleum-derived products and organic solvents. Due to its good mechanical stability and compressibility, the sponge could be readily regenerated by means of either squeezing or distillation in the meantime recovering the sorbed pollutants. It is anticipated that the sponge has numerous applications in environmental remediation, particularly in oil spill cleanup.

Chapter 7 A Hierarchically Nanostructured TiO₂-Carbon Nanofibrous Membrane for Gravity-Driven Oil-Water Separation

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M.H. Tai, Gao, P., B.Y.L Tan, D.D. Sun, and J.O. Leckie (2015) "A Hierarchically-Nano Structured TiO₂-Carbon Nanofibrous Membrane for Concurrent Gravity-Driven Oil-Water Separation". International Journal of Environmental Science and Development, vol. 6, no. 8, pp. 590-595.)

Figure 7.1a shows the bare carbon-silica nanofiber membrane prepared by electrospinning. Prior to TiO₂ coating via hydrothermal treatment, the nanofibers are relatively thin with diameter of ~500 nm. In addition, they have smooth surface. After coating, as shown in Figure 7.1b, the carbon-silica nanofibers are wrapped by assemblies of TiO₂ nanosheets that make the surface very rough. The coating also doubles the nanofiber diameter to ~1μm. TEM observation reveals that the TiO₂ nanosheets wrap around the nanofiber and exhibits a structure similar to core/sheath structure (Figure 7.1c). The TiO₂ nanosheets densely grown on the nanofiber are in polycrystalline phase. The lattice fringe has an interlayer distance of 0.35nm which can be assigned to the (101) plane in anatase TiO₂ (inset of Figure 7.1c) This can be further confirmed by the XRD patterns shown in Figure 7.1d. All the diffraction peaks are assigned to anatase TiO₂ (according to the JCPDS card file. 21-1272) except for the small peak at around 32° that might be caused by the impurity of brookite TiO₂.

The wetting behavior of the fabricated membrane was observed by measuring the contact angle in air (CA_{w/a}) and oil contact angle in water (CA_{o/w}). The results indicate that the membrane has a CA_{w/a} close to zero and CA_{o/w} of ~157°, manifesting the superhydrophilicity and underwater superoleophobicity property of the membrane (Figure 7.2a). Furthermore, the membrane possesses high flexibility. As seen in Figure. 7.2b, the membrane can be bended at an angle of 90° without loss of structural integrity. This phenomenon can be attributed to the entanglement of the continuous and flexible carbon-silica nanofibers (Tai, Gao et al. 2014).

7.1 Characterization of TiO_2 -Nanosheet Anchored Carbon-Silica Nanofiber Membrane

Figure 7.1 FESEM image of electrospun CNFs a) before and b) after TiO_2 nanosheets coating. c) TEM image showing TiO_2 nanosheets are coated onto the surface of carbon-silica nanofibers. d) XRD pattern of TiO_2 nanosheets.

Figure 7.2 a) Photograph of a water droplet on the membrane in air (top) and oil droplet depositing on the membrane in water (bottom). b) The digital photograph showing excellent membrane flexibility.

7.2 Surface Wetting Property of TiO₂-Nanosheet Anchored Membrane

To further examine the wettability of the as-fabricated membrane, the spreading process of a water droplet is recorded by a VCA instrument operated in dynamic mode at a capture speed of 30 frames per second. As shown in Figure 7.3, the membrane shows a high affinity towards water (also due to the strong capillary effect with water) where the water spreads out rapidly at the moment it touches the membrane surface. This wetting property has resulted in a water contact angle close to zero. The entire wetting process only takes 132 ms to complete, thus suggesting that the membrane is superhydrophilic.

Figure 7.3 Spreading and permeating process of a water droplet on the membrane.

The membrane also exhibited underwater superoleophobic character with very low adhesion to oil. When dichloromethane (DCM) was injected onto the membrane that was tilted at an angle of $\sim 10^\circ$ and immersed in methylene blue-dyed aqueous solution, it is observed that DCM droplets rolled off the surface at high speed. It is also observed that the DCM droplet could be readily detached from the surface, suggesting that the membrane has low adhesion to oil. This low adhesion to oil is due to the reduced liquid-solid contact area induced by roughened surface and the formation of water layer which will be discussed in the later section. In contrast, DCM droplets seeped into when came into contact with a pristine CNF membrane (Figure 7.4a and b).

The change in wetting behavior of the membrane can be explained by the standard Wenzel and Cassie-Baxter model. The pristine carbon nanofibrous membrane with smooth surface is underwater oleophilic. In this case, the surface can be fully-wetted by oil and it falls into the Wenzel state. However, after coating with TiO₂

nanosheets, the membrane becomes superhydrophilic and underwater superoleophobic. This is due to the micro/nanohierarchical structure arising from the dense array of vertically aligned, interconnected TiO₂ nanosheets that roughen the surface as well as the intrinsic hydrophilic property of TiO₂. We hypothesized that the membrane with enhanced roughness can then trap water between oil droplet and the surface, yielding an oil-proof surface that prevents oil wetting. As a result, the Cassie-Baxter state occurs.

Figure 7.4 Video snapshot demonstrating the selective wettability characteristic of a) TiO₂ nanosheet-anchored carbon-silica nanofiber membrane and b) pristine carbon-silica nanofiber membrane.

Such wetting transition from Wenzel to Cassie-Baxter regime can be described by the Cassie-Baxter model where the contact angle is given by $\cos\theta' = f_{so}(R_f\cos\theta + 1) - 1$, where $\cos\theta'$ is contact angle of oil in water for a rough surface, θ is contact angle of oil in water for a smooth surface, f_{so} is fractional solid-oil area, R_f is non-dimensional parameter of surface roughness. From the above equation, one can see that solely increasing the surface roughness is insufficient to change the sign of $\cos\theta$ from positive (oleophilic) to negative (oleophobic). However, it is possible if f_{so} is decreased to an extent that it results in a negative value on the left side in the equation. Therefore, the observed underwater superoleophobicity can be ascribed to the decreased f_{so} . The change in wetting behavior of membrane surface is illustrated in Figure 7.5.

