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SUPERHYDROPHILIC TiO_2 NANOMATERIALS FOR EFFICIENT OIL-WATER
SEPARATION

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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Abstract

The rapid growth of industrial activities and occurrences of environmental pollution such as contaminated oil spill evoke situations leading to water source contamination. Furthermore, surfactant-containing oil-water mixtures tend to emulsify the oil into small and stable droplet that are difficult to be separated from water. Currently, conventional techniques have shown their incapability of tackling such problem. Therefore, significant attention has been drawn to introduce advance materials or techniques that are suitable for effective oil-water separation process. This thesis explores the feasibility of TiO_2 -based material and its derivatives in separating oil from water.

In general, the TiO_2 -based materials reported in this thesis are fabricated using hydrothermal method, and the membranes were synthesized via a 2 step process which include filtration and hot pressing. TiO_2 materials has been the most promising candidate for oil-water separation membranes due to its intrinsic superhydrophilic and underwater superoleophobic properties. For the initial part of the work, the pristine TiO_2 nanowire was investigated for its oil-water separation ability with the aid of a flexible scaffold. In this study, it is the first time that we fabricated a novel micro/nanowire hierarchical membrane with flexible, self-cleaning and underwater superoleophobic properties for efficient oil-water separation under vacuum filtration. This novel membrane composed of ultralong copper microwires (MW) and functional TiO_2 nanowires (NW). The ultralong copper microwires act as a scaffold, as well as providing mechanical flexibility for the membrane, which allow it to be operated under vacuum-driven condition. Meanwhile, underwater superoleophobic TiO_2 nanowires membrane provides nano-scale pore size, ensuring the filtration of smaller oil droplets with droplet size $> 600\text{nm}$ under vacuum condition. Moreover, the possession of the self-cleaning function of TiO_2 nanowires allows the degradation of foulants and contaminants under UV irradiation, which promote the facile recovery of the used membrane.

In order to further understand the oil-water separation efficiency and photocatalytic effect corresponding to the TiO_2 nanomaterial morphology, a comparative study of self-cleaning ability and oil-water separation efficiencies of 1D TiO_2 nanostructure

with that of 3D TiO₂ nanostructure was conducted. Various TiO₂ membranes formed by different nanostructures including 1D TiO₂ nanotube, 1D TiO₂ nanowire and 3D nanosheet-decorated TiO₂ nanowire hierarchical structure were synthesized and compared. The oil-water separation results showed that the three membrane portrayed excellent oil-water separation ability due to the formation of water layers represented by their high water capture percentage (WCP). Studies from the self-cleaning experiment indicated that TSW (3D nanosheet-decorated TiO₂ nanowire) membrane has the shortest time to self-clean the oleic acid accumulated on its surface and simultaneously recovers its superhydrophilicity property. In addition, the results for photodegradation activity showed that 3D nanosheet-decorated TiO₂ nanowire has the highest photodegradation efficiency among the investigated TiO₂ nanostructures to eliminate intermediate organic compounds. This is attributed to its high light harvesting capacity resulting from the multiple reflections of incident light and superior electron collection properties due to the hierarchical structure. Essentially, this study paves way for enhancing oil-water separation performance of other photocatalysts through the modification of its nanostructure.

To reinforce the TiO₂ nanomaterials with excellent oil-water separation ability, photocatalytic properties and mechanical flexibility, Fe₂O₃ nanoneedles were grown uniformly on TiO₂ nanowire substrate to provide the clinching effect once compacted together. Hence, the subsequent study introduces a hierarchically nanostructure multifunctional TiO₂/Fe₂O₃ composite membrane, which is capable of separating surfactant-stabilized oil-water emulsions with high separation efficiency. The experimental results showed that the membrane is capable of removing droplet size as small as 400nm. The high oil rejection rate is contributed by the acquisition of an interconnected delicate network and underwater superoleophobic interface. Meanwhile, its self-cleaning function promote the facile recovery of the contaminated membrane. Furthermore, the mechanical flexible characteristic of the multifunctional TiO₂/Fe₂O₃ composite membrane widens its applicability in industrial employment.

The separation performance of multifunctional TiO₂/Fe₂O₃ composite membrane was further evaluated by operating the membrane in a two-step treatment process. The as-prepared membrane was examined for its ability in photodegrading dye contaminants effectively without affecting its oil-water separation efficiency. Methyl blue (MB),

Rhodamine B (RhB) and acid orange (AO7) aqueous solution were the three types of common pollutants employed in this study. The results showed that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes demonstrated excellent oil-water separation ability under vacuum filtration process even after photodegrading the various types of dye contaminant. Ultimately, the introduction of this membrane provides an opportunity to eliminate dye contaminants and separating oil from water effectively.

In sum, the results gathered from this thesis illustrated that TiO_2 -based membrane can be regarded as a practical option in managing polluted surfactant-stabilized oily wastewater.

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5.1 mg/L while the initial TOC reading of the emulsion was 8201 mg/L. From this study, it can be explained that the olive oil present in the feed was efficiently segregated from the olive oil-in-water emulsions. Hence, the combination of the TGA and TOC results justified that the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane displayed an outstanding oil-water separation capability. 98

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List of abbreviations and symbols

μm	Micrometer
AOPs	Advanced oxidation processes
AFM	Atomic-force microscopy
Br^-	Bromide
BrO_3^-	Bromate
CA	Contact angle
Cl_2	Chloride
ClO_2	Chlorine dioxide
Cu	Copper
Cu(OH)_2	Copper hydroxide
Cu_2O	Copper (I) oxide
CuO	Copper (II) oxide
D_p	Particle diameter
EDA	Ethylenediamine
EDX	Dispersive X-ray spectrometer
FESEM	Field emission scanning electron microscopy
H_2O_2	Hydrogen peroxide
HCL	Hydrochloric acid
LBL	Layer-by-layer
MB	Methylene blue
MF	Microfiltration
NaOH	Sodium hydroxide

NF	Nanofiltration
nm	Nanometer
O ₃	Ozone
OH.	Hydroxyl radical
QE	Qualifying Examination
RO	Reverse osmosis
SEM	Scanning electron microscopy
TC	TiO ₂ /Copper
TGA	Thermogravimetric analyzer
Ti	Titanium
TiO ₂	Titanium dioxide
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WCP	Water capture percentage
WHO	World Health Organization
XRD	X-ray diffractometer

1. Introduction

1.1. Background

Daily oily wastewater production from industries such as petrochemical, textile, metal finishing, leather and steel processing has been considered as a common pollutant globally (L. Wang, Chen, Hung, & Shammas, 2010). Moreover, in view of the frequent oil spill accidents caused by unpredicted disposal or natural disaster, this wastewater has created a long term and lethal impact on the ecosystem as well as the environment (Kajitvichyanukul & Hung, 2006; Peterson et al., 2003). Furthermore, the rapid population growth coupled with global warming issues have further worsened the problems of clean water scarcity (Elimelech & Phillip, 2011). Hence, separating oil from water is regarded as a potential solution to resolve these problems.

Surfactant-containing oil-water mixtures are one of the commonly produced oily wastewater, which tend to emulsify the oil into small and stable droplets that are difficult to be separated from water. To date, oil-adsorbing materials, gravity separation, coagulation, flocculation and flotation are various technologies that have been employed to separate oil/water mixtures. However, these methods are limited by their large footprints, low efficiency in treating emulsified oil/water mixtures, complicated instrument setup and high energy usage (Ashraf, 1996; Cheryan & Rajagopalan, 1998; El-Kayar, Hussein, Zatout, Hosny, & Amer, 1993; Mueller, 1997; Tsuneki, 2007). Therefore, significant attention has been drawn to introduce advanced materials or techniques that are suitable for effective oil-water separation process. As such, membrane technology with high treatment efficiency and easy scalability has been widely studied (C. Gao et al., 2013; Kwon et al., 2012; F. Zhang et al., 2013).

Hydrophobic membranes and hydrophilic membranes are two types of membranes that have been applied in oil-water separation process (Kota, Kwon, Choi, Mabry, & Tuteja, 2012). Inspired by the anti-wetting property of oil droplets on fish scales and lotus leaves in aqueous media, materials built with superhydrophilic and underwater superoleophobic characteristics have been extensively studied to treat oil/water mixture (Howarter & Youngblood, 2009; Qunfeng et al., 2011; Zhongxin, Mingjie, & Lei, 2012). In other words, the superhydrophilic materials interface will have low affinity for oil drops, resulted from the formation of water/solid interface, created by the entrapment of water molecules in the micro/nanostructures (Zhongxin, Yingze, Na, Lin,

& Lei, 2014). Notably, studies have shown that hydrophilic membranes portray more advantages as compared to that counterparts due to the following reasons: 1) Clogging of the membrane by viscous oil can be prevented due to its water-liking characteristic, which only encourages water to permeate and 2) the formation of water barrier between the membrane and oil phase can be avoided. Due to the fact that water is denser than oil, water tends to form a barrier between the oil and the hydrophobic surface, which prevents the oil from permeating through the membrane (C. Gao et al., 2013; L. Lin et al., 2010; M. Liu, Wang, Wei, Song, & Jiang, 2009; W. Zhang et al., 2013; Zhu et al., 2013).

With the knowledge on such special wettable surface, diverse materials such as silica gel, hydrogel, TiO_2 , zeolite and nanostructured ZnO surfaces have been investigated for achieving superhydrophilic surface with underwater oil repellent ability (Y. Chen et al., 2014; Sawai, Nishimoto, Kameshima, Fujii, & Miyake, 2013; Tian et al., 2012; Xue et al., 2011b; Zeng & Guo, 2014). Feng and co-workers fabricated a superhydrophilic and underwater superoleophobic hydrogel coated mesh, which consists of nanostructured hydrogel coating and microscale porous substrate. During the test, there was effective separation water from oil-water mixture (Xue et al., 2011b). Furthermore, Zhongxin's group reported on the development of superoleophobic aligned carbon nanotube films and micro/nano hierarchically structured polymer surfaces, and discovered that the nano/micro structures played a significant role for constructing superoleophobic surfaces.

Among the materials mentioned above, titanium dioxide (TiO_2) is regarded as the most promising candidate due to its superhydrophilic surface, photocatalytic efficiency and chemical stability properties (P. Gao, J. Liu, T. Zhang, D. D. Sun, & W. Ng, 2012; Yamamoto et al., 2012). As reported, the structure, morphology, roughness, crystalline phase and dimensionality are essential factors which determine the wettability and photocatalytic activity of TiO_2 materials (Cheng et al., 2011; Lai et al., 2013b). In the last decade, various forms of TiO_2 nanostructures have been introduced, including tubes (M. Wang, Iocozia, Sun, Lin, & Lin, 2014), wires (X. Zhang, Zhang, Ng, & Sun, 2009), fibers (Dharani et al., 2014) and sphere (Gao & Sun, 2014). For example, Zhang's group reported a self-cleaning underwater superoleophobic mesh synthesized via the layer-by-layer (LbL) assembly of TiO_2 nanoparticles on stainless steel mesh, and concluded that this mesh possessed excellent oil/water separation ability as well as self-cleaning properties due to the presence of micro-nano hierarchical structure, hydrophilic nature

and outstanding photocatalytic activity (L. Zhang, Zhong, Cha, & Wang, 2013b). Lai and co-workers fabricated large scale pinecone-like anatase TiO_2 particles (ATP) film through an electrochemical anodizing approach. They suggested that the wettability and adhesion characteristics of the ATP film can be controlled by regulating the topographical structure and surface chemistry (Lai et al., 2013a). Guohui et al. (2011) synthesized three-dimensional (3D) hierarchical flower-like TiO_2 nanostructures using a two-step procedures which include a facile solvothermal method and a calcination process. In their study, they reported that the as-prepared 3D TiO_2 nanostructures possess high light-harvesting capacity, porous structure and more reactive sites, in which inevitably enhanced the photodegradation activity of phenol.

It is worthwhile to note that an oil-water separation membranes built with hydrophobic interface can be constructed via a demixing process known as phase inversion. However, such construction approach is least feasible to be adopted for the assembly of hydrophilic membranes (W. Zhang et al., 2013). Alternatively, coating materials with hydrophilic properties onto a porous substrate such as wire meshes is a typical approach for fabricating hydrophilic membranes. For example, Xue et al. fabricated a superhydrophilic and underwater superoleophobic membrane by coating hydrogel onto a porous metal substrates, and these membranes achieved 99% efficiency for separating surfactant free oil-water mixture (Xue et al., 2011a). Zhang and co-worker grew $\text{Cu}(\text{OH})_2$ nanowire-haired on a copper mesh, and these superhydrophilic and underwater superoleophobic membranes were capable of performing effective oil-water separation process with extremely high efficiency (F. Zhang et al., 2013). Zhang et al. assembled sodium silicate and TiO_2 nanoparticles onto the surface of stainless steel mesh which could separate water from oil-water mixture effectively (L. Zhang, Zhong, Cha, & Wang, 2013a). However, separating surfactant-stabilised oil-water emulsions still remains a challenge for these reported membranes. Primarily, this is potentially due to the intrinsic large pore sizes (usually greater than one micrometre) of the selected porous matrix (Kota et al., 2012). Furthermore, large pore sizes also resulted in a low breakthrough value for the membrane, which restricts its operation to be only efficient under gravity-driven processes. The main disadvantage for employing such process is that it requires the initial de-emulsification process to allow the natural separation of oil and water. In other words, additional operation time will be needed to manage such pre-treatment process, which reduces productivity (i.e. from an economical and practical

stand point) when tonnes of oily wastewater have to be treated daily. On the other hand, a pressure-driven filtration process permits high flux and continuous separation, and this will ultimately outperform the slower filtration rate portrayed by the gravity-driven oil-water separation process. Therefore, for practical oil-water separation, a membrane with superhydrophilic and underwater superhydrophobic properties, coupled with the ability to be employed in a pressure-driven filtration process will be greatly appreciated.

In summary, ceramic membranes are recognised for their hydrophilic property which makes them viable for oil-water separation application (L. k. Wang, Chen, Hung, & Shammas, 2011). However, the widespread application of these membranes are limited by their poor mechanical flexibility and high cost. Among the membrane modules, rolled up membrane such as spiral-wound membranes have been widely adopted for most of the industrial applications due to their capability in reducing the required footprints significantly. In this sense, flexibility of the membrane plays a critical role for membrane application. Therefore, the development of a novel flexible, low membrane fouling and highly hydrophilic oil-water separation membrane with the potential to separate surfactant-stabilized oil-water emulsion at high rejection rate under vacuum filtration is greatly desired.

1.2. Research Objectives

The objective of this PhD Thesis is to present a study on the fabrication and performance of TiO_2 and TiO_2 -based composite oil-water separation membrane. The explicit objectives are as follows;

- I. To fabricate hydrophilic TiO_2 and TiO_2 -based oil-water separation membrane through hydrothermal and filtration procedures.
- II. To examine the TiO_2 morphology that is best suited for application in the oil-water separation process.
- III. To assess the performance of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite oil-water separation membrane with the aid of its hierarchical structures.
- IV. To investigate the ability of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane in maintaining its oil-water separation potential photo degradation process.

1.3. Thesis Overview

This thesis contains 8 chapters and 2 appendices. **Chapter 1, 2 and 3** consist of a brief introduction, literature review and experiment methodology respectively.

Chapter 4 involves the preliminary characterization of a novel oil-water separation membrane composed of functional TiO₂ nanowire and ultralong copper microwires. Basically, the TiO₂ nanowires provide the wetting property while the microwires act as a scaffold, as well as providing mechanical flexibility for the membrane, which allow it to be operated under vacuum-driven condition. This chapter determines the feasibility of employing TiO₂ nanomaterials for oil-water separation process under vacuum filtration.

Chapter 5 reports on the comparative study of self-cleaning ability and oil-water separation efficiencies of 1D TiO₂ nanostructure with that of 3D TiO₂ nanostructure which is still lacking. In general, this chapter elucidates the possibilities of utilising pristine TiO₂ nanomaterial and its best morphology suitable for oil-water separation under vacuum filtration.