Figure 7.5 Illustration of wetting transition in underwater superoleophobic surface of a TiO₂-coated carbon-silica nanofiber membrane.

To verify the presence of oil-proof surface due to the formation of water barrier, we conducted a wetting test to the membrane with and without TiO₂ nanosheets. In the test, droplets of water was first dropped onto the membranes followed by olive oil. For pristine carbon nanofibrous membrane, we observed that the surface could be wetted by water before it contacted with oil. As oil came into contact with the membrane, oil replaced water and the membrane surface was turned into hydrophobic. This suggests that the membrane has a stronger affinity for oil than water. For TiO₂-coated carbon nanofibrous membrane, it exhibits a stronger affinity for water than oil because throughout the test, the membrane remained hydrophilic. The oil did not wet the surface and it could be easily washed away by rinsing with water. Hence, it is postulated that as the dry TiO₂-coated membrane contacts with the wetting phase, a liquid layer will be immediately formed on the surface. This liquid layer serve as a repulsive barrier that prevents the membrane surface from being wetted by the next wetting phase. To verify this postulation, a similar wetting test where the TiO₂-coated membrane was first wetted by olive oil followed by water, was repeated. It is observed that the membrane became hydrophobic and oleophilic. The subsequent water wetting became impossible. The results is clearly shown is Figure 7.6. Combined with the earlier discussion, it is suggested that the large cavities in the rough surface coupled with the hydrophilic property of TiO₂ facilitate the formation of water layer by trapping water between solid surface and oil droplet. By that, the chance for oil droplet to contact directly with the solid

surface is lowered, as depicted in Figure 7.5. The membrane with such wetting behavior can be applied for control separation of oil and water.

Membrane Type	Pure carbon nanofibrous membrane		TiO ₂ -coated carbon nanofibrous membrane	
Initial Wetting Phase	Water	Oil	Water	Oil
	Water on dry membrane	Oil on dry membrane	Water on dry membrane	Oil on dry membrane
	Oil on water-wetted membrane	Water on oil-wetted membrane	Oil on water-wetted membrane	Water on oil-wetted membrane
	Water on water-wetted membrane	Oil on oil-wetted membrane	Water on water-wetted membrane	Oil on oil-wetted membrane

Figure 7.6 Surface wetting behavior of carbon-silica nanofiber membrane with and without TiO₂ nanosheets.

7.3 Oil-Water Separation Performance of TiO₂-Nanosheet Anchored Membrane

Unlike those conventional pressure-driven membranes, it is found that the as-fabricated TiO₂ nanosheet-anchored carbon-silica nanofiber membrane is capable of separating oil from water without requiring additional pressure. For demonstration, both free oil and water and surfactant stabilized oil-in-water emulsions were prepared and poured individually into a home-made separation apparatus in which the as-prepared membrane was sandwiched between a funnel and a flask as shown in Figure 7.7. The oil-water emulsions were stabilized by using Triton X-100 (hydrophile lipophile balance, HLB=13.5). For separation of free oil and water, water is added to the funnel immediately followed by the oil. It is observed that, within a few seconds, the water passed through the membrane by gravity while the oil was retained above the membrane (Figure 7.7). Upon water contacted with the membrane, the surface is immediately wetted (as evidenced from the instantaneous water spreading behavior shown in Figure 7.3) and a water barrier is formed. The formation of water layer prevents the wetting of the incoming oil thus reduces the oil area fraction along the surface. Similarly for oil-in-water emulsions, water

permeated through the membrane within a few seconds whereas the oil was retained by the membrane. The collected permeate was very clear compared to the highly turbid emulsion feed (Figure 7.8). It is observed that the oil retained on the membrane surface can be easily washed away by rinsing the membrane with water. This may be owing to the fact that the oil has low adhesion with solid surface. On the contrary, oil retained on a pristine carbon-silica nanofiber membrane adhered to the surface. It is observed that the membrane eventually lost its water permeability. The oil-water separation was unable to continue after 2-3 times of operation (picture not shown).

Figure 7.7 Batch separation of free oil and water. Separation apparatus with olive oil added above water a) before and b) after separation by gravity. Inset, water permeates through the membrane while olive oil is retained.

Figure 7.8 Gravity-driven separation of oil-water mixture a) before and b) after separation. Inset, water permeates through the membrane while olive oil is retained.

Figure 7.9 Left: A representative optical microscopy image of the Triton X-100 stabilized feed mixture of vegetable oil, water. The oil droplet has a size range of 5-85 μm . Right: A representative optical microscopy image of the permeate after separation. Result shows that the membrane can separate oil droplets of <10 μm .

The separation efficiency of the membrane is characterized by measuring the water purity in the permeate. The water purity was estimated based on the weight loss of the permeate after heating at 105 °C. The results show that the permeates from oil-water separation have water purity higher than 99.5 %. The water purity percentage of the permeates from the separation of various oils is shown in Figure 7.10.

Figure 7.10 The water purity in the filtrate after permeating a series type of oil-water mixtures through the as-fabricated TiO_2 nanosheet-anchored membrane.

The separation efficiency was also estimated by comparing the density of permeates with the density calibration curves. In the curve, different oil compositions (0wt%, 1wt%, 2wt%) in the oil-water mixtures are plotted against the corresponding densities of the mixtures. The densities of the permeates from the separation of free vegetable oil-water, olive oil-water, used pump oil-water and hexadecane-water were measured to be 1.006 ± 0.005 g/ml, 1.008 ± 0.002 g/ml, 1.006 ± 0.0004 g/ml and 1.007 ± 0.001 g/ml, respectively. Comparing these values with the calibration curves shows that the permeates have oil content significantly lower than 1wt% (Figure 7.11).

Figure 7.11 Density of various oil-water mixtures as a function of oil composition.

To further confirm, TGA was performed by using the permeates obtained from free vegetable oil and water as well as vegetable oil-in-water mixture. Pure vegetable oil was also used for comparison. As seen in Figure 7.12, after heating at 100°C for 30 min, the weight of samples was decreased close to zero percent, revealing that almost all the water was boiled off. The results show that the permeates obtained from free vegetable oil and water and vegetable oil-in-water mixture contain only ~0.001 wt% and ~0.33 wt% vegetable oil, respectively. These experimental results indicate that the membrane can separate oil from water with very high separation efficiency (>99%).

Figure 7.12 TGA data for the feed and the permeates after separation of various mixtures (free water and oil and oil-in-water emulsion).

The breakthrough height ($H_{\text{breakthrough}}$), defined as the allowable maximum height of the liquid before it permeates through the separation medium, was used to further characterize the separation ability of the membrane. A superhydrophilic and superoleophobic membrane with large pore size usually results in low breakthrough height of oil or possesses no oil-water separation capability. In practice, oil will gradually accumulate on a separator and exert corresponding pressure to the beneath layer of wetting phase that could engender the permeation of oil through the membrane. Hence, design of a membrane with high breakthrough height of oil is favorable and more practical. Theoretically, $H_{\text{breakthrough}}$ can be obtained by using the relationship: $P_{\text{breakthrough}} = \rho g H_{\text{breakthrough}}$. To predict $P_{\text{breakthrough}}$, the equation derived by Kota et al (Kota, Kwon et al. 2012) was used in this work. According to the equation, for a membrane already saturated by the wetting phase, the required $P_{\text{breakthrough}}$ for the non-wetting phases is given by $(2R\gamma/D^2) * ((1-\cos\theta) / (1+2(R/D)*\sin\theta))$ where R is the cylinder radius, γ the interfacial tension between the wetting phase and the non-wetting phase, D the half of the distance between fibers and θ the contact angle of the non-wetting phase on the solid surface. For the case of free olive oil (average density = 860 g/ml) and water separation, $H_{\text{breakthrough}}$ is predicted to be 3.88 m ($P_{\text{breakthrough}}=32724$ Pa) by substituting $R= 0.5 \mu\text{m}$, $D= 0.77 \mu\text{m}$, $\gamma = 16.42$ mN/m and $\theta = 152.6^\circ$ into the equation. The D is estimated to be $0.77 \mu\text{m}$ (or $2D = 1.54 \mu\text{m}$) based on the rejection efficiency of polystyrene particles by

the membrane. Results showed that the membrane is capable of rejecting 96% of 2.061 μm particles and 72.5 % of 1.025 μm particles based on the TOC removal result. Hence, the membrane has a pore size range of $1.025 \mu\text{m} < x < 2.061 \mu\text{m}$. For calculation, the average pore size (2D) of the membrane is estimated to be $(2.061+1.025)/2 \approx 1.54 \mu\text{m}$. For comparison, the $H_{\text{breakthrough}}$ is experimentally measured by using free oil and water. It is observed that olive oil started permeating through the membrane when a pumping pressure of around 30659 kPa (230 mmHg) was applied. This indicates that the experimental $H_{\text{breakthrough}}$ for olive oil is around 3.63 m which closely matches the theoretical value.

Figure 7.13 The effect of TiO_2 coating to the effective fiber radius (R) and intercylinder spacing ($2D$). a) Before TiO_2 coating, the fiber diameter is approximately $0.5 \mu\text{m}$ and the membrane has larger pore size (smaller R but larger D). b) After TiO_2 coating, the fiber diameter is increased to $1 \mu\text{m}$ and the membrane pore size is considerably reduced (larger R but smaller D).

The high $P_{\text{breakthrough}}$ value implies that the membrane is highly resistant to pressure perturbations. The small pore diameter is expected to be the major contributing factor. The electrospun membrane used in this work is capable of rejecting PS particles larger than 2.061 μm (up to 96 % rejection efficiency), implying that the membrane has small apparent pore size. Furthermore, after TiO_2 nanosheets were grown on the fiber, the spacing between fibers ($2D$) was shortened owing to the

increase in fiber diameter (R). The effect of TiO_2 coating can be illustrated in Figure 7.13. According to Kota's equation, as D becomes smaller and R is larger, a greater $P_{\text{breakthrough}}$ will be resulted.

7.4 Stability of TiO_2 -Nanosheet Anchored Membrane and its Permeate Flux

The chemical stability of the fabricated membrane was examined by investigating its changes with respect to the structural morphology, permeate flux and surface wettability after immersed in different pH solution. Prior to the analysis, the membranes were separately immersed in solutions with pH of 1, 7, and 14 for 7 days. The membrane immersed in pH 7 solution was used as a reference.

Figure 7.14 The pH stability of the membranes in terms of permeate flux, water contact angle in air and oil contact angle in water. The insets show the morphology of the membrane at each pHs.

Interestingly, the membrane was able to sustain a $\text{CA}_{\text{o/w}}$ above 150° after 7-day exposure to strong acid (pH 1) and strong alkaline (pH14) conditions. In addition, all of the membranes remained $\text{CA}_{\text{w/a}}$ close to zero (Figure 7.14). As a water droplet ($5\mu\text{l}$) is added to the membrane, it quickly spreads out and wets the membrane. The wetting process can be completed in very short time: 198ms and 462ms for

membrane immersed in pH 1 and 14, respectively (Figure 7.15). This observation study suggests that the superhydrophilic and underwater superoleophobic character of the membrane can be preserved under harsh chemical conditions.

Figure 7.15 The wetting behavior of water droplets on membrane surface after treated with different pHs.

The permeate flux of the membranes was also determined. As seen in Figure 7.14, all three membranes maintain high permeate flux between 400-700 L/m²-hr. These values are comparable to other MF membranes reported elsewhere (Kołtuniewicz and Field 1996; Hyun and Kim 1997). The variation in permeate flux may be a consequence of the inconsistent membrane thickness. According to Hagen-Poiseuille equation, as the membrane thickness is small, the allowable flux of water permeating through the membrane is higher and vice versa. SEM observation reveals that the average thickness of membrane immersed in pH 1, 7, and 14 is 127.7±5 μm, 188.7±5 μm, and 124.3±2 μm, respectively. This is in good agreement with the permeate flux result. Structurally, the membrane's morphology is also well-preserved. There is no noticeable change in the TiO₂ nanosheets coated on the fiber surface. The surface is remained porous and rough as previously seen in inset in Figure 7.14.