Chapter 6 introduces a superhydrophilic and flexible TiO₂/Fe₂O₃ composite membrane built with superhydrophilic and underwater superoleophobic properties. The individual structures was formed by growing Fe₂O₃ nanoneedles uniformly onto the surface of TiO₂ nanowires. In this study, the water wetting behaviour, oil-water separation ability and photodegradation activities of the TiO₂/Fe₂O₃ composite membrane were investigated. Notably, the applicability study on separating surfactant-stabilised oil-water emulsion was also assessed.

Thereafter, research was conducted to describe the effectiveness of employing a membrane formed using a three-dimensional structured TiO₂/Fe₂O₃ composite nanomaterial to deal with polluted oily wastewater. This study demonstrated that the membrane's ability in separating surfactant-stabilised oil-water emulsion was not affected by the presence contaminants such as dyes.

Chapter 7 concludes the findings obtained from the above experimental details and discussions. Moreover, recommendations and suggestions are also provided for the continuation of future work.

Chapter 8 compile the list of references applied in this thesis.

Appendix A demonstrates the method of obtaining the water capture measurements for the oil-water separation membrane. **Appendix B** illustrated the Langmuir-Hinshelwood kinetics theory used to determine the photodegradation rates.

2. Literature review

2.1. Overview

Oil and gas industries such as petroleum refineries have been unavoidably generating a large volume of oily wastewater. As a result, meeting the environmentally acceptable disposal standards is regarded as one of their major challenges. Therefore, the need to improve the conventional oily wastewater treatment has become an urgent issue. This is important because the improper discharge of oily wastewater will eventually affects the marine life and human health.

The literature review will discuss the importance of water treatment and comparing various conventional oily wastewater treatment methods and expose their limitations. Besides that, it will also include fundamental theories relating to membrane based oil-water separation and membrane fouling mechanisms. Lastly, the important characteristics of TiO₂ materials will also be discussed.

2.2. Importance of water treatment

Water is one of the most important natural resources in the world, which covers almost 70% of the earth surface. In spite of this, water is still considered as a scarce resource in most countries. One of the major concerns is the accessibility to safe drinking water; this has been extremely crucial to support the livelihood of mankind and animals. In other words, water should be free from disease-causing substances. Apart from drinking water, people have employed water for various uses such as cooking and washing. As a consequence, water from rivers, lakes and oceans would tend to be contaminated by the over-use and wastage of human beings if no proper water treatment processes are available. This contamination not only affects the natural environment; it will also potentially create adverse effects to the human health. Point source (single source) and non-point source (many sources) are the two main groups to consider when classifying water pollutant (Mehrotra, Yablonsky, & Ray, 2003). Water pollution is commonly generated from some major sources such as industrial waste, sewage and wastewater, agricultural waste, oil spills, marine dumping and nuclear wastes. In 2008, the World Health Organization (W.H.O) revealed that 884 million people were still relying on unimproved water sources - among those, 84% of them were living in rural areas. Many more are depending on drinking microbiologically unsafe water for survival, which is

infected with waterborne diseases such as typhoid, hepatitis and cholera (Byrne et al., 2011; Statistics, 2011)

In order to solve the concerns over improper water supplies, elimination of harmful matters, detoxification and removal of pollutant from wastewater, surface water and groundwater has been maintained as a top priority in water issues around the world. In a water treatment process, there is secondary and tertiary treatment. During the secondary treatment, organic matters are partially decomposed. Subsequently, Cl_2 , O_3 or UV light will be introduced at the tertiary stage to disinfect the wastewater through an oxidation process. Biological, chemical and physical oxidation processes are methods that can be widely employed in a tertiary water treatment. Biological oxidation treatment is considered to be inexpensive but the presence of the toxic substances has created concerns over human health and the environment. Similarly, the application of the high temperature treatment method (thermal) is also effective in treating remaining pollutants, although the cost of such a method is not economically feasible. On the other hand, chemical oxidation does not encounter such difficulties. This method employs several oxidants such as H_2O_2 , Cl_2 , O_3 and ClO_2 in the treatment process. However, there are still limitations present in this method such as inability to provide complete mineralization of water pollutants (D. Li & Qu, 2009). For example, the presence of Cl_2 and ClO_2 contribute to the formation of disinfection by-products.

USEPA has initiated stringent regulations on the standards for wastewater discharge. To comply with these implemented regulations, advanced oxidation processes (AOPs) have been recommended to enhance or replace the traditional processes. This is because AOPs have the ability to remove various potentially harmful compounds which the traditional processes cannot deal with (Zhou, 2002). Some examples of AOPs are O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ and TiO_2/UV (Legrini, Oliveros, & Braun, 1993). From the mentioned AOPs, TiO_2/UV based photocatalysts have been receiving remarkable attention over recent years. Furthermore, it has also been regarded as an alternative for water detoxification. Figure 2.1 illustrates wastewater treatment procedures in general (Metcalf, 2002). In order to enhance the performance of TiO_2 - based material, solar light has to replace UV lamps as the main source of energy. Substantially, modifications on TiO_2 and TiO_2 - based material are required to move towards the solar visible spectra.

Figure 2-1: Wastewater treatment steps(Metcalf, 2002)

2.3. Conventional oily wastewater treatment methods

Various treatment technologies have been recommended previously for oily wastewater treatment in oil and gas industries. Some of the common conventional methods are discussed below.

2.3.1. Coagulation

Coagulation has been widely regarded as a proven technology for removing contaminants such as metals, suspended solids, fats, oils and grease from wastewater. Basically, this process causes the dissolved or suspended contaminants to form a solid precipitate through a precipitation process, which is subsequently filtered or centrifuged from the liquid portion. The precipitation process is performed with the assistance of coagulants which promote the formation of larger aggregates by smaller particles. In other words, these coagulants act as a bridge between the particles in solution (EPA, 2000). Some of the commonly used coagulants include Fe, Mg and Al (Fakhru'l-Razi et al., 2009).

In this process, oils and greases tend to bind together and form "slick" on the water surface due to their non-polar and non-solubility in water characteristics. Consequently, these oils and greases can become emulsified, thus creating globules due to the presence of compatibly charged particles. As a result, the emulsion must be disintegrated by destabilising the electrical charge attraction. One of way is to introduce a polymer to

perform charge neutralization. In this way, the charge attraction of the oily contaminants will be disassembled, allowing the easy removal of oily particles from water (EPA, 2000). As reported, this method is able to achieve a oil removal efficiency of approximately 92 to 97% (Fakhru'l-Razi et al., 2009)

However, this treatment method has certain limitations which include 1) polymer can be costly, 2) large amount of chemical is required, 3) increase in the chemical usage will generate large amount of sludge, 4) the resulting water may contain high metal content and 5) frequent jar tests are required to prevent overdosing of chemical. As a result, it is not an optimum method for a small water treatment plant due to its high capital and operation cost.

2.3.2. Gravity Separation

This method is regarded as the cheapest and most widely used method for the removal of free oil ($D_p \geq 150 \mu\text{m}$) from oily wastewater with an oil removal efficiency of 52 - 87% (Joseph & Yung-Tse, 2004). Basically, this method is fully dependent on the density difference between the oil phase and water phase. Due to the fact that oil is less dense than water, it will upsurge to the surface of the treatment module. Subsequently, this floating oil will then be skimmed off. The key parameters for such process can be obtained from Stokes' law, i.e density difference, size of the droplet and degree of viscous. Feasible hydraulic design and wastewater retention time are the two main factors that determine the efficiency of the treatment process (Coca, Gutirrez, & Benito, 2011; Falconer, 2003). Some common gravity separation methods include American Petroleum Institute (API) separators, plate coalescers and flotation units.

Nonetheless, there are limitations relating to this treatment method which include 1) not effective for recovering fine molecule droplets, 2) requiring a large amount of water during operation, 3) cleaning in a daily basis cleaning is essential and 4) requiring large footprint (Falconer, 2003).

2.3.3. Flotation

Flotation is a physico-chemical method that is suitable for removing emulsified oil from wastewater with a removal efficiency of 70 - 90% (Joseph & Yung-Tse, 2004). Compared to gravity separation, it is capable of discarding oil that cannot be separated due to on oil-water density differential. During the process, small air bubbles are injected into the wastewater to form oil droplets adhesion, as well as increasing the

buoyancy force, hence, allowing the oil droplets to rise quickly to the surface where it can be skimmed off. Furthermore, addition of chemicals is also essential for enhancing the coagulation of the oil droplets. Figure 2.2 illustrates the synergy effects between air bubbles and oil droplet (Gary F. Bennett, 2009). The steps are summarised as follow,

- a) Attachment of fine air bubble to the oil droplet
- b) Formation of agglomerates through collision
- c) Entrapment of more air bubbles while rising
- d) Rising of flocs in a sweeping action known as sweep flocculation.

Figure 2-2: Diagrams showing the flotation mechanism (Coca et al., 2011)

On the other hand, the drawbacks of employing this process include 1) a cover is require to protect the flocs from wind and precipitation, 2) highly power intensive and 3) it is not suitable for high-turbidity water (Hoboken, 2012).

2.3.4. Adsorption

Adsorption is a physical process that adheres polluting compounds onto a solid surface, and this process has been widely employed in wastewater treatment plants. Activated

carbon, bentonite, coal and fibreglass to mention a few are some common adsorbents which have been used in adsorption treatment. Among them, activated carbon is extensively used for removing organic compound such as oil from water (Emam, 2013; Joseph & Yung-Tse, 2004; Okiel, El-Sayed, & El-Kady, 2011). The United States Environment Protection Agency (USEPA) has recommended activated carbon adsorption as one of the best technologies available for organic compounds removal (Okiel et al., 2011). Generally, adsorption processes are able to achieve an average oil removal efficiency of 80-90% (TIGG, 2014).

However, activated carbon is expensive, and is heavily dependent on activation and reactivation procedures. As a consequence, this method is not suitable for use in developing countries (Coca et al., 2011).

2.3.5. Biological treatment

Biological treatment is mostly employed in areas that generate wastewater with low oil content, i.e. synthetic or semi synthetic metalwork industries (Coca et al., 2011). For a typical biological treatment, organic compounds such as oil are consumed as food source by the microbes, which use them as a source of carbon and energy. In addition to that, nutrients such as nitrogen and phosphorus are crucial for sustaining the growth of the microbes, if the wastewater does not supply sufficient amount of these nutrients. There are three different types of microbes which mainly include aerobic microbes, anaerobic microbes and facultative microbes.

Aerobic microbes need oxygen to survive, while anaerobic microbes can develop in the absence of oxygen. On the other hand, facultative microbes can survive in both aerobic and anaerobic environments. Biological treatment is heavily dependent on several factors such as pH, temperature, type of pollutants, availability of required nutrients and the presence of inhabiting compounds. For instance, heavy metals can be harmful to the microbes; therefore pre-treatment process is necessary for eliminating these compounds (USEPA, 2000). Currently, membrane bioreactors are one of the widely used biological treatment methods for treating oily wastewater. As reported, it is capable of obtaining oil and grease removal efficiency of 92 - 95%(R. Kurian, 2006).

However, the major limitation of this method include 1) Growth of microbes can be affected by various factors if proper system control is not in place, 2) high capital and operating cost compared to conventional methods, 3) operation and maintenance cost

for cleaning and replacement of membrane and 4) high energy cost due to the air scouring process for controlling the growth rate of the microbes (USEPA, 2008) .

2.3.6. Membrane filtration

Membranes can be defined as a physical barrier that controls the passage of particles and pollutants presence in wastewater. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are the common membrane technologies employed in water treatment processes. They can be fabricated using different materials such as polymers, ceramic and metal. Generally, MF and UF are capable of removing pollutants with molecular size of $\geq 0.1 \mu\text{m}$ and $0.01\text{-}0.1 \mu\text{m}$, whereas NF and RO are used to remove salts and organic compound with pollutant molecular size of $0.001\text{ - }0.01 \mu\text{m}$ and $\leq 0.001 \mu\text{m}$ respectively. Figure 2.3 shows the species and compounds that can be rejected by individual types of membrane materials and processes (Coca-Prados, Gutiérrez, & Benito, 2013).

Figure 2-3: Summary of the species and compounds rejected by various filtration processes (Coca-Prados et al., 2013)

Lots of research has highlighted the effectiveness of membrane separation for oily wastewater treatment (Benítez, Acero, & Leal, 2006; Marchese, Ochoa, Pagliero, & Almandoz, 2000; Norouzbahari, Roostaazad, & Hesampour, 2009; Salahi, Abbasi, & Mohammadi, 2010). In general, these studies were conducted in laboratory and pilot scale. From these studies, the various researchers reported an average oil removal efficiency of 95 - 98% by analysing the UF permeate after treating the oily wastewater. Reed reported an oil/grease removal rate of 92 - 96% using UF membrane technology based on the results achieved from a pilot test experiment (Reed, Lin, Dunn, Carriere, & Roark, 1997). Recently, Madaeni and co-workers reported on the performance of hydrophilic MF and UF membrane as a treatment option for oil separation through

pressure driven and cross-flow velocity effects, and they found that both MF and UF are capable of exhibiting a high oil removal rate of approximately 95% (Madaeni, Gheshlaghi, & Rekabdar, 2013).

Although there is an increase in the application of membrane processes for treating oily wastewater, the main drawback of membrane technology is the decline in permeate flux owing to membrane fouling. Therefore, pre-treatment for the oily wastewater are always advisable to minimise such an occurrence. Therefore, the physical properties of the membrane has to be further modified to enhance the oily wastewater treatment processes. For example, a membrane with self-cleaning capability will effectively resolve the issues of fouling experienced during the treatment process.

2.4. Membrane based oil-water separation

A membrane acts as a selective barrier which control the passage of certain components while rejecting the others. Recently, inspired by the fact that fish are able to survive in oil-polluted water due to the remarkable oil-repellent ability exhibited by their fish scales, membrane with hydrophilic and superoleophobic properties have been considered to be promising for oil-water separation (K. K. Arun, Gibum, Wonjae, Joseph, & Anish, 2012; L. Lin et al., 2010; M. Liu et al., 2009; Zhu et al., 2013).

Compared to the traditional hydrophobic and oleophilic materials, the water-loving separation membrane allows water to pass through easily, and thus minimising the pore blocking effects created by the viscous oil. Furthermore, the traditional membranes tend to create a water barrier between the membrane and oil phase due to the fact that water is heavier than oil, in which restraining the oil from contacting with the separation membrane. As a consequence, this evidently deteriorates the oil-water separation function.

For separating oil from water using the membrane filtration method, it is essential that the membrane possess with high production work rate, selective wetting behaviour and reusability ability. Furthermore, in the view of an industrial oily wastewater treatment plant, the application of such membrane should expect to create a low cost opportunity.

In general, the introduction of selective wetting property onto a membrane can be achieved by different methods such as surface geometry modification (P.-C. Chen & Xu, 2013; Kota et al., 2012; Xue, Cao, Liu, Feng, & Jiang, 2014; Xue et al., 2011a; Yang, Zhang, Xu, & Shi, 1998) and surface chemical composition (Nyström & Järvinen,

1991; Rana, Matsuura, Narbaitz, & Feng, 2005; Wavhal & Fisher, 2003). It is worthwhile to note that Zhang et al. fabricated a self-cleaning hydrophilic and underwater superoleophobic membrane by depositing sodium silicate and TiO₂ nanoparticle onto a stainless steel mesh via a layer-by-layer (LbL) method (L. Zhang et al., 2013a). On the contrary, Gao and co-workers reported a superhydrophobic and superoleophilic TiO₂ coated mesh that is capable of separating insoluble oil from water, as well as degrading soluble pollutant under UV irradiation (C. Gao et al., 2013). However, their works can only be employed under gravity-driven condition which required de-emulsification process to allow the natural separation of oil and water phases. In other words, a longer operation time is resulted from such additional oil-water phase separation, which is not economical for a large scale operation where tonnes of oily wastewater have to be treated daily. Consequently, these factors have impeded the practical application of these membranes for oil-water separation treatment in oil and gas industries. On the other hand, a vacuum-driven operation allows a continuous separation process, and this will inevitably outperform the slower filtration rate exhibited by gravity-driven oil-water separation. Based on this, a facile and low cost approach for synthesizing an oil-water separation membrane that is able to be operated under a vacuum-driven operation with self-cleaning capability is greatly desired.

Some of the major advantages of employing hydrothermal synthesis include the ability to fabricate substances that are unstable when reaching melting point, and the capability of producing large high quality crystal. Nonetheless, the process of the substances or crystal growth cannot be monitored during the hydrothermal reaction (Maksimov, Meskin, & Churagulov, 2007; Meskin, Ivanov, Barantchikov, Churagulov, & Tretyakov, 2006; Shlyakhtin.Oleg, Zaitsev.Dmitry, & Churagulov.Bulat, 2009).

2.5. Membrane fouling mechanism

Membrane technologies have been widely employed in various water treatment processes. However, the decrease in filtration performance with time is one of the major imperfections which hinders its initial performance. This phenomenon is known as membrane fouling. Membrane fouling commonly occurs either on the membrane surface or within the membrane pores. This result in the blockage of membrane pores which emanates from the sieving and adsorption process during filtration. Owing to such occurrence, the permeate production rate and the membrane operation becomes greatly

affected. Thus, membrane fouling is considered the most challenging obstacles to be overcome for future membrane design and development.

Figure 2.4 illustrates the flux-time curve of an ultrafiltration (UF) process. Three different stages are shown in the graph where; (I) depicts rapid initial drop of permeate flux, (II) shows the gradual decrease in flux and (III) represents a steady state flux.

Figure 2-4: Three stages of flux decline (Li, Fane, Ho, & Matsuura, 2008)

The decline in flux is caused by two major factors which include pore blockage and cake layer formation on the membrane surface. These factors are capable of increasing the membrane resistance during the filtration process, where pore blockage increases the resistance of the membrane and the cake layer formation further cause a decline in permeate flow. In general, pore blockage and cake layer formation are two common factors that contribute to membrane fouling.

During a typical membrane filtration process, the permeate flux can be rapidly affected in the initial stage of the process due to pore blockage mechanism. Thus, the maximum flux rate is normally considered at the start of the filtration process when the pores of the membrane are clean. The decline in flux begins when the particles are within the membrane pores, and the severity of pore blockage depends on the shape and size of the particles and membrane pores. As a result, a complete blockage will occur when the particles and membrane pores have similar shape and sizes (Belfort, Davis, & Zydney, 1994; Hlavacek & Bouchet, 1993). Compared to cake formation, pore blockage requires

a shorter period of time to reach complete blockage since less than 1 layer of particles is sufficient to achieve such phenomenon (Hlavacek & Bouchet, 1993; Song, 1998).

The flux decline effect contributed by cake layer formation will only take place after the complete pore blockage mechanism. The accumulation of such cake layers is attributed to the increase in the amount of particles retained on the membrane surface. Consequently, the membrane resistance increases with the growth of the cake layer thickness, which results the permeate flux to further decline with time.

2.5.1. Mathematical models for membrane fouling

Different mathematical models have been developed to study and describe membrane fouling phenomenon. Cake filtration model is one of the widely used empirical model which emphasises on the importance of particles larger than the membrane pore sizes. Equation 2.1 as follow illustrates this model, where the hydrodynamic resistance of cake layer is represent by $[R_c, m^{-1}]$

$$R_c = R_c^{\wedge} . md \text{ ----- Equation 2.1}$$

where $R_c^{\wedge}$ [m/Kg] represents the cake resistance contributed by the cake layer presence on the membrane surface and md [kg/m²] is the mass of deposit per unit membrane surface area. Subsequently, Darcy's Law and resistance in series model (RIS) is applied to determine the permeate flux (J , m³/m².s) as shown below;

$$J = \frac{\Delta P}{\mu (R_m + R_c)} \text{ ----- Equation 2.2}$$

where ΔP (Pa) represents the transmembrane pressure, μ (Pa-s) is the viscosity of the fluid and R_m (1/m) is the hydrodynamic resistance of clean membrane. Previous research has been conducted to relate $R_c^{\wedge}$ to the cake layer structures resulted from particles and aggregates, in which reasonable filtration data and results were obtained (Chellam, Jacangelo, & Bonacquisti, 1998; A. S. Kim & Hoek, 2004; M. Zhang & Song, 2000). Nonetheless, this model only explains the proportionality between the build-up of hydrodynamic resistance and deposit mass on the membrane surface during filtration process under certain conditions. Studies have shown that $R_c^{\wedge}$ values vary from 10¹⁰ to 10¹⁶ m/kg for various aquatic substances. For example, $R_c^{\wedge}$ value for Chlorella algae culture ranged from 10¹⁰ to 10¹² m/kg when its growth became inhibitive. Furthermore, it was also discovered that $R_c^{\wedge}$ depends on several other factors which include cell

morphology, surface properties, time and operating pressure. Although the resistance in series model (RIS) model is easy to apply for the study of membrane fouling phenomenon, one has to take note that this model excludes the consideration of pore blockage mechanism.

Another model was introduced by Kosvintsev and co-worker who studied membrane fouling phenomenon attributed to physical sieving by particles larger than the pores of membrane under low pressure condition (S. Kosvintsev, Holdich, Cumming, & Starov, 2002). From their analysis, they suggest that fouling attributed to cake filtration does not occur at the start of the filtration process, and the fouling is governed by pore blocking to an extent when the membrane surface is covered by the particles. This pore blocking dominated model which describes volume as a function of permeate time under constant pressure is presented as follows:

$$V = \frac{1}{\gamma n \beta} \ln(1 + \beta \tau^*) \text{ ----- Equation 2.3}$$

Where V is the permeate volume (cm³), β is the ratio between particle-fouled membrane area to the area of clean pores. This constant has to be determined through experimental procedures for a given membrane which should be greater than unity. n is the number of particles contained in per unit volume of feed, γ represents the fraction of pores area to total membrane area and τ^* is the filtration time (dimensionless), where $\tau^* = \gamma n \int_0^t \frac{dV}{dt}$.

In general, this model only focuses on fouling caused by pore blocking while the effect on cake layer formation is not taken into account, and more information can be obtained from the authors' subsequent research publication (s; Kosvintsev, Cumming, Holdich, Lloyd, & Starov, 2004).

Ho and co-worker then proposed a model which incorporated both pore blockage and cake layer formation fouling mechanisms under low pressure condition caused by proteins and humic acids (Ho & Zydney, 2002; W. Yuan, Kocic, & Zydney, 2002) This model again assumes that the fouling is attributed to presence of large particles formed mainly by proteins and humic acids aggregates, operated under constant pressure and varying flux. The combined model is as follows:

$$\frac{J}{J_0} = \exp\left(-\frac{k_b \Delta P C_b}{\mu R_m} t\right) + \frac{R_m}{R_m + R_c} \left[1 - \exp\left(-\frac{k_b \Delta P C_b}{\mu R_m} t\right)\right] \text{ ----- Equation 2.4}$$

Where J and J_0 (m^3/s) represent the permeate flux at a given time and initial flux of the cleaned membrane respectively, K_b (m^2/kg) is the parameter for pore blockage which can be measured experimentally (blocked membrane area per unit mass of aggregates passing through the membrane). C_b (kg/m^3) represents the large aggregate concentration, R_m ($1/\text{m}$) is the resistance of the unfouled membrane, R_c ($1/\text{m}$) is the resistance of the cake layer formation, μ is the viscosity of the solution and ΔP is the transmembrane pressure (Pa). Equation 2.4 describes both the pore blockage and cake layer formation respectively. First term represents pore blocking which occurs during the initial stage, and the second term indicates cake layer formation which dominates fouling for a longer time.

Fouling attributed to adsorption caused by particles smaller than the pore size of the membrane can be represented using the following model (Srebnik, 2003). The effect on the membrane's permeability due to the adsorptive layer can be estimated using the modified Hagen-Poiseuille capillary filtration model as shown below:

$$\frac{J}{J_0} = \left(1 - \frac{\delta}{r_p}\right) \text{----- Equation 2.5}$$

Where J and J_0 (m^3/s) represent the permeate flux after the adsorptive fouling at a given time and initial flux of the cleaned membrane respectively, under a given transmembrane pressure, δ (m) is the thickness of the adsorptive layer (measured experimentally) and r_p (m) indicates the pore radius of the membrane. However, there is a limitation for such model to be applied in a filtration process of natural surface water which contain high content of aquatic NOM. Thus, the δ value cannot be determined easily using either theoretical or experimental explanation, which is further worsened by heterogeneity of membrane surface properties.

2.5.2. Factors affecting fouling

The factors that contribute to membrane fouling includes 1) Properties of membrane; 2) Properties of solution; and 3) Operating conditions

2.5.2.1. Properties of membrane

Typically, membrane can be attractive or repulsive to water environment. The wettability of membrane is mainly dependent on its composition and surface chemistry, which can be determined through measuring the membrane contact angle. As shown in

Figure 2.5, membrane contact angle measures the angle of contact between the membrane surface and a water droplet.

Figure 2-5: a) Hydrophobic behaviour on a membrane surface; b) hydrophilic behaviour on a membrane surface (Li et al., 2008)

Membranes that are equipped with hydrophilic properties contain active groups that are capable of forming hydrogen-bonds with water (Figure 2.5b). On the other hand, hydrophobic membranes react in an opposite interaction with water compared to its counterpart, and they have little or no tendency to adsorb water. In other words, water droplets tend to repel away from the membrane surface as illustrated in Figure 6a. The low wettability of such membrane can be explained by the lack of active groups present on the surface to establish hydrogen-bonds with water. Furthermore, foulants tend to possess hydrophobic characteristics, and thus escalate fouling of the hydrophobic membrane. Due to their low interfacial energy, these foulants have the tendency to group together and form cluster. Usually, membrane with a high degree of hydrophilicity has greater charge density on its surface. For example, polysulfone, cellulose acetate, ceramic and thin-film composite membrane employed in water treatment and wastewater recovery applications contains a greater amount of negatively surface charge and hydrophilicity. As a result, the occurrence of fouling can be scaled down when using membrane with surface charge, and such membranes have been modified to enhance their hydrophilic properties.

Moreover, morphology of the membrane such as pore size, pore size distribution and pore geometry, especially those present on the membrane surface, also contribute to the fouling effect. These mainly involve fouling mechanisms namely pore blockage and cake layer formation as discussed previously in section 2.5.1.

2.5.2.2. Properties of solution

Membrane fouling can also be attributed to the properties of the feed solution such as solution concentration, particles properties, pH and ionic strength. In general, the permeate flux tend to be affected when there is an increase in the feed concentration. This can be explained by the presence of high foulant concentration which escalate membrane fouling. Particles found in the feed solution may be due to either the feed nature or through precipitation of soluble components. With the presence of such particles, pore blocking, pore narrowing or cake layer formation can occur, depending on the size of the particles. Large particles are the ones that result in higher membrane flux and cake thickness because they inhabit deposition (Vyas, Bennett, & Marshall, 2000). On the other hand, fine and coarse particles have the tendency to form cake layers with lower porosity. This is because the interstices form by the larger particles can be filled by the finer ones when it slides through the pores. Thus, the particle size distribution plays a significant part in determining the membrane selective deposition. Furthermore, particle shape does influence the porosity of the cake layer assembled on the membrane, in which particles with lower sphericity will result in higher porosity (Vyas et al., 2000).

pH, ionic strength and electric charge are some factors that have an impact on membrane fouling. The feed solution pH and ionic strength affect the membrane charge, particle charge, conformation and stability of particles which further enhance the adhesiveness of particles/molecules, and thereby the size of the cake layer. For instance, a study focusing on the impact of membrane fouling relating to the pH of latex emulsion demonstrated that high pH condition will prohibit coagulation of latex particles, and thus enhance the anti-fouling properties. On the contrary, it also known that a decline in pH will lead to NOM with reduced molecular size, which increase membrane adsorption and lead to severe fouling (A. Abdelrasoul, H. Doan, & A. Lohi, 2013).

2.5.2.3. Operating conditions

Investigation of temperature effect on permeate flux shows that permeate flux increased at a higher temperature, which represent a decline in fouling. For example, the permeate flux was increased by a margin of 60% when the temperature was raised from 20°C to 40°C, and this could be attributed to the possibility where permeate diffusion rate through the membrane was altered due to the temperature change (Salahi et al., 2010)

Cross-flow velocity is also known as the superficial velocity of the feed flow that is moving parallel to the surface of the membrane. A wide variety of feed solutions had been tested to discover the effect of cross flow velocity. It was noted that the mass transfer coefficient and mixing mechanism near to the membrane surface were enhanced by increasing the cross-flow velocity, in which the permeate flux was increased. Furthermore, high mixing mechanism gained from the increase in cross-flow velocity reduces the feed solid aggregation on the membrane surface (Abdolhamid, Toraj, Ali Rahmat, & Fatemeh, 2012). This can be explained by the enhanced diffusion process in which the components were diffused back into the bulk, resulting in lower effect of concentration polarization (A.Abdelrasoul et al., 2013).

Transmembrane pressure (TMP) is another essential factor to be observed. TMP can be defined as the difference in pressure between the feed and permeate flow, and this affect the permeation rate. At a point with higher TMP, the force pushing the fluid through the membrane will increase which result in an increase in permeate flux. Figure 2.6 illustrates the pattern of flow where the increase in pressure leads to an increase in permeate flux. At P_1 (very low pressure), flux is similar to pure water flux at the same pressure. As pressure increases to P_2 , the concentration polarization effect on the retained component increases due to the upsurge of flux. At P_3 which is also known as the critical pressure, concentration polarization is sufficient for the retained solutes present on the membrane surface to form gel concentration, C_{gel} . Owing to the gel layer formation, there will not be any impact on the increase in flux even if the applied pressure is increased. However, the gel layer thickness and the retained solute density will continue to increase. Therefore, permeate flux passing through the membrane will be constrained, and thus, a steady state flux can be observed. Notably, it was reported that fouling phenomenon was not observed under critical flux conditions (Li et al., 2008).

Figure 2-6: Effect of membrane Flux relating to pressure (A.Abdelrasoul et al., 2013)

2.5.3. Impact on Membrane properties

The interaction between the solute and membrane can be influenced by the membrane properties, which impact on adsorption and fouling. For example, while filtering proteins that are hydrophobic in nature, it is not advisable to utilise hydrophobic membranes because they will strongly adhere to the hydrophobic surfaces. Therefore, a hydrophilic membrane is more favourable in such a situation to reduce membrane fouling. Enhancing membrane properties using chemical modification is one option in improving the membrane properties, for example, sulfonation of polysulfone.

Alternatively, blending hydrophobic component with hydrophilic ones can also enhance the membrane anti-fouling properties. Pretreatment of membrane using hydrophilic surfactants is another way to improve solute and membrane interaction. There are various methods that can be employed to introduce hydrophilic properties onto conventional ultrafiltration membranes via surface modification, and these methods are listed as follow (Hazlett, 1995; Y. G. Park, 2002);

- a) Plasma treatment on membrane surfaces
- b) Polymerization using UV, heat or chemicals
- c) Interfacial polymerization
- d) Introduction of polar or ionic group to membrane surface

Pre-coating of membrane with non-ionic surfactants can also be done to promote hydrophilization, and this method is very practicable for industrial applications due to its simple procedures. Report shows that such treatment significantly improves rejection rate and flux permeation rate (R.D.Noble & S.A.Stern, 1995). Besides that, ozone can be used to modify a hydrophobic membrane hydrophobic nature. This treatment enhances the membrane hydrophilicity by grafting monomers with hydrophilic groups onto the membrane surface via introducing a peroxide group. The effectiveness of such processes can be determined by observing the concentration of peroxide group formed. A study was conducted to investigate the extent of permeate flux after ozonation, and the result shows that this treatment increased the flux be 10%. However, ozonation only prolongs the period of reaching fouling rather than eliminating it. Thus, introduction of ways in preventing fouling is essential to membrane filtration (Y. G. Park, 2002).

2.5.4. Membrane cleaning

For most membrane systems, chemical cleaning is one of the most commonly employed methods to alleviate membrane fouling. However, the entire process is cumbersome, and the plant unit that undergoes cleaning requires shutting down. As a result, the overall plant capacity can be affected and harmful wastes may be generated. In chemical cleaning, the cleaning process involves chemical reaction between chemicals and foulant, and there are several factors that can affect the cleaning efficiency. These factors include temperature, concentration, length of cleaning period and hydrodynamic reactions. Chemical concentration is important because it not only maintains equilibrium of the reaction rate, it is also essential to overcome the mass transfer barrier

caused by fouling layer. In most cases, cleaning chemical concentration is sufficient to maintain a reasonable reaction, while mass transfer is the factor that determine the limitation of the chemical concentration required for the cleaning process.