Figure 7.16 TGA data for pristine CNFs and TiO₂-coated CNFs.

To study the thermal stability of the fabricated membrane, TG analysis was performed. The result shows that the membrane was stable at a temperature up to 500 °C in air (beyond which it starts to degrade) (Figure 7.16). Additionally, TG analysis provides information on the mass percentage of each species in the sample. As seen, the pristine CNFs has a residual weight of ~2.65% after TGA. The residue is contributed by the SiO₂ present in the sample. On the other hand, the TiO₂-coated CNFs show a residual weight of ~47.5% due to the presence of both inorganic SiO₂ and TiO₂ in the sample. This indicates that the TiO₂-coated CNFs has TiO₂ content of ~45%. The wetting property was studied after the membrane was heated at 500 °C in N₂. It was found that the value of CA_{o/w} was remained at above 150°, showing that the membrane wettability was thermally stable. Furthermore, It was also found that the TiO₂ assembly remained stable even after 20 min ultrasonic irradiation, as seen in Figure 7.17.

Figure 7.17 FESEM image of TiO_2 -coated carbon nanofibrous membrane after ultrasonication for 20 mins.

7.5 Conclusions

A novel TiO_2 -nanosheet anchored carbon-silica nanofiber membrane with superhydrophilic and underwater superoleophobic character by using solvothermal method has been fabricated. The oil-water separation test shows that the as-fabricated membrane is capable of separating a range of different oil-water mixtures (free water and oil and oil-in-water emulsion) at high separation efficiency. Similar with other surface modified meshes, the fabricated membrane permits gravity-driven oil-water separation while sustaining high permeate flux. On top of that, the membrane has the advantage of high breakthrough height for oil which is essential for large-scale application. On the other hand, the excellent chemical and thermal stability allow the membrane to function well even under harsh conditions. Therefore, it is anticipated that the membrane will have numerous applications, including oil spill cleanup, oil purification and oily water treatment.

Chapter 8 Carbon-Silica Composite Nanofiber Membrane for High Flux Separation of Water-in-Oil Emulsion - Performance Study and Fouling Mechanism

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8.1 Characterization of Carbon-Silica Nanofiber Membrane

The as-fabricated carbon-silica nanofiber membrane used in the experiment has an average fiber diameter of 481 ± 57 nm. The bubble point analysis reveals that the membrane has a mean pore diameter of 1.203 ± 0.251 μm with the smallest pore size being 0.902 ± 0.182 μm . Figure 8.1 shows the representative pore size distribution of the membrane.

Figure 8.1 Representative Pore Size Distribution of Silica-Carbon Nanofiber Membrane.

8.2 Pure Oil Flux

The permeation flux of pure hexadecane at various operating pressures is shown in Figure 8.2. As seen, the flux was increased with increasing applied pressure in a nonlinear manner. It appeared that the flux is approaching a plateau at higher pressure. Due to its unique characteristics of high porosity and interconnected open pore structure, the electrospun carbon-silica nanofiber membrane is capable of producing a large amount of oil at very low pressure. For instance, a high flux of 2481 L/m²-hr could be readily achieved at a pressure of 0.07 bar which is equivalent to 35961 L/m²-hr-bar. The discussion in the later section shows that the electrospun membranes could achieve a flux greater than 100 L/m²-hr for water-in-oil emulsions. This is higher than the other reported membranes which are in different structures (Scott, Mahmood et al. 2000; Scott, Jachuck et al. 2001; Ezzati, Gorouhi et al. 2005; Hu and Scott 2008) and materials (Hu and Scott 2007). For example, under its optimum operating conditions, a hydrophobic polytetrafluoroethylene (PTFE) membrane is only capable of producing a permeate flux smaller than 100 L/m²-hr (Ezzati, Gorouhi et al. 2005). Such high oil throughput makes the electrospun membrane a potential candidate for energy efficient treatment of waste oil.

Figure 8.2 Pure oil flux as a function of operating pressure.

Figure 8.3 shows the representative filtration model of an electrospun nanofiber membrane. It is observed that the flux declines very rapidly with operation time. This is followed by a gradual flux decline before it reaches its equilibrium state. This filtration model is similar to that of the colloidal solution (Zhang and Song 2000). However, depending on the operating conditions including cross-flow velocity and applied pressure, the rate of flux decline, initial flux, rejection efficiency and the final flux will vary. These factors have direct impact to the performance of the electrospun membrane.

Figure 8.3 Typical Oil Flux Model of An Electrospun Nanofiber Membrane. Curve is obtained by performing smoothing to irregular and noisy data.

8.3. Effect of Applied Pressure on Permeate Flux

Figure 8.4 shows variation of the initial permeate flux at applied pressure from 0.07 to 0.206 bar when water-in-oil emulsion was used. It can be clearly seen that the initial flux increased with increasing applied pressure. However, a different trend was observed when it comes to the final flux which is measured at the end of the runs. As seen in Figure 8.5, the permeate flux was reduced as the pressure was increased to 0.138 bar. However, the flux was bounced back as pressure was further increased to 0.275 bar, reaching a value of 1839 L/m²-hr. Obviously, the pressure has both positive and negative effect on the permeate flux which can be explained from the aspect of breakthrough pressure.

Figure 8.4 Initial Oil Flux Over A Range of Applied Pressure Under Constant Cross-Flow Velocity of 0.5421 m/s.

Figure 8.5 The Variation of Final Permeate Flux and the Corresponding Decline in Permeate Flux as a Function of Applied Pressure under constant Cross-flow Velocity of 0.5421 m/s.