Temperature conditions can also affect the cleaning of the membrane by 1) altering the nature of chemical reaction, 2) modifying the reaction kinetics, and 3) altering the foulants and reaction products solubility. In general, membrane cleaning portrays better results at higher temperatures. However, not all membranes are capable of withstanding elevated temperatures.

Hydrodynamic conditions are equally important to create interactions between the cleaning chemicals and fouling materials. This is because the mass transfer between the chemicals and fouling layers will reintroduce the reaction product back into the bulk phase. In practice, in order to allow efficient dynamic cleaning, employing circulating cleaning methods are more effective compared to the static cleaning method such as soaking.

However, the life of a membrane can be affected due to prolonged and repetitive use of the chemical cleaning method, hence, using this method should be minimised.

In cases where chemical cleaning is not effective in recovering the permeate flux, mechanical cleaning can be an alternative option. For example, sponge balls can be used for cleaning tubular membrane modules, in which the balls eliminate the materials that are deposited on the membrane surface through scrapping. Nonetheless, this method requires a long cleaning period, and thus, it is not widely used.

Membrane with self-cleaning abilities is an alternative option for solving these problems. The advantages of such membrane are 1) self-cleaning properties, 2) capable photocatalytic degradation of target compounds and 3) reducing operational costs for membrane filtration. In this thesis, a novel self-cleaning oil/water separation membrane will be introduced.

2.6. Titanium Dioxide material

2.6.1. General remarks of titanium dioxide (TiO₂)

TiO₂ can be classified under the family of transition metal oxides. In the early 20th century, TiO₂ was used to replace toxic lead oxides as pigments for white paint. Nowadays, approximately 4 million tons of TiO₂ are produced annually(international,

1996; Natara NC, 1998). Over the years, the demand for TiO_2 as pigment has increased. They are widely used in fabricating materials such as paints, plastics, paper, food, leathers, pharmaceuticals and UV absorber in sunscreen cream (for high sun protection factor). Furthermore, with its high refractive index, TiO_2 can be employed as an anti-reflection coating on a solar cell and thin film optical devices (Macleod, 1986).

TiO_2 possesses various properties such as chemical stability, non toxicity and low cost etc (kazuhito Hashimoto, 2005). With such advantageous characteristics, it has received a huge deal of attention. Figure 2.7 shows the increment of TiO_2 publications in each year. This reflects the importance of TiO_2 mediated reactions and its potential for applying in an industrial scale. In a catalytic reaction, TiO_2 is capable of playing the role of a promoter, a carrier for metal and metal oxides, an additive and a catalyst (Hadjiivanov & Klissurski, 1996). Reduction of NO_x to N_2 , breaking down volatile organic compound (VOCs) (van der Grift, Woldhuis, & Maaskant, 1996), oxidising CO by O_2 (S. D. Lin, Bollinger, & Vannice, 1993), oxidising H_2S to S (Woo Chun, Yeol Jang, Won Park, Chul Woo, & Shik Chung, 1998), reducing SO_2 to S (H. Kim, Won Park, Chul Woo, & Shik Chung, 1998) and NO_2 storage (Despres, Koebel, Kröcher, Elsener, & Wokaun, 2003) are some reactions that utilise TiO_2 catalysts.

Figure 2-7: Number of TiO_2 publications per year (Jr. et al., 2013)

Figure 2.8 summarises the photo-induced phenomena of TiO_2 (Carp, Huisman, & Reller, 2004). The band gap of the semiconductor determines the entire photo-induced process. This process will only initiate when energy of the photon is higher than the semiconductor's band gap. Subsequently, an electron is transferred to the conduction band, which results in the formation of holes in the valence band. These excited electrons can be employed in a photovoltaic solar cell to produce electricity. Furthermore, it can also act as a driving force for a chemical reaction to take place. The entire process is known as photocatalysis.

Figure 2-8: TiO_2 induced processes (Carp et al., 2004)

With its photocatalysis attribute, TiO_2 has been regarded as an important photocatalyst for environmental decontamination process. It is capable of degrading and mineralising a variety of organics, virus and bacteria into carbon, water and harmless inorganic anions. This process is caused by the presence of highly oxidizing holes and hydroxyl radicals ($\text{OH}^\cdot$). The generated holes and radicals are also known as indiscriminate oxidizing agents. Ultimately, the ability to regulate the photocatalytic activity is crucial for some applications such as the cosmetics industry. For this application, the product should possess low photocatalytic activity. Otherwise, this reaction may damage the DNA in cells.

2.6.1.1. Crystal Structure and properties

The four polymorphs of TiO_2 which can be found in nature include anatase, brookite, rutile and $\text{TiO}_2(\text{B})$. The different formations of anatase, rutile and brookite can be explained using an octahedral structure. Three of these crystals can be recognised by observing the distortion of individual octahedral, as well as the assembly patterns of the octahedral chains. Figure 2.9 illustrates the crystal structures of three different TiO_2 phases. The structure of anatase crystal is constructed from an octahedral geometry that are connected by their vertices. For rutile, the structure is formed by connecting the edge. In brookite, the structure is formed by connecting both the vertices and edges (Carp et al., 2004).

Figure 2-9: Formation of a) Anatase, b) rutile and c) brookite structure(Carp et al., 2004)

Studies have shown that anatase, rutile and brookite are most thermodynamically stable at particle sizes of 11 nm, 11-35 nm and sizes greater than 35 nm respectively (H. Zhang & F. Banfield, 1998). The conversion from anatase to rutile has been widely studied to determine their mechanistic and application driven potential (Suresh, Biju, Mukundan, & Warrier, 1998). This is because the identification of the TiO_2 phase is an important parameter to determine the potential of the material to be employed as a photocatalyst, catalyst or ceramic membrane material (Amy L. Linsebigler, 1995). Ultimately, the transformation of the different TiO_2 phase can be achieved by adjusting the temperature and pressure during the synthesis process.

2.6.2. Photocatalysis reaction

In general, photocatalysis refers to catalytic reactions occurring under the provision of light, and these reactions are dependent on the number of photocatalytically active centres. Thus, specific surface area of the catalyst is often been used to characterise the catalytic activities of the catalyst. Furthermore, photocatalysis can also be denoted as an overall phenomena relating to both photochemical and catalytic processes (Braslavsky et al., 2011) .

As mentioned, the term photocatalysis refers to a reaction that employs light as a driving force to modify the rate of reaction. Figure 2.10 shows that green plants' photosynthesis process can be regarded as a typical example for photocatalysis reaction. During photosynthesis, the chlorophyll photocatalyst capture the energy from the sun to convert water and carbon dioxide into O_2 and glucose. In other words, photocatalysis can also be described as a natural phenomenon.

Figure 2-10: Similarities between photocatalysis and photosynthesis(Science, 2013)

The principle of photocatalytic reactions was originally discovered by Dr Fujishima in 1960's using titanium metal under the irradiation of UV light for water splitting process. Furthermore, TiO_2 also possesses photodegradation characteristics. Therefore, with such properties, titanium dioxide has been employed in various applications such as paint, cosmetics and sun blocks. Moreover, photocatalysis reactions have been attracting diverse attention for chemical waste remediation due to its low temperature and non-energy intensive approach. Most importantly, through water splitting process, this

reaction will potentially aid in accelerating the path in generating green energy such as hydrogen for future applications.

In general, The term 'heterogeneous photocatalysis' is tricky and the detailed mechanism of its reactions has not been properly explained in most cases. For a photocatalytic reaction, a solid photocatalyst (semiconductor) will obtain energy from a light source to react with the liquid or gas phase reactants or product (Schiavello, 1997). Generally, the operation of AOPs results in the formation of low sensitivity hydroxyl radical (OH $\cdot$). These radicals are capable of performing complete mineralization cycle through oxidation process. Moreover, this radical is not only effective for less reactive pollutant; it is also able to destroy highly chemically stable biologically refractory pollutants (Andreozzi, Caprio, Insola, & Marotta, 1999).

ZnS, ZnO, TiO $_2$, Cds and GaP are semiconductors that have effectively shown potential in degrading pollutants, as well as performing complete mineralization in a typical heterogeneous photocatalysis reaction. Among them, TiO $_2$ has been proposed to be the most active photocatalyst under the photon energy range between 300 nm to 390 nm. Furthermore, it also portrays higher stability characteristic compared to other photocatalysts belonging to the same class (Malato, Fernández-Ibáñez, Maldonado, Blanco, & Gernjak, 2009). Figure 2.11 broadly illustrated the photocatalytic oxidation process performed by a TiO $_2$ photocatalyst. To date, TiO $_2$ has been involved in extensive applications relating to water treatment and air purification. This is due to its thermal stability, chemical stability, excellent mechanical properties and cost effectiveness characteristics.

Figure 2-11: Principle of photocatalytic oxidation

The benefits of applying heterogeneous photocatalytic oxidation process are (a) complete mineralization cycle can be achieved by the presence of strong and less selective oxidant, (b) the photocatalyst are stable, reusable, non-toxic and available at low cost, (c) processes are favourable under ambient condition and (d) acquisition of expensive oxidizing chemical is not required (Chong, Jin, Chow, & Saint, 2010; Mehrotra et al., 2003).

2.6.3. Processes in photocatalytic activities

As mentioned, TiO₂ has been discovered to be the most active photocatalyst within the energy range of 300 nm to 390 nm as compared to the available semiconductor. An ideal photocatalyst need to acquire several factors such as oxidation potential and energy of the band gap. Firstly, oxidation potential is crucial as the formation of photogenerated valence band holes (h^+_{vb}) and to create hydroxyl radicals (HO•) in water contribute an important role in oxidizing organic molecules for a photocatalyst. Similarly, the reducing power of the excited conduction band electron (e^-_{cb}) need to acquire sufficient energy to create superoxide from the reduction of molecular oxygen (Mills, Holland, Davies, & Worsley, 1994). Ultimately, these are the two key chemical processes for the photocatalysis of organic molecules which lead to the formation of simple gaseous products (H₂O, CO₂) and inorganic ions (NO₃⁻, SO₄²⁻).

Band gap energy can be defined as the light energy that is required to excite an electron to the conduction band, and results in the formation of a positively charged hole in the

valence band, h^+_{vb} (X. Li, Cubbage, & Jenks, 1999). Titanium dioxide (TiO_2) possess with both high oxidation potential and band gap which support the absorption of UV portion of sunlight. Unfortunately, the solar emission spectrum only comprises of five percent UV.

Despite the low solar absorbance portray by Titania material, it is still being regarded as the most effective option for general photocatalytic needs owing to other desirable criteria. For example, TiO_2 is low in cost, non-toxic, chemically stable, photolytically stable, and reusable. Moreover, the physical and chemical characteristics of TiO_2 can be simply modified, such as absorption edge and particle size. The modification of these factors can potentially enhance the Titania's oxidation capabilities. Methods for advancing the band gap of TiO_2 to a higher wavelength will be discussed later.

Equation 1-9 explained the chemical mechanism of TiO_2 in water, and the pictorial representation of these processes is illustrated in Figure 2.12. The initial reaction of TiO_2 with light is represented by equation 1. This reaction results in the creation of holes and electrons which act as the active excited species, and thereafter react with water and oxygen as shown in equation 2–5. Considering in the aqueous conditions, hydroxyl radicals appeared to be one of the major sources due to the abundant Ti-OH groups (X. Li, Cubbage, Tetzlaff, & Jenks, 1999). Superoxide ($O_2^{\cdot -}$, equation 3) and hydroxyl radical ($HO\cdot$, equation 5) are two downstream products resulted from the reaction with

molecular oxygen, which reacts with the nearby organic molecule. Subsequently, the introduction of hydrogen peroxide in equation 5 and 6 can effectively split up into two hydroxyl radicals through either aqueous photolysis or accepting an electron as shown in equation 6(X. Li, Cubbage, & Jenks, 2001). As presented in equation 7, the hole, h_{vb}^+ can also react with the adsorbed organic donor (**D**) directly. The reduction of an adsorbed molecule by the conduction band hole is demonstrated in equation 8, in which **A** is the adsorbed molecule that accept electrons. However, the reductive photocatalysis of TiO_2 is less evaluated due to the lower reducing power of e_{cb}^- as compared to the high oxidizing power provided by the h_{vb}^+ (Sun & Pignatello, 1995). Lastly, equation 9 explains the recombination of both e_{cb}^- and h_{vb}^+ which release heat, and this process occurs in almost ninety percent of all charge carriers formed, which compete with all “useful” chemistry available in the system. Thus, much efforts have been presented to understand surface recombination and many modifications of Titania relating to reducing recombination(Cunningham & Al-Sayyed, 1990).

Figure 2-12: Illustration for TiO_2 excitation(Timothy, 2009)

Hence, to prevent equation 9 from being the dominating reaction, electron acceptor needs to be constantly added to the reaction to physically separate the charges. Molecular oxygen is one of the common oxidant (equation 8), which is added to the reaction since it is a stoichiometric oxidant (equation 1). Owing to its ability in producing superoxide which lead to the introduction of more hydroxyl radicals (equation 3-5), O_2 portray as an ideal trap for e_{cb}^- . Furthermore, since O_2 has been regarded as a better electron acceptor than most organic molecules, equation 3 becomes more important in aqueous photocatalysis.

Intense studies have been done to modify the electronic structure of TiO_2 to improve its absorption into visible range. Some of the common approaches include pure Titania modifications and doping with other semiconductors. Pure Titania modifications include customizing the morphology and surface area of the material. For example, introducing two different photoactive crystal phases into the material such as Degussa P25, which contains 80% anatase and 20% rutile. In this way, it can heightened photocatalytic activity by having the ability to trap the excited electron from the anatase surface in the lattice of the rutile phase, and thus minimizing the recombination rate (Fujishiro & Mitamura, 1988; Kudo & Miseki, 2009). In other words, crystal structure and crystallinity alter the photocatalyst performance, in which influence the photocatalytic activity. In addition, optimal particle size or surface area has also been largely investigated over the years. The objective of this finding relates to the amount pollutants that can be attached to the surface, as well as the amount of charge carrier recombination that occurs. Other morphological modifications comprise of coating TiO_2 onto the polymer surfaces formed with various shape and sizes in realistic water and air treatment (De Laat & Gallard, 1999). In general, factors such as crystal structure, crysallinity and particle sizes will greatly affect the overall photocatalytic reactions shown in Figure 2.16 (Anpo, Shima, Kodama, & Kubokawa, 1987; Kudo & Miseki, 2009; McLaren, Valdes-Solis, Li, & Tsang, 2009; Z. Zhang, Wang, Zakaria, & Ying, 1998). Anpo et al had shared that a reduction in particle size will effectively improve the absorption and photoluminescence spectra. In other words, this shows that the physical and chemical properties of a small particle are different from its bulk material (Anpo et al., 1987). Ischenko et al also discussed the importance of particle morphology control as this will influence several properties significantly (Ischenko et al., 2005). Previous study had shown that a smaller particle is capable of improving the photocatalytic decomposition by 5 times (McLaren et al., 2009). This can be explained by the fact that when the particles become smaller, the distances provided for the migration of electrons and holes to active sites shrink. Thus, emerging a lower recombination probability. Moreover, doping of TiO_2 is also a fast progressing field, in which metals, non-metals and other metal oxides are coated onto the Titania crystallites to improve visible light absorption and decrease the electron-hole recombination rate.

In general, the oxidizing chemistry of TiO_2 is attributed to the presence of oxidizing species such as hydroxyl radical, $\text{HO}^\cdot$, which are formed by the aqueous photolyses of

TiO₂. The mechanism for the degradation of organic pollutant is largely dependent on the reaction conditions and the organic molecules structure. For most circumstances, TiO₂ surface acts as the adsorption center which can either bind the organic molecules or onto a water molecule ad-layer within a few angstroms of the surface. Thereafter, the molecules will be oxidized either by direct electron transfer or by addition of hydroxyl radicals. After this, a cascade of reactions leads to the formation of CO₂ and H₂O. However, in some cases, recalcitrant species are created which cannot be further degraded by TiO₂ alone (Fox & Dulay, 1993; X. Li & Jenks, 2000).

Over the past decades, it has been reported that Titania materials can degrade any type of compounds which it encounters. However, there are exceptions, one of the example is cyanuric acid which is a final degradation product of triazines species (Tachikawa, Fujitsuka, & Majima, 2007; Tachikawa, Tojo, Fujitsuka, & Majima, 2004). Previously, Hidaka group reported the complete degradation of cyanuric acid to inorganic products using TiO₂, and this was only feasible upon the addition of extra oxidants such as O₃ and H₂O₂. (X. Li & Jenks, 2000)

Ultimately, based on the equations as shown in equation 1-9, it explained the effectiveness of employing TiO₂ nanomaterials under UV irradiation. Furthermore, owing to its excellent photocatalytic reactions, Kazuhito group had reported that the hydrophilicity of TiO₂ can be under UV exposure (Kazuhito, Hiroshi, & Akira, 2005), and this will be discussed in the follow section.

2.6.4. Hydrophilic characteristics of TiO₂

In addition to photocatalytic properties, TiO₂ is also well known for its hydrophilic surfaces. Based on several reports, TiO₂ has demonstrated its hydrophilic characteristics in several applications (Bolis et al., 2012; Fateh, Dillert, & Bahnemann, 2013; Sakai, Wang, Fujishima, Watanabe, & Hashimoto, 1998). In 1995, the water wettability of TiO₂ surface resulting from UV light irradiation was documented. With this discovery, a wide range of possible applications for TiO₂ materials have been uncovered (Kazuhito Hashimoto, 2005).

In general, the hydrophilicity can be determined based on the evaluation of water contact angle (CA). Basically, CA represents the solid surface and the tangent line of the liquid phase in a solid-liquid-gas phases. It can also be regarded as the free energies between the three phases. For a hydrophilic surface, water droplet will completely spread out and

attract to the solid surface, resulting in a CA close to 0° . In other words, it allows water to pass through the solid surface. As shown in Figure 2.13, a less hydrophilic surface will obtain a CA up to 90° , while CA for a highly hydrophilic surface will range from $0 - 30^\circ$. For a hydrophobic surface, there is a tendency to prevent water from wetting the surface or entering the pores. As a consequence, the water droplet will only simply rest on the surface of the solid. Typically, a hydrophobic surface will achieve a CA of $150 - 180^\circ$ (MemRE, 2014).

Figure 2-13: Definition of different wettability properties based on contact angle (Cenano, 2014)

Many researchers have described TiO_2 as a UV-sensitive hydrophilic surface, in which hydrophobic surfaces can be converted to being hydrophilic when irradiated with UV light (M. Miyauchi et al., 2002; Watanabe et al., 1999; J. Yu & Zhao, 2001). Watanabe and co-workers reported that the conversion between hydrophobic and hydrophilic properties could be explained by the photoreduction of Ti^{4+} to Ti^{3+} (Watanabe et al., 1999). In the subsequent study, they realised that the presence of sodium ions in TiO_2 materials act as an electron-hole recombination center. As a result, this inevitably affected the photocatalytic properties of TiO_2 material. On the contrary, the results showed that the hydrophilic property of TiO_2 is not affected by presence of sodium ion. This is because hydrophilicizing effect only took place in the topmost layer of TiO_2 and their studies found out that the presence of sodium does not greatly affect the top layer of the structure. Ultimately, they concluded that photocatalytic oxidation power and hydrophilicity are two independent properties, which can be controlled independently (Toshiya Watanabe, 2000).

In summary, TiO_2 has been proven possess the hydrophilic property which can be measured through a water contact angle test. Furthermore, hydrophilicity is not easily affected by the presence of secondary ions such as sodium.

2.7. Perspectives

To conclude the findings based on the literature review, oil and gas industries such as petroleum refining have been unavoidably generating a large volume of oily wastewater. Improper discharge of this wastewater can potentially lead to serious environmental concerns such as polluting the water sources. Although water embraces almost 70% of the earth surface, it is still considered as a scarce resource in most countries. One of the major concerns would be the accessibility to safe drinking water, this has been extremely crucial to support the livelihood of mankind and animals. Therefore, the attention on improving the conventional oily wastewater treatment has become an urgent issue.

Generally, oily wastewater can be treated using physical, chemical and biological methods. Some of the conventional methods include coagulation, gravity separation, flotation, adsorption, biological treatment and membrane filtration. Table 1 shows the advantages and disadvantages of the various conventional methods available for treating oily wastewater. Furthermore, it also presents the oil removal efficiency for employing the individual method. However, most of these methods are not able to treat oil-water emulsions containing low oil concentration and finely dispersed oil droplets. For example, these techniques are only capable of eliminating oil droplets with a diameter more than 10 μm . Among them, membrane filtration has been considered as a preferred option for treating complex oily wastewater. As shown in Table 1, membrane filtration has the highest oil removal efficiency as compared to the rest. However, severe membrane fouling caused by the effluent nature has limited the application of membrane filtration for oily wastewater treatment. As a result, pre-treatment by conventional methods are required in most situations, and this had led to a complicated and expensive treatment process. Therefore, the characteristic of the membrane has to be further modified to enhance the oily wastewater treatment processes. For example, a membrane with self-cleaning property will effectively resolve the issues of fouling experienced during the operation

TiO_2 material has been involving in extensive applications relating to water treatment. This is mainly due to the fact of its thermal stability, chemical stability, excellent mechanical properties and cost effectiveness characteristics. Most importantly, TiO_2 has been discovered to be the most active one under the photon energy range between 300 nm to 390 nm. With its possession of photocatalysis characteristics, TiO_2 has been regarded as an important photocatalyst for environmental decontamination process. In

addition of photocatalytic properties, TiO_2 is also well known for its hydrophilic surfaces. As report, TiO_2 has demonstrated its hydrophilic characteristics in several applications. With the discovery of such property, the range of possible applications for TiO_2 materials has been boosted. The details of the TiO_2 oil-water separation ability will be furthered discussed in the following chapters.

Table 1: Summary of the available technologies for oil-water separation

Treatment Technology	Advantages	Disadvantages	Oil removal efficiency	References
Chemical Precipitation	<p>Formation of solid precipitate</p> <p>Gather smaller particles</p>	<p>Formation of slick</p> <p>Costly Polymer</p> <p>Large amount of chemical usage</p> <p>High metal content in treated water</p> <p>Frequent cleaning</p>	92 - 97 %	(EPA, 2000; Fakhru'l-Razi et al., 2009)
Gravity Separation	<p>Simple process</p> <p>low capital and operating cost</p>	<p>Not effective for removing fine molecules</p> <p>Require large amount of water</p> <p>Require daily cleaning</p>	52 - 87 %	(Coca et al., 2011; Falconer, 2003; Joseph & Yung-Tse, 2004)
Flotation	<p>Simple process</p> <p>Small and shallow plant</p>	<p>Flocs protection is required</p> <p>Power intensive</p>	70 - 90 %	(Gary F. Bennett, 2009; Hoboken, 2012; Joseph

		Not suitable for high-turbidity water		& Yung-Tse, 2004)
Adsorption	Widely employed in oil/water separation Recommended by USEPA	Expensive adsorbent (activated carbon) Heavily dependent on activation and reactivation procedures	80 - 90 %	(Emam, 2013; Joseph & Yung-Tse, 2004; Okiel et al., 2011; TIGG, 2014)
Biological treatment	Efficient in treating organic and inorganic compounds Low operating costs	Only suitable of low oil content wastewater Stringent control require O & M cost for clearing and replacement of membrane High energy due to air scouring	92 - 95 %	(Coca et al., 2011; R. Kurian, 2006; USEPA, 2000, 2008)
Membrane filtration	Able to remove a wide range of compounds	Fouling problems Expensive replacement	95 - 98 %	(Benítez et al., 2006; Coca-Prados et al., 2013; Madaeni et al., 2013;

	Excellent performance for oil/water separation	Pre-treatment require		Marchese et al., 2000; Norouzbahari et al., 2009; Reed et al., 1997; Salahi et al., 2010)
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3. Methodology

3.1. Materials

All reagents used in the experiments were of analytical grade and were used as received without further purification. Degussa P25 (80% anatase and 20% rutile) was purchased from Evonik Degussa (Germany). Copper (II) Chloride Dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99% pure) was purchased from Scientific Resources. Ferric Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Sodium Hydroxide (NaOH, 99%), Hydrochloric Acid (HCl, 36.5%), Titanium(IV) Isopropoxide (TTIP, 97%), Diethanolamine, Hydrazine and Methylene Blue were obtained from Sigma-Aldrich. Urea and Absolute Ethanol was bought from Merck Ltd (Singapore), and Ethylenediamine was purchased from Fluka. Moreover, deionized (DI) water was collected from a Millipore Milli-Q water purification system.

3.2. Characterisation and Instrumentation

3.2.1. Field Emission Scanning Electron Microscopy (FESEM)

The morphologies of the nanomaterial were analysed using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) operated at 5kV. Prior to analysis, samples were placed onto a carbon tape and sputter-coated with platinum for 20 seconds. This measure was adopted to prevent electron charging which would interrupt the analysis process. Generally, FESEM was employed to observe the surface and diameter of the nanomaterials.

3.2.2. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM, Leica LT 7480) was used to examine the morphologies of the as-prepared materials. Similarly, samples were mounted onto a carbon tape and sputter-coated with platinum for 20 seconds before analysis to prevent electron charging.

3.2.3. Transmission Electron Microscopy (TEM)

TEM analyses were performed to observe the as-prepared material at a higher resolution using a JEOL JEM-2010 microscope with an operating specification of 200kV accelerating voltage. Before the analysis, a small section of the membrane was initially dispersed in ethanol through an ultrasonication process, and subsequently applied dropwise onto the copper grid. This step was adopted to promote uniform dispersion of sample on the copper grid.

3.2.4. X-Ray Diffractometer (XRD)

X-ray diffraction (XRD, Shimadzu XRD-6000) with monochromatic high-intensity Cu K α radiation ($\lambda = 1.5418\text{\AA}$) operating at 40kV and 30 mA was used to study the crystal phase of the as-prepared materials.

3.2.5. Energy Dispersive X-ray spectrometer (EDX)

The energy dispersive X-ray spectrometer with monochromatic high-intensity Cu K α radiation ($\lambda = 1.5418\text{ \AA}$) operating at 40 KV and 30mA (EDX, Oxford instrument, X-Max, 80 mm²) was employed to investigate the elemental composition of the as-prepared materials.

3.2.6. Atomic Force Microscopy (AFM)

Atomic Force Microscopy (Park Systems, XE-100) was used to investigate the surface roughness of the as-prepared membrane. Both 2D and 3D AFM images were attained to study the effect of roughness relating to hydrophilicity.

3.2.7. Contact Angle Measurement

The contact angle measurements were carried out on a Video Contact Angle (VCA) device (AST product inc. Optima series) at room temperature. A video camera was used to determine the hydrophilicity and underwater oleophobicity of the individual membrane surface. For CAs in air, 3 μL of water was placed onto the membrane surface, in which readings were collected from three different positions. For underwater CAs, 5 μL of dichloromethane (DCM) droplet was dropped onto the membrane surface which was submerged in water. Thereafter, the final CA reading was obtained from the average measurement of three distinct positions.

3.2.8. N₂ Adsorption-Desorption

The specific surface area of the as-prepared materials was investigated using BET (Quantachrome instruments, Autosorb-6B supplied by ITS Science & Medical PTE LTD). The condition was set at nitrogen ranges from 0.05 m²/g to unknown upper limit at liquid nitrogen temperature of 77K. Prior to sample analysis, degassing of sample was done overnight to eliminate any moisture present within the samples.

3.2.9. Thermogravimetric Analyzer (TGA)

The oil content present in the feed and permeate was examined using PerkinElmer Thermogravimetric Analyzer TGA 4000. At the start of the analytical work, the sample holder was sterilised and cleaned by heating up from 30°C to 300°C in air. Subsequently,

the sample was loaded and held at 110°C for 40 min with a temperature increment of 10°C min⁻¹.

3.2.10. UV-vis Spectrometer

UV-vis spectrometer (Shimadzu UV2450) was employed to identify the materials' light adsorption ability. For each analysis, 3 mL of the photo-reacted solution was extracted with a syringe at a given interval.

3.2.11. Particle Size of Oil Droplet

The optical microscopy image of the feed (oil-in-water emulsions) was captured using Olympus TH4-200 microscope. The droplet size of the oil present in the feed was measured by Malvern Instruments Mastersizer-2000 particle size analyser.

3.3. Sample Preparation

3.3.1. Synthesis of TiO₂ Nanowire

TiO₂ nanowire was fabricated via a conventional hydrothermal method (X. Zhang, Du, Lee, Sun, & Leckie, 2008). In a typical process, 3 g of P25 was thoroughly dissolved in 100 mL of 10 M NaOH aqueous solution. Subsequently, the mixture was transferred to a 125 mL Teflon-lined stainless-steel autoclave and heated at 180°C for 48 h. Thereafter, the white precipitate was washed with HCl aqueous solution and DI water for to achieve a neutral pH. Finally, the resulting white pulp suspension underwent a calcination process in air at 650°C for 2 h to obtain TiO₂ nanowire.

3.3.2. Synthesis of TiO₂ Nanotube

TiO₂ nanotube was produced through a hydrothermal process that was previously reported (S. Xu, A. Du, J. Liu, J. Ng, & D. Sun, 2011). First, a mixture was prepared by adding 3 g of P25 into 100 mL of 10 M NaOH aqueous solution and was stirred for 6 h. Thereafter, the mixture was loaded into a 125 mL Teflon-lined stainless-steel autoclave where it underwent a heating process at 150°C for 48 h. Subsequently, the precipitate was washed with HCl aqueous solution and deionised (DI) water to achieve a neutral pH. Finally, the product was annealed at 450°C for 2 h.

3.3.3. Synthesis of Copper Microwire (MW)

The copper microwire was fabricated following a modified approach discovered by Rathmell and co worker (Rathmell, Bergin, Hua, Li, & Wiley, 2010). Compared to previous study, the amount of ethylenediamine (EDA) added was adjusted in order to

promote the growth of copper microwires. In short, hydrazine aqueous solution was prepared by mixing 100 ml NaOH (15 M), 5 ml copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Scientific Resources, 99% pure) (0.2 M), 1.0 ml ethylenediamine (EDA) and 0.1 ml hydrazine homogenously in a glass bottle. Then, the mixture was transferred into a water bath and heated at 80 °C for 1 hour. Finally, the end product was washed with 3 wt% of hydrazine solution, filtered and dried at 80 °C for 6 hours. During the fabrication process, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was reduced by hydrazine, in which the mixture transform from blue to reddish brown.

3.3.4. Synthesis of Nanosheet-Decorated TiO_2 Nanowire (TWS) Hierarchical Structure

Nanosheet-decorated TiO_2 nanowire (TWS) hierarchical structure was synthesized by a two-step hydrothermal process. Firstly, 0.5 M of Ti^{4+} stock solution was prepared by mixing TTIP and triethanolamine (molar ratio of 1:2 respectively) with distilled water. Then, the pH of the prepared stock solution was adjusted to 11 by adding 0.4 M ethylenediamine drop wise. Subsequently, the prepared nanowires were added into the stock solution and soaked for 18 h. After soaking, the solution was heated at 110°C for 20 h (first hydrothermal process). Thereafter, the gel product was loaded into an autoclave and heated for 160°C for 20 h (second hydrothermal process). After undergoing the two hydrothermal processes, the as-prepared TWS hierarchical structures were washed with NaOH, HCl and distilled water before it was dried in a freeze dryer. Finally, the end product was annealed at 550°C for 2 h.

3.3.5. Synthesis of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ Composite Hierarchical Nanomaterials

A portion of the as-prepared TiO_2 nanowires were dispersed using ultrasonicator in 30 mL of deionized water. 0.243 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.25 g urea were added into the mixture and stirred vigorously for 60 min. Thereafter, the resulting mixture was poured into a 50 mL Teflon-lined autoclave. After hydrothermally treated for 6 h at 90°C, the composite nanomaterial were collected and dried in an oven (50°C) for 12 h after washing with ethanol and deionized water. Finally, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite nanomaterials were synthesised following the calcination of the collected composite materials for 2 h at 500°C (H. Wang, Ma, Huang, Huang, & Zhang, 2012).