A breakthrough pressure is defined as the maximum allowable pressure of a solute before it permeates through the membrane. As the pressure was lower than 0.138 bar, increasing the pressure decreased the permeate flux because more emulsified water-hexadecane droplets accumulated on the membrane surface due to increased build-up of concentration polarization layer. This effect is likely to squeeze the emulsion droplet into the membrane pore and eventually led to pore blocking that caused the flux to decline. Hence, the flux decline percentage was high. However, at pressure equal to and beyond 0.206 bar, increasing the pressure increased the flux due to the fact that the water-hexadecane droplets permeated through the membrane as observed during the experiments. In this pressure region, the percentage of flux decline was reduced at the expense of water rejection efficiency. To sustain production of high quality permeate, the membrane shall be operated at a pressure below 0.206 bar which is also the breakthrough pressure for hexadecane in this case.

Figure 8.6 Representative Optical Microscopy Image of a) Feed water-in-oil Emulsion and the Permeate Collected at b) 0.07 bar c) 0.138 bar and d) 0.275 bar.

Figure 8.6 shows the representative optical microscopy images of feed emulsion and permeates collected at different operating pressures. It is clearly seen that the as-prepared feed emulsion contains water-oil emulsion droplets of different sizes. After membrane filtration, no droplets were observed in the collected permeate except for that collected at 0.275 bar. It was observed that at 0.206 and 0.275 bars, emulsion droplets broke through the membrane and flowed into the permeate. Hence, it is postulated that the permeate collected at 0.206 bar also contains emulsion droplets. However, it is worth to note that the breakthrough pressure for emulsion droplets may vary with shear rate, surface tension coefficient and droplet viscosity. It is reported that at a fixed shear rate, the breakthrough pressure is higher for more viscous droplets (Darvishzadeh, Tarabara et al. 2013).

8.4 Effect of Cross-flow Velocity on Permeate Flux

The effect of cross-flow velocity varied from 0 to 0.8387 m/s on final flux under a constant pressure of 0.138 bar is shown in Figure 8.7. The results showed that higher cross-flow velocity gave rise to higher final permeate flux and therefore lower percentage in flux decline. This phenomenon could be explained by the increase in shear rate which is expressed as $S = 4Q/\pi r^3$, where Q is cross-flow volumetric rate (m^3s^{-1}), and r the inner radius of pipe (m). As cross-flow velocity was varied from 0 to 0.8387 m/s, the shear rate was increased from 0 to 2236.4 /s. This made the shear force sufficient to scour off the water-hexadecane droplets accumulated on the membrane surface. The retained water-hexadecane droplets could form a gel layer that added up additional hydraulic resistance to the total resistance and hence induced a pressure drop. The difference in flux decline observed in Figure 8.7 was a result of different cake layer thickness. At high shear rate, the gel layer thickness was kept minimum that the hydraulic resistance did not cause a significant pressure drop. Therefore, a higher final flux was resulted. A 34.8% flux decline was achieved when the cross-flow velocity was maintained at 0.8387 m/s. It is noted that cross-flow velocity operated beyond 0.8387 m/s is not feasible because the corresponding minimum pressure required is above 0.138 bar which exceeds the hexadecane breakthrough pressure.

Figure 8.7 The Variation of Final Permeate Flux and the Corresponding Decline in Permeate Flux as a Function of Cross-flow Velocity under constant Applied Pressure of 0.138 bar.

8.5 Membrane Fouling Characterization

To characterize the fouling mechanism, the internal and external fouling models derived from Darcy's law are employed. For internal fouling model, the corresponding resistance curve increases with an increasing slope over the time whereas external fouling model yields a curve with a decreasing slope. This offers a simple yet straightforward mean of identifying the membrane fouling mechanism.

Figure 8.8 Total Resistance as a Function of Time for Membranes Operated at Various Pressures under Constant Cross-flow Velocity of 0.5421 m/s. Curves are obtained by performing smoothing to irregular and noisy data.

Figure 8.8 shows the total resistance curve of the membrane operated at different pressures while keeping the cross-flow velocity unchanged. At 0.07 bar, the resistance curve increase with a decreasing slope throughout the entire experiment and is concave down. This indicates that the membrane was fouled externally. However, as the pressure was increased to 0.138 bar, the resistance curves are changed. Initially, the resistance increases with an increasing slope (concave up) until to the point of inflection (at 100 min), beyond which the resistance increases with a decreasing slope (concave down). This shows that the fouling is governed by internal fouling followed by external fouling. It is postulated that, during the early stage, the water droplets deposit within the pores (but do not permeate across the membrane), causing a corresponding decline in pore volume. As a result, the resistance rises rapidly. At approximately 100 min, most of the pores are blocked and the depositing droplets start to grow a layer on the membrane surface, engendering further increase in total resistance. During the surface deposition, it is likely that the water droplets aggregate into bigger droplets which serve as sites for

further deposition. It is noticed that there is a sudden resistance decline at 110 min. This might be due to the unexpected escape of water droplets from the membrane pore as a result of scouring effect during the permeate collection. Hence, it caused a temporary drop of total resistance before the water droplet deposition site was quickly refilled. After 110 min, the fouling layer started building up which led to the rapid rise in total resistance. Similarly, at 0.206 bar, the membrane is initially fouled from within for the first 85 min and then the growth of cake layer on the membrane surface induce the external fouling. It appear that resistance decreases after it reaches the maximum resistance at 135 min. This may be due to the permeation of water droplets that originally clog the internal pores across the membrane. The water droplets found in the permeate when collected at 0.206 bar could support this hypothesis. Lastly, when the pressure is increased to 0.275 bar, only external fouling dominates. This is because the applied pressure is sufficient enough to push the water droplets through the membrane. Under such condition, it is unlikely for the water droplets to deposit in the pores and thus the internal resistance cannot be built up.