3.3.6. Assembly hierarchical TiO₂/Fe₂O₃ multifunctional membrane

A certain amount of the as-prepared sample were firstly scattered in 80 mL deionised water. A vacuum filtration setup was employed to filter the suspension through a commercial cellulose acetate membrane (Φ 47 mm, 0.45 μ m, ADVANTEC, USA). The multifunctional membrane was formed by the build-up of as-prepared sample on the membrane surface. After drying the membrane overnight, the multifunctional membrane underwent a hot pressing cycle at 100°C under a pressure of 5 bar to enhance its mechanical strength. In general, the membranes reported in this thesis were fabricated using the same method.

3.3.7. Preparation of Surfactant-Stabilized Oil-in-Water Emulsions

Surfactant-stabilized oil-water emulsions were prepared by mixing surfactant (Triton X-100), water and oil (namely lubricant oil, vegetable oil and olive oil) in a ratio of 2 : 100 : 2. The mixing process was carried out using an ultrasonicator, in which a white and milky solution was obtained after mixing for 1 h under a power of 1 kW. After several week of storage, the surfactant-stabilized oil-water emulsions remain stable, and no de-emulsification was observed.

3.4. Application study

3.4.1. Study on Oil-Water Separation Ability

The as prepared multifunctional membranes were pre-wetted and positioned in an all-glass vacuum filter holder (vacuum resistant) which was connected to a vacuum pump. During the separation process, the surfactant-stabilized oil-water emulsions were initially poured into the filtration cup. Subsequently, a vacuum pump was triggered to filter the water through the membrane into the collection point, while rejecting the oil droplets on the membrane surface. Thereafter, the oil content remaining in the permeate was investigated using a Thermogravimetric Analyser (TGA, Q500).

3.4.2. Self-Cleaning of Contaminated Membrane

The multifunctional membranes were contaminated with oleic acid by immersing the membrane in a 1.0% (v/v) acetone solution of oleic acid for 5-10 min. After contamination, the membrane was subjected to UV irradiation, and the CA before and after UV irradiation was measured to evaluate the self-cleaning ability of the membrane.

3.4.3. Photocatalytic Degradation Under Ultraviolet (UV) Light Irradiation

Methyl blue (MB), Rhodamine B (RhB) and acid orange (AO7) aqueous solution were the three types of common pollutants employed in this study. The photocatalytic degradation of these pollutants under UV irradiation was examined. These experiments were carried out individually in 3 identical 100 mL glass beakers with a magnetic stirrer each to promote homogenization and aeration conditions. Prior to UV irradiation process using a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA), 30mg of the individual nano-catalyst sample (TiO₂ nanowire, TiO₂ nanotube, nanosheet decorated TiO₂ nanowire and TiO₂/Fe₂O₃ nanocomposite) was added into 50 mL of 30 ppm MB solution and stirred in the dark for 60 min to establish adsorption-desorption equilibrium. After 60 min of dark adsorption, the initial concentration was then recorded. The UV light had an emission energy centred at 365 nm with a light intensity of 1150 mW/cm². During the reaction, the UV lamp was positioned at a fixed height in each glass beaker to provide the energy source. Subsequently, the photo-reacted solution (2-3 mL) was extracted using a syringe at regular intervals. Then, the extracted solution was analysed with a UV-visible spectrometer. Finally, photolysis experiment (without sample dosage) was performed under identical condition for analytical comparison.

3.4.4. Study on The Two-Step Photodegradation and Oil-Water Separation Process

This study was carried out individually for each pollutant. First, the as-prepared membranes were mounted at the bottom of the filtration cup of an all-glass vacuum filter holder (vacuum resistant), which was connected to a vacuum pump (Figure 3.1). Then, 50 mL of the pollutant was poured into the filtration cup and underwent dark adsorption for 60 min to achieve equilibrium. Subsequently, a low-pressure UVP Pen-ray mercury lamp (model no. 11SC-1L, UVP. LLC, California, USA) with an emission energy centred at 365 nm and a light intensity of 1150 mW/cm² was switched on to commence the photodegradation experiment. Thereafter, the photo-reacted pollutant solution (3 mL) was extracted with a syringe at set intervals. The UV-visible adsorption values of these extractions were obtained using a UV-visible spectrometer. After the photodegradation process, the sample remaining in the filtration cup was filtered through the membrane, in which the permeate was examined using the UV-visible spectrophotometer. For comparison study, the TiO₂ nanowire membrane was tested

within the same procedures to study its photodegradation ability. The photolysis study for each pollutant (in the absence of TiO_2 nanowire and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite nanomaterial) was conducted ahead of each photodegradation experiment.

Figure 3-1: Vacuum filtration setup for photodegradation study

The oil-water separation study was conducted immediately after the photodegradation process using the photo-reacted membrane (namely MB treated membrane, AO7 treated membrane and RhB treated membrane) and filtration setup as mentioned above. The feed for this study was prepared by mixing surfactant (Triton X-100), water and lubricant oil in a ratio of 2:100:2. A white and milky solution was obtained after mixing in an ultrasonicator for 60 min at 1 kW. The surfactant-stabilised oil-water emulsion was observed to remain stable and de-emulsified after several weeks of storage. During the oil-water separation experiment, the surfactant-stabilised oil-water emulsion was poured into the filtration cup where the membrane was mounted, in which the separation was performed via a vacuum filtration process. Thereafter, the permeate collected was examined using a Thermogravimetric Analyser (Perkin Elmer, TGA 4000) to determine the oil content remaining in the water.

4. Preliminary Study of TiO₂ Nanomaterials on Oil-Water Separation Application

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Tan, Benny Yong Liang., Liu, Zhaoyang., Peng, Gao., Tai, Ming Hang., & Sun, Delai Darren. (2016). Oil-Water Separation Using a Self-Cleaning Underwater Superoleophobic Micro/Nanowire Hierarchical Nanostructured Membrane. ChemistrySelect, 1 (2016) 1329-1338. doi: 10.1002/slct.201600141

4.1. Morphology of TiO₂ nanowire , copper microwire and TC membrane

First of all, field emission scanning electron microscopy (FESEM) and scanning electron microscopy (SEM) were employed to study the morphology of TiO₂ nanowires, copper microwires and TC membrane. These studies revealed that copper microwires could be characterized easily based on their larger diameter compared to its counterpart, TiO₂ nanowires. Figure 4.1a shows the morphology of the calcined TiO₂ nanowires fabricated by hydrothermal method. The diameter of such TiO₂ nanowires consistently measured between 80-90 nm, with a length of more than 10 μ m long. Furthermore, the surface of the nanowires appeared to be very smooth. Notably, it is also worth mentioning that this hydrothermal method is capable of producing large-scale amount of TiO₂ nanowires, with precise morphological control.

On the other hand, Figure 4.1b shows a FESEM image of the assembled copper microwires that was fabricated via a water bath process. We synthesized copper microwires by reducing CuCl₂ 2H₂O with hydrazine prepared in a NaOH and EDA aqueous solution. These microwires have a distribution of diameters between 250 nm - 450 nm, with a length range from several micrometers to several tens micrometers. Owing to their ultra-long properties, it was mentioned in elsewhere that copper microwires possessed with flexible characteristics (Lo & Yu, 2009; J. Wang et al., 2013; Yiin-Kuen & Li-Chih, 2013; Y. Zhang et al., 2009). Moreover, these microwires have a rougher surface compared to TiO₂ nanowires.

The representative morphology of the as-prepared TC membrane is presented in Figure 4.1c, which was prepared using a mixing and filtration processes (Figure S1a). Firstly, the mixture was prepared by mixing TiO₂ nanowires with copper microwires using a weight ratio of 14:1. During the mixing process, both TiO₂ nanowires and copper microwires spontaneously interlock with each other, forming a unique interlocking

alignment. Subsequently, a simple filtration method was employed to fabricate the 36mm diameter membrane as shown in Figure S1b. Considering the simplicity of such method, a membrane of a larger diameter could be easily fabricated. Furthermore, the advantages for adopting such filtration method are: (1) Homogenous distribution of the nanowires and microwires through filtration process and (2) Membrane thickness can be easily controlled by adjusting the concentration and volume of the micro/nanowires suspension (X. Zhang et al., 2008). The cross section view in Figure 4.1d shows that the as-prepared membrane has an active layer thickness of approximately 120 μm . Moreover, by comparing the pure TiO_2 nanowire membrane (Figure 4.1e) and TC membrane (Figure 4.1f), the TC membrane was built with remarkable flexible characteristic, in which no significant defects was detected after repeated flexure. This occurrence was mainly due to the presence of the ultra-long copper microwires which primarily acted as a scaffold to contain the TiO_2 nanowires. In order to retain the shape of the membrane, the filtered product was dried and hot-pressed. From Figure 4.1c, it was supported that the formation of the TC membrane were attributed to the overlapping and interpenetrating of the TiO_2 nanowires and copper microwires. Additionally, both TiO_2 nanowires and copper microwires could be easily differentiated by observing the diameter and surface roughness of the materials. Due to the incongruity of their diameters, the membrane resulted in a porous structure with a high water flux of 1385.9 $\text{L}/\text{m}^2/\text{hr}/\text{bar}$ (235.6 $\text{L}/\text{m}^2/\text{hr}$) operated under 0.17 bar (16.93 kPa).

Figure 4-1: Morphology of TC membrane. (a) FESEM image of TiO₂ nanowires with diameters of 80-90 nm. (b) FESEM image of copper microwires with diameters of 850-1000 nm. SEM images of TC membrane: (c) membrane surface and (d) cross section. (e) Optical image showing the surface cracks of pure TiO₂ nanowires membrane after repeated flexure, indicating its poor flexibility. (f) Optical image showing the TC membrane with no signs of defects after repeated flexure, indicating its remarkable flexibility.

Figure 4-2: Fabrication of TC membrane; (a) The schematic sketch of TC membrane synthesizing process. (b) Digital Image of the 36mm diameter TC membrane

4.2. Characterization of TC membrane

The image obtained from the dark field FESEM-STEM in Figure 4.3a (insert) confirms that the membrane was made up from the cross linking of several nano/micro structured wires with different diameters. This clearly indicates the different types of wires present in the membrane structure. Furthermore, due to the fact that copper (Cu) element has a heavier atomic weight compared to titanium (Ti), the wire with a brighter surface could be attributed to copper microwire (S. S. Lee, Bai, Liu, & Sun, 2012). The corresponding energy dispersive X-ray spectrometer (EDX) spectrum in Figure 4.3b confirmed that the membrane comprised both Ti and Cu elements and the result also shows that the as prepared material contain a higher fraction of Ti elements. The co-existence of Ti and Cu elements is further supported by the mapping images as shown in Figure 4.3c and Figure 4.3d. These images also indicate that the membrane contained a smaller ratio of copper microwire compared to TiO₂ nanowire. As mentioned in the earlier part of this report, the primary purpose for the inclusion of copper microwire is to provide a flexible support and mechanical strength for the TC membrane. However, a higher content of copper microwire would affect the photocatalytic performance of TiO₂ nanowires. This phenomenon can be explained by the possible coverage of the TiO₂ semiconductor with increase in amount of copper microwires which could impede the access of the light, thus restricting the initiation of photocatalytic reaction (C. Wang, Shao, Zhang, & Liu, 2009). Hence, it is important to note that the amount of copper microwires added during the fabrication process should be controlled and much be lower than the amount of TiO₂ nanowires.

Figure 4-3: Surface composition of TC nanowire membrane. (a) High magnification dark field FESEM-STEM image of TC nanowire membrane, (b) EDX spectrum of TC nanowire membrane, (c – e) Elemental mapping images for Ti element, Cu element and O element respectively, which present in (a).

X-ray diffractometer (XRD) analysis was conducted to characterise the crystal structure of the as-prepared TC membrane. Figure 4.4 illustrates the crystalline phase of TiO_2 nanowire, copper microwire and TC membrane respectively. After the calcination at 700°C , the TiO_2 nanowire were crystallized into anatase TiO_2 with a highly crystalline nature, and this XRD result agrees well with the XRD patterns communicated in literatures (JCPDS file No.21-1272) (Dong, Cogbill, Zhang, Ghosh, & Tian, 2006; Zhaoyang Liu, Sun, Guo, & Leckie, 2006; Zhong-Yong & Bao-Lian, 2004). As earlier mentioned, anatase TiO_2 acquires the best photocatalytic properties compared to other TiO_2 phases (T. A. Arun et al., 2014; Wei, Zhu, Fang, & Chen, 2013), and this plays an

important role when performing self-cleaning process which will be elaborated later. On the other hand, the XRD pattern for the copper microwire indicates the presence of metallic copper components. Diffraction peaks at $2\theta = 43.64$, 50.8 and 74.42 were ascribed to the respective (111), (200) and (220) planes of metallic copper (JCPDS file No. 04-0836) (T.Theivasanthi, 2010). The XRD pattern for TC membrane shows that metallic copper is not discernible in the separation membrane, owing to the relatively low amount of copper microwire added during the synthesizing process. In other words, the presence of TiO_2 nanowire in greater quantity had resulted the copper microwire to exist in a dimension below the detection limit of XRD.

Figure 4-4: Crystallinity studies. (a) XRD pattern of TiO_2 NW, (b) Copper MW, and (c) TC membrane. Wherein, A: anatase TiO_2 , Cu: metallic copper

Contact angle (CA) assessments were employed to evaluate the wettability of the TC membrane, and the data are presented in Figure 4.5. For a typical material, the wettability properties are established based on its surface morphological micro and nano

structure, as well as its chemical composition along its surface (Feng et al., 2002). Generally, the hydrophilic or hydrophobic characteristic is determined by the surface chemical composition, and this property can be further enhanced by the surface morphology. In other words, the wettability of a material is primarily governed by its surface chemical composition and geometrical structures. TiO_2 has gained a lot of attention for its impressive performance for possessing superhydrophilic characteristics, which is an inherently interfacial property (Y. C. Lee et al., 2003; Masahiro Miyauchi & Tokudome, 2007; Nakajima, Koizumi, Watanabe, & Hashimoto, 2000; J. C. Yu, Ho, Lin, Yip, & Wong, 2003). Furthermore, the hydroxyl group present along the surface of TiO_2 also aid to the improvement on the hydrophilic property of the membrane. TiO_2 nanowires were introduced to overcome the significant drawbacks faced by TiO_2 nanoparticles while fabricating an oil-water separation membrane on a glass fibre filter. This is because high concentration of TiO_2 nanoparticles can induce aggregation, which will eventually reduce the hydrophilicity and permeability of the separation membrane (Wu, Gan, Cui, & Xu, 2008). In addition, it was also reported that nanoparticles tend to leach out from the membrane partly during filtration process (J.-F. Li, Xu, Yang, Yu, & Liu, 2009). As a consequence, we fabricated a hybrid TiO_2 nanowire/copper microwire membrane with copper microwires acting as a scaffold on the surface of a glass fibre filter. As shown in Figure 4.5a, the as-prepared TC membrane exhibited a superhydrophilic behaviour with a water CA of 0° . During the CA test, when the water droplet contacted with the surface of the TC membrane, it quickly spread and penetrated the membrane completely. To ascertain the superhydrophilic property of the membrane, more water droplets were tested on the membrane. The latter results showed that the water could continuously permeate through the membrane, indicating good hydrophilic and permeability properties. These outcomes can be explained by the effect of TiO_2 hydrophilic nature as well as the presence of the nano/micro hierarchical structures. Meanwhile, the TC membrane also portrayed an underwater superoleophobic property with an oil contact angle of 151° (Figure 4.5b) above the membrane surface.

Figure 4-5: Wetting behaviour of TC membrane. (a) Video snapshots of the water contact angle measurement of a 3.0 μl water droplet in air. (b) Shape of a oil droplet on TC membrane in aqueous media.

From these characterisation tests, we have shown that the TC membrane is made up of anatase TiO_2 nanowire and copper microwire. In addition, this membrane is built with superhydrophilic and underwater superoleophobic properties.

4.3. Oil-water Separation Test

In accordance to the superhydrophilic and underwater superoleophobic properties demonstrated by the as-prepared TC membrane, it possesses with great ability to separate water from oil-water emulsion. In order to evaluate the oil-water separation efficiencies, a series of tests were conducted to achieve these results. Figure 4.6a and 4.6b show the set up of the oil-water separation experiment. The as-prepared membrane was placed in an all-glass vacuum filter holder (vacuum resistant), which was connected to a vacuum pump. Subsequently, the oil-water emulsion was poured onto the membrane. Owing to the membrane's underwater superoleophobic and low oil-adhesion characteristics, the oil present in the mixture was separated while water could selectively permeate through the membrane and flowed to the collection point below. This phenomenon can be observed from the optical microscopy images in Figure 4.6c and 4.6d, which show that the membrane is capable of separating oil droplet $> 1 \mu\text{m}$. As shown in Figure 4.6e, oil-water emulsion containing vegetable oil, silicone oil, olive oil and used crude oil were successfully separated by the above treatment process, with an oil removal rate of $\geq 99.9\%$. Moreover, in order to reuse the membrane, the oil remained on the membrane's surface could be easily removed by rinsing it with deionised water. During the separation process, the membrane did not experience any loss of its superhydrophilic and underwater superoleophobic properties, it was able to maintain oil removal efficiencies of $\geq 99.9\%$ even after several rounds of vacuum-driven operations (Figure 4.7a). Furthermore, no sign of defect on the membrane was observed during the

entire process. The stability of the membrane could be attributed to the superhydrophilic properties of TiO_2 nanowire, alongside with the flexibility and mechanical strength provided by the inclusion of copper microwire.

Figure 4-6: Oil-water separation by TC membrane. (a) Oil-water separation setup with TC membrane. The as-prepared membrane was placed in an all-glass vacuum filter holder (vacuum resistant), which was connected to a vacuum pump. (b) Photograph shows the collected permeate and oil retentate. Visibility of oil and water was not

observed in the permeate and oil retentate respectively, representing an effective separation process. (c) Optical microscopy image of Triton X-100 stabilized olive oil feed, with oil droplet range from 1 μm to 10 μm . (d) Optical microscopy image of permeate shows that TC membrane can separate oil droplets as small as 1 μm . (e) Oil removal efficiency for vegetable oil (99.90%), silicone oil (99.95%), olive oil (99.93%) and used crude oil (99.92%).

In comparison with the as-prepared TC membrane, the similar experiment was conducted using the pure glass fibre filter. As shown in Figure 4.7, water and oil could permeate through the pure glass fibre filter easily. On the contrary, oil deposit was found on the surface of TC membrane after the oil-water separation process. Based on water capture percentage (WCP), the existence of TiO_2 nanowires and copper microwires exhibited a significant increase in the amount of water uptake with a WCP value of 238%. In other words, the TC active layer was able to take in an amount of water that was more than two times its original mass. Therefore, the failure displayed by glass fibre filter to segregate oil from the mixture is probably due to the absence of surface nano and micro structure of TiO_2 and copper content, which are capable of forming water layer through hydrogen bonds by trapping water molecules. The introduction of such water layer would eventually minimise the contact area between the oil and the membrane, thus, preventing the oil molecules from passing through. The removal efficiencies of the various oil-water separation processes were examined using the thermogravimetric analysis (TGA) based on the collected water purity. During the TGA operation, the sample was heated up to 100°C to evaporate the water content present in the sample tray. After heating, the final weight of the sample was obtained, in which the purity of the water could be determined by comparing with the results with the feed sample.

Figure 4-7: Comparison of oil-water separation by TC membrane and pure glass fibre filter. Schematic diagram of oil-water separation using TC membrane (left) and pure glass fibre filter (right). This diagram illustrates the functionality of TiO_2 nanowires and copper microwires in separating oil from water.

4.4. Self-cleaning properties of TC membrane

As highlighted earlier, it is desirable for the TC membrane to build with self-cleaning property. TiO_2 material has been regarded as an important photocatalyst for environmental decontamination process owing to its possession of photocatalysis characteristics. Under the irradiation of ultraviolet (UV) light, it is capable of degrading a variety of organics into carbon dioxide, water and harmless inorganic anions (A. Houas, 2001). This phenomenon is attributed to the generation of highly oxidizing holes and hydroxyl radicals ($\text{OH}^\bullet$) (Amy L. Linsebigler, 1995; Schwitzgebel, Ekerdt, Gerischer, & Heller, 1995; Wold, 1993). Therefore, with the incorporation of TiO_2 material, organic contaminants and fouling species that are deposited onto the membrane surface can be decomposed, thus providing a self-cleaning potential. In order to study and understand the self-cleaning potential of the TC membrane, the membrane was contaminated with oleic acid, which has been widely used for the investigation of self-cleaning capability for oil-water separation membranes (Gao, Liu, Sun, & Ng,

2014; Zhifu Liu & Miyauchi, 2009; L. Zhang et al., 2013a). Oleic acid was chosen as the model contaminant because it is also recognized as a fatty acid, in which resembles the properties and characteristics of an oil contaminant. After the oleic acid contamination, the surface of the membrane was found to lose its superhydrophilic and underwater superoleophobic properties, indicating its inability to perform oil-water separation process. The disappearance of such properties was further confirmed through a CA test, in which the contaminated membrane portrayed a hydrophobic property with water contact angle of $\sim 93^\circ$ in air. Subsequently, the contaminated membrane was exposed to a UV light (360 nm) irradiation for 75 minutes. Thenceforth, the water contact angle was significantly reduced and restored to its original value close to 0° (Figure 4.9a), representing the recovery of the membrane's hydrophilic property. The recovery of the hydrophilic property for the membrane can be explained by the elimination of the oleic acid adsorbed on the membrane's surface.

As discussed, TiO_2 is capable of converting organic compounds such as oleic acid into water, CO_2 and other inorganic final product (NO_3^- , SO_4^{2-}). However, these conversions involve several procedures, which lead to the formation of intermediate organic compounds that are still contaminants in water. Therefore, we used methylene blue (MB) as a target compound to further evaluate the photocatalytic properties of TC membrane. As shown in Figure 4.8b, the concentration of the MB solution was determined through a light absorption analysis. From the graph, the peak values of different adsorption curves recorded after various photodegradation times represent the concentration of MB remaining in the aqueous solution. Through comparisons, we are able to observe the shift in MB concentration while undergoing the UV light photodegradation process. During the UV photodegradation analysis, it is important to take note that MB in aqueous solution would experience a decrease in concentration with the presence of TiO_2 material even in the dark, and this phenomenon can be explained by the adsorption effect of TiO_2 material (Ammar Houas et al., 2001). As a consequence, the TC membrane was soaked in the MB aqueous solution in the dark for 2 hours before exposing to UV light. After soaking, we spotted a slight drop in the adsorption peak (from peak start to peak 0min). However, after 90 minutes of UV light irradiation, we realized a significant drop in the peak value, indicating a close to completion photodegradation process with a degradation rate of 0.035 min^{-1} . To further elaborate on the strong photodegradation ability of TC membrane, Figure 4.8c shows

that the TC is capable of degrading 100% of MB. On the hand, a MB solution without the presence of TC membrane shows that the UV light is only capable of degrading 35% of MB given the same period of time. Based on this study, it showed that photocatalytic effect of TiO_2 played a more dominant role in decontamination cycle compared to physical adsorption. Furthermore, Figure 4.9 illustrates that the TC membrane was able to exhibit remarkable photocatalytic performance even after 5 cycles of MB degradation under UV irradiation. Ultimately, these analytical results portray the excellent photocatalytic properties of TiO_2 . Furthermore, it can maintain its performance even after going through several rounds of degradation cycles. From this study, it once again demonstrates that the TC membrane possess with the capability in degrading organic compounds, in which further support its self-cleaning ability.

Figure 4-8: Self-cleaning ability of TC membrane. (a) Change of water contact angles of the contaminated TC membrane with respect to UV irradiation time. (b) UV-vis absorbance curves showing the decrease in the concentrations of methylene blue aqueous solution after different UV exposure time. (c) Changes of MB concentration during photodegradation of MB with and without the presence of TC membrane.

Figure 4-9: Study on consecutive oil-water separation process; a) Oil removal efficiency for silicone oil by TC membrane in five cycles of vacuum-driven operations. b) UV-Vis absorbance curve showing the decrease in the concentration of methylene blue (MB) aqueous solution after the fifth cycle of MB degradation under UV irradiation.

4.5. Practical oil-water separation

In this study, the practical oil/water separation ability of the novel TC membrane was investigated, it was adopted to separate crude oil-in-water emulsions at different temperature and ionic concentrations. Figure 4.10a shows that the separation ability of this novel membrane was slightly affected with the increase in temperature, and this phenomenon can be attributed to the increased in solubility of oil in water at higher temperatures (Shiu et al., 1990). From the experimental results, the separation efficiency at 40°C has decreased insignificantly from 99.93% to 99.9 %, indicating the membrane's potential to be employed within a wider temperature range. Subsequently, NaCl solutions with different concentrations were prepared and mixed with oil to study the applicability of the TC membrane under different ionic concentrations. Figure 4.11b shows that the novel TC membrane was able to achieve an overall separation efficiency as high as 99.93% under different NaCl concentrations, which illustrates that the effects of ionic concentrations has almost no influence on affecting the TC membrane separation efficiency. In essence, the above experimental results demonstrate that the novel TC membrane can be potentially employed in industrial oily wastewater treatment and oil spill clean-up activities.

Figure 4-10: Practical oil-water application. (a) Study on separation efficiency of crude oil-in-water emulsions at different temperature. (b) Study on separation of crude-oil-in-water at different ionic concentrations.

4.6. Conclusions

In summary, we successfully fabricated a flexible and hierarchically-structured membrane by assembling TiO₂ nanowires and copper microwires for efficient oil-water separation. This novel membrane exhibits both hydrophilic and underwater

superoleophobic properties, which shows great capability in treating oily wastewater. Experiments showed that the as-prepared TC membrane was capable of separating various oil-water emulsions under a vacuum-driven conditions with remarkably high oil removal efficiencies. Moreover, TC membrane is also endower with the photodegradation property, allowing the membrane to perform self-cleaning process and degradation of pollutants. Owing to these properties, it can potentially enhance the efficiency in water treatment without giving rise to any secondary pollution. Ultimately, this novel TC membrane portrays promising potential for numerous application relating to oily wastewater treatment.

5. A study on the performance of self-cleaning oil/water separation membrane formed by various TiO₂ nanostructures

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5.1. Characterization study of TiO₂ nanostructure

Figure 5.1 depicts the representative FESEM images of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire (TSW) respectively. Figure 5.1a and 5.1b show the as-synthesised TiO₂ nanotubes which is similar to our previous studies, the nanotube structures agglomerate easily and form a cluster of micro-sized aggregates (S. Xu, A. J. Du, J. Liu, J. Ng, & D. D. Sun, 2011; Xu, Ng, Zhang, Bai, & Sun, 2011; Xu & Sun, 2013). As a result, the morphology of the individual nanotube cannot be detected easily. Furthermore, due to their aggregation nature, the photocatalytic activities of the nanotube will be affected. Figure 5.1c illustrates the morphology of the TiO₂ nanowire, which has lengths over several tens micrometers. From a closer observation of the TiO₂ nanowire (Figure 5.1d), it shows that the individual nanowire possessed consistent diameter between 50nm to 90nm. Furthermore, some of the nanowires tend to bind together to form bundles. Figure 5.1e shows the FESEM of the nanosheet-decorated TiO₂ nanowire, in which the TiO₂ nanosheet were successfully grown along the surface of the TiO₂ nanowire through a two-step hydrothermal process. In addition, the high definition FESEM image (Figure 5.1f) revealed that the nanowire hosts were uniformly and densely covered by 200nm long and 150nm wide nanosheet structures. This incorporation of nanosheet onto nanowire form a single "heterostructure" that possesses enhanced specific surface area for mass transfer and reactive sites, which are important factors to improve the photocatalytic properties as well as oil-water separation ability (Bai, Liu, & Sun, 2011; Gondal et al., 2014). As shown in Figure 5.2, the thickness of a typical TiO₂ nanostructured membrane is approximately 120µm. Furthermore, the distribution of the active layer (TiO₂ nanostructures) is uniform and compact, and this is resulted from the compression by the hot-press during the fabrication process. The specific surface area of the TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated

TiO₂ nanowire will be investigated by BET, which will be discussed in the following section.

Figure 5-1: Morphology of TiO₂ nanostructures. FESEM images of TiO₂ nanotube (a) and (b), TiO₂ nanowire (c) and (d), and nanosheet decorated TiO₂ nanowire (e) and (f).

Figure 5-2: Cross section view; FESEM images showing the cross section of a TiO₂ nanostructured membrane

XRD patterns of the nanostructures obtained from the as-prepared and calcined samples of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire are presented in Figure 5.3. Well resolved and sharp TiO₂ anatase peak was observed in all 3 samples, with 2θ of 25.3°, 37.8°, 48° and 62.7°, indexed to the (101), (004), (200) and (204) peaks respectively (JCPDS 21-1272). In addition, these sharp peaks also represent good crystallinity formed by the different TiO₂ nanostructures (Gao, Li, Sun, & Ng, 2014). Compared to the rutile phase, anatase phase has been reported to possess better efficiency for photocatalytic activity (N. G. Park, van de Lagemaat, & Frank, 2000), due to the presence of lower surface area resulting from the close packing structure of the rutile polymorph (Kalyanasundaram & Grätzel, 1998). Moreover, the anatase phase has higher conduction-band energy, which hasten the electron transfer phenomenon (Wold, 1993) and reduces the opportunity of charge recombination (Jimmy, Yu, Ho, Jiang, & Zhang, 2002). From both the FESEM and XRD study, it can be confirmed that anatase TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire with similar

photocatalytic activity have been successfully synthesized as illustrated from the set of XRD spectra with similar diffraction peaks.

Figure 5-3: Crystallinity studies. XRD spectrum of TiO_2 nanowire, TiO_2 nanotube and nanosheet decorated TiO_2 nanowire respectively.

The wetting behaviours of water on the TNT, TNW and TSW membranes that were fabricated using the TiO_2 nanotube, TiO_2 nanowire and nanosheet-decorated TiO_2 nanowire respectively, were determined by contact angle measurement. In air, the water wettability of the TiO_2 membranes was greatly enhanced as compared to the original glass fibre membrane. As shown in Figure 5.4a and 5.4b, the water droplet spread and penetrated the TSW membrane quickly when it contacted with the surface of the membrane. In order to demonstrate the good hydrophilicity and permeability properties of the TiO_2 membranes, more water droplets were added onto the membrane surfaces, and the observations showed that the water could pass through the membrane easily. This phenomenon could be attributed to the combined effects of the hydrophilic nature as well as the nano hierarchical structures of the TiO_2 materials.

Figure 5-4: Wetting behaviour of TSW membrane. Video snapshots of the water contact angle measurement of a 5.0 μ l water droplet in air (a) and (b). Shape of an oil droplet on TSW membrane in aqueous media (c).

Meanwhile, the underwater oil wetting behaviour was determined by immersing the TiO₂ membranes in an aqueous media. Figure 5.4c illustrates the contact angle of oil droplet appearing on the TSW membrane, which had an oil contact angle of 154°. In general, the various TiO₂ membranes possessed an oil contact angle greater than 150° on their surfaces, indicating the presence of good underwater superoleophobic properties. Additionally, the observations showed that these oil droplets had a low adhesion to the surface of the TiO₂ membranes, in which they appeared to be quite unstable on the membrane surfaces. This could be explained by the hydrophilic nature possessed by the various TiO₂ membranes which was discussed previously. Owing to this property, water could be trapped by the TiO₂ nanostructures when the membranes were immersed in the aqueous medium, in which resulted in high repellency created by the formation of polar surfaces and non-polar oil phase. These characteristics were further enhanced by the nano hierarchical structures present on the membrane surfaces, leading to an underwater superoleophobic property (K. K. Arun et al., 2012; Lianbin, Zhonghai, & Peng, 2012; L. Lin et al., 2010; M. Liu et al., 2009; Tian et al., 2012; Wen, Di, Jiang, Yu, & Xu, 2013; Xue et al., 2011b; Zhu et al., 2013).

The integration of hydrophilicity and underwater superoleophobicity characteristics rendered TNT, TNW and TSW membranes suitable to perform oil-water separation process.