On the other side, it is noted that the resistance curves for water-oil separation operated at 0.07 and 0.275 bar are similar. Except that the cake layer buildup takes place immediately on the membrane surface, both exhibit very steady resistance over the operation time. This is due to the slow growth of cake layer. At low pressure (0.07 bar), the liquefied cake layer could be scoured off whereas water droplets permeate through the membrane at high pressure (0.275 bar). Both situations do not favor the growth of cake layer and hence the resistance cannot be built up. However, it can be deduced that the cake layer thickness is larger at 0.275 bar than at 0.07 bar because the total resistance is greater at 0.275 bar. For 0.138 and 0.206 bar, the total resistance starts off lower but increases to 2-4 times the resistance at 0.07 and 0.275 bar by the end of runs. This is because the total resistance combines the resistance from both internal and external fouling.

Figure 8.9 Total Resistance as a Function of Time for Membranes Operated at Various Cross-Flow Velocities under Constant Operating Pressure of 0.138 bar. Curves are obtained by performing smoothing to irregular and noisy data.

The effect of cross-flow velocity to the membrane fouling was also studied. Figure 8.9 shows the total resistance curve when the membrane was ran at 3 different cross-flow velocities. At 0.5421 m/s, the membrane fouling is a combination of internal and external fouling. However, the external fouling prevails when the cross-flow velocity is increased to and above 0.769 m/s. At high cross-flow velocities while keeping relatively low pressure, the chance for the water droplets to clog the pores or accumulate on the membrane surface is lessened because the tangential feed flow traveling across the membrane surface will wash away the retained droplets. By that, the accumulation of cake layer can be mitigated or even eliminated. This can be manifested from the relatively low total resistance at 0.769 and 0.8387 m/s as compared to that at 0.5421 m/s. Furthermore, it is observed that the accumulation rate of cake layer is lower when a higher cross-flow velocity is applied. At 0.5421 m/s, the induced scouring effect is insignificant so that pore blocking can still take place.

8.6 Fitting of Membrane Fouling Models

To determine the model parameters, the fouling models are applied to the experimental data. For internal fouling, models for standard pore blocking and complete pore blocking are applied to the experimental data occurring before the point of inflection. However, for external fouling, cake filtration model is employed after point of inflection. For the cases in which cake filtration is deemed to be governing fouling mechanism for the entire time period, only cake filtration model is applied. Table 8.1 summarizes the values of fouling constants determined from the slopes, initial permeate flux determined from the intercepts together with the regression coefficients. Figure 8.10-8.11 show the fitting of each model to the data. Note that the regression of data in the figures was not performed for the entire experiment although the dominant mechanism is deduced to be external fouling. This is owing to the fact that the rejection coefficient was not constant for earlier times (Tracey and Davis 1994).

As seen in the table, cake filtration model fit the data very well with regression coefficient (r^2) greater than 99% for all cases. However, the initial flux obtained from the intercepts does not yield accurate values. This is simply because the cake filtration model applies at later times instead of initial times. Since K_3 is proportional to specific cake resistance according to $K_3 = \mu C_3 \rho / (2A^2 \Delta P)$ where μ is solution viscosity, C_3 specific cake resistance, ρ the mass of cake deposited per volume filtrate, A membrane surface area and ΔP the transmembrane pressure (Belter, Cussler et al. 1987), a lower value of K_3 means that the specific cake resistance is lower. Among the various operating conditions, It is found that the membrane operated at 0.138 bar and 0.8387 m/s experiences from the least resistance resulted from cake filtration whereas the highest cake resistance is resulted when cross-flow velocity is 0.5421 m/s under the same applied pressure. In fact, K_3 decreases with increasing cross-flow velocity. As mentioned earlier, the plausible explanation can be the shear effect at high cross-flow velocity. These results are in good agreement with the total resistance data.

Table 8.1 Internal and External Fouling Model Constants from Linear Regression of Filtration Data.

Cross-flow Velocity (ms^{-1})	Pressure (bar)	Initial Permeate Flux, J_o ($\text{L/m}^2\text{-hr}$)	Complete Blocking Model			Standard Blocking Model			Cake Filtration Model		
			J_o	K_1 (L^{-1})	R^2	J_o	K_2 (min^{-1})	R^2	J_o	K_3 (min/L^2)	R^2
0.5421	0.07	2014.3	N.A	N.A	N.A	N.A	N.A	N.A	420.2	13.3	0.993
0.5421	0.138	2817.3	2946.5	5.11	0.94	3258.4	3.85	0.851	-120.25	372.56	0.996
0.5421	0.206	3534.7	3865.7	5.404	0.906	3085.6	3.649	0.8182	-98.51	353.89	0.994
0.5421	0.275	2796.1	N.A	N.A	N.A	N.A	N.A	N.A	197.4	50.38	0.998
0.769	0.138	1660.8	N.A	N.A	N.A	N.A	N.A	N.A	204.31	210.1	0.998
0.8387	0.138	2244.9	N.A	N.A	N.A	N.A	N.A	N.A	470.95	8.23	0.997

Figure 8.10 Cake Filtration Model Applied to Experimental Data for the Membrane Operated at a) 0.07 bar, 0.5421 m/s b) 0.138 bar, 0.8387 m/s c) 0.138 bar, 0.769 m/s d) 0.275 bar, 0.5421 m/s e) 0.138 bar, 0.5421 m/s and f) 0.206 bar, 0.5421 m/s.

Figure 8.11 Complete Pore Blocking Model Applied to Experimental Data for the Membrane Operated at a) 0.138 bar, 0.5421 m/s and b) 0.206 bar, 0.5421 m/s.

Figure 8.12 Standard Pore Blocking Model Applied to Experimental Data for the Membrane Operated at a) 0.138 bar, 0.5421 m/s and b) 0.206 bar, 0.5421 m/s.

For cases in which internal and external fouling take effect, both complete and standard pore blocking models are applied to the data before the cake layer is developed. Compared to standard pore blocking model, complete pore blocking model appears to better fit the data because the regression coefficient is higher ($> 90\%$). Furthermore, the initial fluxes determined from the complete blocking model is closer to the experimentally measured data. These lead to the postulation that the water droplets deposit on instead of within the pores during the early stage.

8.7 Optimization of Operating Conditions

The collective effect of operating pressure and cross-flow velocity to the oil permeation is studied by constructing contour (Figure 8.13) which is useful for visual explanation and figuring out the optimum operating conditions. The color gradient clearly shows the distribution of flux decline percentage as a function of both pressure and cross-flow velocity. Within the experimental data boundary, it can be seen that flux decline percentage decreases with increasing cross-flow velocity and applied pressure. A maximum flux decline (grey region) is resulted when a low cross-flow velocity and a considerably high pressure is employed. As discussed earlier, the reason for it is due to the accumulation of cake layer which exerts additional hydraulic resistance to the oil permeation. Therefore, it shall be avoided. By taking the grey region as a starting point, one can clearly see that both increasing and decreasing the pressure while holding the cross-flow velocity constant have a positive effect to the oil permeation. However, by taking the consideration that the pressure greater than 0.206 bar will lead to the undesirable penetration of water droplets across membrane and filtration ceases at pressure lower than 0.07 bar, hence the optimum operating conditions for efficient oil-water filtration shall be at high cross-flow velocity and low pressure (not smaller than 0.07 bar) which is located at the right bottom corner in the contour plot.

Figure 8.13 Contour Plot as a Function of Pressure, Cross-flow Velocity and Flux Decline Percentage.

8.8 Conclusions

With its unique interconnected pore structure, the electrospun carbon-silica nanofiber membrane enables water-oil separation at high flux under low pressure. High flux and low pressure imply higher energy efficiency and thus lower operating cost. Separation of water-in-oil emulsion was performed using the membrane and both the cross-flow velocity and operating pressure have direct influence to the flux and rejection efficiency. The effect of operating pressure to the final flux is dependent on the breakthrough pressure for oil as the cross-flow velocity is remained unchanged. A greater flux decline was resulted if the filtration was carried out at above the breakthrough pressure and vice versa. The analysis based on rejection efficiency suggests that the breakthrough pressure is higher than 0.206 bar. On the other side, the shear effect induced by cross-flow velocity mitigates the fouling problem by scouring off the foulant layer accumulated on the membrane

surface. Therefore, flux decline is reduced. The scouring effect is also reflected in the reduction of specific cake resistance.

The membrane fouling models derived from Darcy's law can fit the experimental data with greater than 80% confidence level. Of the internal fouling model, complete pore blocking model offer a better fit than standard blocking model. However, whether a membrane is fouled internally, externally or both highly depends on the operating conditions. The optimization study indicates that the membrane achieves its optimum performance (in terms of flux decline in conjunction with rejection efficiency) at high cross-flow velocity and considerably low applied pressure.

Chapter 9 Conclusions and Recommendations

9.1 Conclusions

A nonwoven membrane made of CNFs can be fabricated by using electrospinning followed by heat treatment. The physical characterization reveals that the CNFs have average fiber diameter ranging between 200 nm and 300 nm with pore size being ~3 nm. TEM analysis shows that the CNFs are turbostratic and have carbon atomic sheets randomly stacked together. Under an oxidative condition, the CNF can withstand a temperature up to 500°C without degrading its structure. However, the nanofibers lack of sufficient toughness and flexibility that are very essential for further material processing, thus making the membrane problematic for handling. By virtue of its intrinsic hydrophobicity and oleophilicity property, the CNF membrane are capable of sorbing various oils and organic solvents with uptake greater than 20 times its weight.

After addition of silica, CNFs become more flexible. Mechanical strength analysis suggests that the membrane toughness varies with the silica loading. The membrane toughness is found to be maximum when the silica loading is 2.7 wt%. Elemental characterization (TEM, XRD and EDX) shows that the silica is in amorphous state and evenly distributed across the fiber in the form of linear network. Furthermore, with increase in silica loading, the thermal stability of carbon-silica composite nanofibers is improved. The folding test shows that the composite nanofibers are stable over a wide spectrum of temperature (-196°C to 500°C). Despite the presence of silica, the CNFs did not lose much its hydrophobicity and oleophilicity. However, owing to the porosity-driven hydrophilicity, the carbon-silica membrane exhibits nonhomogenous wettability across the surface area. Hence, a hydrophobic coating is necessary to ensure hydrophobic-oleophobic surface pattern. The characteristic of high porosity and selective wettability renders the membrane an effective medium for gravity-driven separation of free oil and water at high flux. Due to its high

thermal stability, the membrane is advantageous when dealing with low and high temperature oils.

Other than utilizing membrane technology, mixture of oil and water can also be separated through selective sorption. Hence, a sponge-like sorbent comprised of carbon-silica nanofibers is made via electrospinning. The sponge possesses 5 major features: (1) superhydrophobicity and superoleophilicity, (2) high porosity, (3) reversible structural deformation, (4) recyclability and (5) high uptake of oil and organic solvents. On top of that, the sponge is lightweight. Sorption test shows that the sponge exhibits a maximum sorption capacity of 140 times its own weight. Such high oil uptake amount is mainly attributed to the low density and high porosity of the sponge although oil and organic solvents of higher density can apparently increase the sorption capacity. As the sorbates get into contact with the sorbent, they are rapidly sorbed due to the superoleophilic surface of nanofibers as well as the induced capillary force. The irregular pores and microroughness of the nanofiber surface present in the sponge further promote the sorption. Nevertheless, the sponge's sorption rate is reduced for sorbates of high viscosity. To recover the sorbed oil, mechanical squeezing and distillation are found to be effective. Moreover, the electrospun sponge can be designed with favourable functions such as magnetic sponge as fabricated in the work to tackle with oil removal under more complicated conditions.

In the study of oil-water separation using hierarchically nanostructured TiO_2 -carbon-silica membrane, it was found that the membrane's wettability property is shifted from hydrophobic and oleophilic into hydrophilic and underwater oleophobic. This is attributed to the hydrophilic TiO_2 nanosheets that grows on the surface of electrospun CNFs as well as the enhanced roughness. The transition from Wenzel state into Cassie-Baxter state can be used to theoretically explain such change in wetting behaviour. Similar for flat-sheet carbon-silica membrane, the TiO_2 -coated CNF membrane enables gravity-driven separation of water and oil at high flux with the permeating phase for TiO_2 -carbon membrane being water instead of oil. On the other hand, the growth of TiO_2 nanosheets on the nanofibers increases

the average fiber diameter, thus reducing spacing distance between fibers. This reduction in membrane pore size gives rise to an oil breakthrough pressure of 32.724 kPa which is equivalent to 3.88 m high water column. The stability test shows that the morphology of TiO₂-coated CNF membrane was well preserved even under extreme acidic and alkaline condition. Moreover, no degradation in structure integrity and selective wettability was observed after the treatment at elevated temperature and under ultrasonication.

The functionality of flat-sheet carbon-silica nanofiber membrane is further explored in the cross-flow microfiltration experiment. Results show that the membrane is able to separate not only free water and oil but also water-in-oil emulsion. In the 150 min cross-flow filtration, the membrane exhibits high water rejection efficiencies below 0.138 bar which is the breakthrough pressure for water. In addition, the flux decline is largely affected by the cross-flow velocity as well as the applied pressure. At constant pressure, a higher cross-flow velocity engenders lower flux decline and vice versa. This is due to the fact that the induced shear rate helps to scour off the foulant layer on the membrane surface. On the other hand, increasing pressure will reduce the final flux until it reaches the critical pressure, beyond which the final flux is bounced back. This observed trend can be ascribed to the fact that the water permeates across the membrane at high pressure. The total resistance data indicates that the membrane can be fouled externally, internally or both, depending on the collective effect of cross-flow velocity and applied pressure. The contour plot suggests that the membrane will function better and longer when operated at high cross-flow velocity and relatively low pressure.

9.2 Recommendations for Future Research

This thesis has covered the works pertaining to the separation of water-oil mixture (free oil and water, water-in-oil emulsion and oil-in-water emulsion) using carbon-silica nanofibers in the form of flat-sheet membrane and sponge. However, further studies are required to compliment the thesis. The recommendations for future research include:

(i) Seeking for substitute for silica. Although silica has notable toughening effect to the CNF, the silica precursor is readily hydrolyzed. As a result, the atmospheric humidity has to be controlled, thus making the electrospinning more difficult to monitor. To mitigate the hydrolysis problem, other inorganic reinforcing fillers that are hydrostable such as glass beads, powdered barium sulphate (Ziegel and Romanov 1973) and silicon carbide (Liang 2002) are the potential options.

(ii) Designing CNFs with multi-functionalities through electrospinning. Although TiO₂ nanosheets have been successfully anchored onto the CNFs, the synthesis requires high pressure and temperature which undoubtedly incur higher cost. In fact, electrospinning is a versatile technique that enables the encapsulation of many functional materials or precursors into CNFs in one step. By employing electrospinning, CNFs with several desirable functionalities could be fabricated in a more economical and convenient way as compared to the various post-treatments performed to the pristine CNFs. The fabrication of multifunctional CNFs are beneficial for simultaneous environmental applications.

(iii) Studying cross-flow filtration of hierarchical CNF membrane for separation of water from oil. It has been reported that corrugated membrane has remarkable flux enhancement compared to the flat-sheet membrane. (Scott, Jachuck et al. 2001) Given that the hierarchically structured CNFs are rougher, it is of interest to explore its potential for energy efficient and high flux purification of oil.

(iv) Investigating the influence of the factors that control the stability of water-in-oil emulsion on the membrane's separation performance. This also includes to what extent the separation performance is affected.

Appendix A Sponge Porosity Measurement

Porosity Determination (1) - Direct Method

Porosity = Pore volume / Total bulk volume

Pore volume = total bulk volume - material volume

For the as-prepared carbon-silica sponge,

mass = 3.3 mg or 0.0033g, bulk volume = $(0.9 \times 0.4 \times 0.6) \text{ cm}^3 = 0.216 \text{ cm}^3$

It is reported that CNF has a density(ρ) ranging from 1.95 to 2.17 g/cm³, hence

Pore volume = $0.216 \text{ cm}^3 - 0.0033 \text{ g} / 1.97 \text{ gcm}^{-3} = 0.2143 \text{ cm}^3$ (using $\rho = 1.95 \text{ gcm}^{-3}$)

Porosity = $(0.2143 / 0.216) \times 100 = \underline{\underline{99.21\%}}$

or

Pore volume = $0.216 \text{ cm}^3 - 0.0033 \text{ g} / 2.17 \text{ gcm}^{-3} = 0.2145 \text{ cm}^3$ (using $\rho = 2.17 \text{ gcm}^{-3}$)

Porosity = $(0.2145 / 0.216) \times 100 = \underline{\underline{99.30\%}}$

Porosity Determination (2) - Fluid Saturation Method

In this experiment, the porous sponge was immersed in hexadecane until the adsorption reaches its maximum capacity. Hexadecane was selected because it is relatively stable and non-volatile. The saturated sponge was then weighted on a digital balance.

Pore volume = (mass of saturated sample - mass of dry sample)/density of hexadecane

$$\begin{aligned} &= (247.4 \text{ mg} - 5.4 \text{ mg}) / 770 \text{ mgcm}^{-3} \\ &= 0.3141 \text{ cm}^3 \end{aligned}$$

Bulk Volume = $(0.9 \times 0.8 \times 0.45) \text{ cm}^3 = 0.324 \text{ cm}^3$

Porosity = $(0.3141 / 0.324) \times 100 = \underline{\underline{96.94\%}}$

Appendix B Sorption Capacity Comparisons

Sorbent Materials	Maximum sorption capacity, g/g	Ref.
Twisted carbon fiber sponge	192	1
Graphene Sponge	86	2
CNF sponge	139	3
Electrospun PVC-PS fiber	149	4
CaCO ₃ -functionalized foam	13	5
Porous boron nitride nanosheet	33	6
Manganese oxide nanowire membrane	20	7
Macroporous CNF film	138	8
PDMS-coated CNF sponge		9
Synergistically assembled carbon sponge	743	10
Bacterial cellulose-derived CNF sponge	312	11
Electrospun carbon-silica sponge	140	Present work

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