5.2. Oil-water separation efficiencies by TNT, TNW and TSW membranes

Pictorial views of the oil-water separation setup employed for this study are shown in Figure 5.5. For each experiment, the as-prepared TNT, TNW and TSW membranes were

initially wetted with water and placed in a vacuum pump supported all glass-vacuum filter holder respectively. Vacuum filtration was selected as a separation approach due to its straightforward setup and feasibility of performing a continuous separation process. The oil-water emulsion was then poured into the top glass funnel and the permeate was collected in a flask placed underneath. In order to demonstrate the critical role of the TiO_2 nanostructures, the oil-water separation process was firstly carried out using an uncoated glass fiber filter. As shown in Figure 5.5a, both oil and water percolated through the uncoated glass fibre filter rapidly. On the other hand, when TNT, TNW and TSW membranes were used in the setup at each time, the water in the emulsion percolated through the membrane while the oil was retained on the top glass funnel as illustrated in Figure 5.5b.

Figure 5-5: Oil-water separation by uncoated glass fibre filter and TSW membrane. Both membranes were pre-wetted and placed in a vacuum pump supported all glass-vacuum filter holder. An oil-water emulsion was poured into the top glass funnel respectively. Oil-water separation setup using (a) uncoated glass fibre filter where oil and water passed through the filter rapidly and (b) TSW membrane where the water permeated through the membrane while the oil was separated and left behind.

For the oil-water separation experiment, all synthesized TiO_2 membranes were tested with oil-water emulsion sample prepared using used crude oil with a water/oil ratio of 9:1. In each experiment, 60 mL of the oil-water sample was used, and the separation process was completed within 30 – 35 seconds on average. Subsequently, the oil-water

separation efficiencies of the TNT, TNW and TSW membranes were evaluated using thermogravimetric analysis (TGA). After every cycle of oil-water separation process, a simple membrane cleaning method was adopted to remove the rejected oil. As the as-prepared TiO_2 nanostructured membranes were built with hydrophilic and underwater superoleophobic properties, only water permeated through while the oil molecules were repelled off the membrane surface during the separation process. Due to this phenomenon, the oil present on the surface of the membrane can be easily removed by washing with water, as shown in Figure 5.6a. Thereafter, the recovered membrane could be reused for the subsequent oil-water separation process. During the TGA experiment, the sample was heated up to 110°C to evaporate the water content present in the sample tray. After heating, the final weight of the sample was obtained, and the amount of oil present in the sample was determined. Therefore, the separation efficiencies of the membrane were calculated by comparing the oil content presence in the feed and permeate for each membrane. Figure 5.7a shows the TGA curve showing the oil content present in the feed and permeate treated using TSW, TNT and TNW membranes. The separation efficiencies of the three TiO_2 membranes are shown in Figure 5.7b. Remarkably, these membranes exhibit high separation efficiency ($>95\%$) with TNW, TNT and TSW membrane achieving 95.6%, 96.5% and 99.89%. Such efficiencies can be attributed to the hydrophilic and underwater superoleophobic properties possessed by the synthesised TiO_2 membranes. Moreover, the result also demonstrates that the introduction of nanosheet along the surface of nanowire (nanosheet-decorated TiO_2 nanowire) significantly improves the oil-water separation efficiency of TNW membrane. This is due to the higher surface area available for the water intake during the initial wetting procedure, in which the water capture percentage (WCP) for TNT, TNW and TSW membranes are 397%, 267% and 563% respectively. The WCP experiment shows that TSW membrane is capable of forming more water layer by trapping more water molecules. Owing to this characteristic, the TSW membrane tends to outperform its counterparts.

Figure 5-6: Effect of cleaning membrane; a) Digital image of TSW membrane after oil-water separation process (left) and digital image of TSW membrane after washing with water (right) and; b) separation efficiency of TSW membrane in its original state (99.88%) and after membrane washing (99.86%)

Figure 5-7: Oil-water separation ability. (a) Thermogravimetric analysis (TGA) curve graph determining the oil content remaining in the permeate after each separation process performed by TNT membrane, TNW membrane and TSW membrane respectively; and (b) separation efficiency using different TiO_2 nanostructured membrane.

5.3. Photocatalytic self-cleaning application

As mentioned earlier, it is imperative to fabricate an oil-water separation membrane built with self-cleaning property. In the past decades, TiO_2 material is widely recognised for its ability to generate photo-electrons and holes under ultraviolet (UV) irradiation. Consequently, highly reactive hydroxyl radical and superoxide anions species are produced from the reactions between the electrons and holes with oxygen and water (Akira Fujishima, 1972; Linsebigler, Lu, & Yates Jr, 1995). These reactive species have the ability to disintegrate and remove organic contaminants as well as the fouling species accumulated on the surfaces of the separation membrane. For this study, the self-cleaning capability of TNT, TNW and TSW membranes will be evaluated. First of all, the three TiO_2 membranes were contaminated with a model contaminant, oleic acid. After the oleic acid contamination, the membranes lost their hydrophilic and underwater superoleophobic characteristics, and the contaminated TNT, TNW and TSW membranes displayed water contact angle of 73.6° , 76.2° and 74.2° in air respectively (Figure 5.8). From these results, it indicates that the oil-water separation ability of the TiO_2 membranes will be affected once contaminated. The contaminated membranes allowed oil and water to pass through indiscriminately, which led to their inability to

separate oil and water. In order to study the self-cleaning characteristics of the TNT, TNW and TSW membranes, the contaminated membranes were subjected to UV irradiation for a maximum of 105 minutes. The self-cleaning process was then assessed by observing the water contact angles of the individual membrane at a fixed interval in air using VCA instrument. Figure 5.9 graphically illustrates the decrease in water contact angle in air under UV irradiation. Among the TiO_2 membranes, TSW membrane has the fastest recovery, followed by TNT membrane and then TNW membrane, which required recovery duration of 45 mins, 90 mins and 105 mins respectively. After the desired self-cleaning process, the TiO_2 membranes regained their original water contact angle value and their hydrophilic characteristics.

a) TNT membrane

b) TNW membrane

c) TSW membrane

Figure 5-8: Self-cleaning cycle. Video snapshots illustrating the decrease in water contact angles of the contaminated a) TNT, b) TNW and c) TSW membranes respectively over time under UV exposure

Figure 5-9: Self-cleaning ability of TNW membrane, TNT membrane and TSW membrane. Changes of water contact angles of the contaminated TNW membrane, TNT membrane and TSW membrane with respect to UV irradiation time.

In general, the specific surface area and light absorption ability of the photocatalysts are two significant components that determine and influence the photodegradation activities of the photocatalysts. Therefore, BET and UV-VIS experiments were conducted to further explain such phenomenon. As shown in Figure 5.10, the specific surface area and adsorption/desorption isotherms of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire were investigated by N₂ adsorption/desorption analysis. The obtained BET specific surface area of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire are 105 m²g⁻¹, 63.4 m²g⁻¹ and 71.3 m²g⁻¹ respectively. From the result, it shows that TiO₂ nanotube has a larger BET surface area compared to its counterparts, which enhances its physical adsorption capacity. Furthermore, the self-cleaning efficiency of TiO₂ nanotube is better than that of TiO₂ nanowire, which required a shorter recovery duration. This is attributed to the larger BET specific surface area of the photocatalyst which increased the available active sites for the photodegradation process, as well as providing more surfaces for contact by the incident light. However, the nanosheet-decorated TiO₂ nanowire has the best self-cleaning efficiency amongst the three photocatalyst despite having a lower BET specific surface

area than that of the TiO₂ nanotube. This clearly suggests that the BET specific surface area is not the only factor that governs the photocatalytic self-cleaning process.

Figure 5-10: Specific surface area; N₂ adsorption/desorption isotherms of a) TiO₂ nanowire, b) TiO₂ nanotube and c) nanosheet decorated TiO₂ nanowire respectively.

As shown in Figure 5.11, the light absorption experiment was employed to measure the UV-vis spectra of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire. From the result, it can be observed that the three TiO₂ nanostructures have similar absorption edges in the UV region. This phenomenon can be explained by the intrinsic band-gap absorption of the TiO₂ material. Furthermore, due to the wide band gap of anatase TiO₂, visible light absorption could not be observed for all the synthesised TiO₂ nanostructures (Chai, Peng, Zeng, & Mao, 2011). Among the synthesised TiO₂ nanostructures, the nanosheet-decorated TiO₂ nanowire portrayed a stronger light absorbance within the UV region from 300 nm to 380 nm, as illustrated in Figure 5.11. Scheme 1 delineates this outcome, resulting from the morphological enhancements to the TiO₂ nanowire from the growth of the nanosheet. In general, the nanosheet-

decorated TiO_2 nanowire was constructed by growing secondary nanosheet along the surface of TiO_2 nanowire. It is interesting to note that the formation of this unique structure allows multiple scattering and reflection of incident light, which enhances the utilisation of light compared to its counterparts. Moreover, the transfer of photogenerated electrons can also be improved by the formation of intricate transportation network resulting from the interconnecting nanowire and nanosheet. Interestingly, the anatase nanosheet is believed to have fewer surface trap sites and grain boundaries, which essentially reduces the electron-hole recombination process. As such, the nanosheet-decorated TiO_2 nanowire acquire excellent electron generation attributes due to its superior electron transfer characteristics and suppressed recombination properties (D. H. Kim et al., 2013). Hence, the combination of larger BET specific surface area contributed by the growth of TiO_2 nanosheet, scattering property which results in high light absorption capacity and superior electron collection properties due to the hierarchical structure of the nanosheet-decorated TiO_2 nanowire which synergistically account for its superior self-cleaning performance.

Figure 5-11: Light absorption analysis. UV-VIS of nanosheet decorated TiO_2 nanowire, TiO_2 nanotube and TiO_2 nanowire respectively.

Scheme 1: Schematic diagram illustrating the multiple reflection effects within nanosheet decorated TiO₂ nanowire as compared to TiO₂ nanowire

Owing to TiO₂ photocatalytic property, it is possible to convert organic compounds such as oleic acid into CO₂ and other inorganic products (SO₄²⁻, NH₄⁺ and NO₃⁻). However, these conversions require several steps and organic intermediates, which are still pollutants in water (Changrui et al., 2013). Therefore, there is a need to study and compare the photodegradation activity of the synthesised TiO₂ nanostructures. For this study, the photodegradation activity of TiO₂ nanotube, TiO₂ nanowire and nanosheet-decorated TiO₂ nanowire were investigated through a process of degrading methylene blue (MB), which is commonly used as a target molecule to evaluate preliminary photocatalytic activity for TiO₂ material. During the UV photodegradation process, the variation of MB concentration in aqueous solution can be determined by observing the peak value of the individual absorption curves formed after different photodegradation times. As shown in Figure 5.12a, TiO₂ nanotube exhibited strong physical absorption for MB within 60 min, and this can be explained by its possession of larger BET specific surface area and mesoporous structure, which was discussed in our previous study (Shiping Xu, Jiawei Ng, et al., 2011). The TiO₂ nanotube degraded approximately 94% of MB whilst the TiO₂ nanowire degraded less than 60% of MB during the 30 min of

UV irradiation. On the other hand, it was observed that the nanosheet-decorated TiO₂ nanowire was capable of degrading almost 100% of MB within the same time frame. These outcomes showed that the incorporation of nanosheet effectively enhances the photodegradation performance of the nanowire, owing to its increased BET specific surface area, scattering and reflecting effects and enhanced electron transport pathway. As shown in Figure 5.12b, the detailed photodegradation process performed by the nanosheet-decorated TiO₂ nanowire was illustrated by the UV-vis absorption spectra of MB, in which the concentration of MB in the aqueous solution was represented by the absorbance of light. Moreover, the distinct changes in colour of MB degraded by nanosheet-decorated TiO₂ nanowire are shown in Figure 5.12c, and the overall degradation rates for the individual nanostructure are presented Figure 5.13.

Figure 5-12: Photodegradation of organic contaminants. (a) Changes of MB concentration during photodegradation of MB by TiO₂ nanotube, TiO₂ nanowire and nanosheet decorated TiO₂ nanowire respectively; (b) UV-vis absorption spectra of MB degradation by nanosheet decorated TiO₂ nanowire during 30 min; and (c) Photographs showing the changes in colour of MB degraded by nanosheet decorated TiO₂ nanowire during 30 min.

Figure 5-13: Degradation rate of TiO₂ nanostructures; Pseudo-first-order reaction rate performed by a) TiO₂ nanotube, b) TiO₂ nanowire and c) nanosheet decorated TiO₂ nanowire.

5.4. Condition study for oil-water separation

To investigate the adaptability of the TiO₂ nanostructured membrane in performing oil-water separation process under different conditions, TSW membrane was adopted to separate the oil-water mixture at different temperatures and ionic concentrations. Figure 5.14a shows that the separation efficiency of the TSW membrane decline slightly with the increase in the temperature of the oil-water mixture. This phenomenon could be attributed to the increase in solubility of the oil-water mixture when exposed to a higher temperature condition (Shiu et al., 1990). The experimental outcome shows that the separation efficiency at 40°C only experiences a slight decrease from 99.90% to 99.87%. Thus, this study indicates that this membrane can be employed in a wider range of temperature without compromising its performance. Subsequently, various oil-water mixtures were prepared by mixing with different concentration of NaCl solutions to

study the effects of ionic concentrations on the oil-water separation efficiency of TiO_2 nanostructured membrane. Figure 5.14b shows that there is minimum influence on the separation efficiency under different NaCl concentration, and an overall separation efficiency as high as 99.90% can be achieved. As a result, the main findings of the above experiment revealed that the TiO_2 nanostructured membrane can be applied to oil-water separation process occurring in various conditions (e.g. temperature and ionic strength condition).

Figure 5-14: Condition study for oil-water separation. (a) Separation efficiency of oil-water mixture at different temperature; and separation efficiency of oil-water mixture at different ionic concentrations.

5.5. Conclusion

In summary, 1D TiO₂ nanotube, 1D TiO₂ nanowire and 3D nanosheet-decorated TiO₂ nanowire have been successfully fabricated, and subsequently assembled into TNT, TNW and TSW membrane respectively. Generally, the three anatase TiO₂ nanostructured membranes are equipped with hydrophilic and underwater superoleophobic characteristics, which portrayed great potential for treating oily wastewater under vacuum filtration approach. Studies shown that these membranes are capable of separating oil from water with the possession of remarkable oil/water separation abilities. From this study, the results demonstrated that the oil/water separation ability of TSW membrane is the best among the three TiO₂ nanostructure membranes. This performance can be attributed to the TiO₂ nanosheet ability to intake more water which boost the water capture percentage (WCP) and form more water layers. Furthermore, owing to the possession of photodegradation properties by TNT, TNW and TSW membranes, they are able to self clean and degrade intermediate organic pollutants. From the experiments conducted, it revealed that the TSW membrane has the most outstanding self-cleaning and photodegradation properties. The TSW membrane was able to self clean the oleic acid (foulant) accumulated on the membrane surface in 45 min. Further, it was also capable of degrading close to 100% of MB (intermediate organic compound) within 30 min of UV irradiation. Through this analysis, the scattering and reflecting effects coupled with high light utilization capacity and hierarchical mesoporous structure are the three main factors that synergistically enhance the photodegradation performance of TSW membrane. Ultimately, it was found that through the growth of nanosheet along the surface of nanowire (3D nanosheet-decorated TiO₂ nanowire), it significantly enhanced the oil/water separation and degradation performance of the authentic TiO₂ nanowire, this finding can contribute to references for other photocatalysts used to perform oil/water separation study in future.

6. Flexible hierarchical $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane with high separation efficiency for surfactant-stabilized oil-water emulsions

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6.1. Surface morphology of as-synthesized membrane

As shown in Figure 6.1, the XRD pattern of the as-prepared $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane suggests that the composite nanostructures are all well-crystallized into anatase TiO_2 and Fe_2O_3 .

Figure 6-1: Crystallinity study; XRD spectrum of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane

Figure 6.2a shows the vulnerability of the pure TiO_2 membrane. Owing to its poor mechanical strength, it can be easily damaged and cracked by slight bending. The surface morphology of the pure TiO_2 nanowire membrane indicates that the TiO_2 nanowires have smooth surface and are loosely gathered together, as illustrated in Figure 6.2b and 6.2c respectively. As a result, the poor mechanical strength can be attributed

to the lack of cross linking between the nanowires which leads to a large pore size formation. Iron oxide material has been reported to have high mechanical properties and flexible characteristic which can inevitably improve the strength of a material (A.Ahmed, Hassanean, Assaf, & Shawkey, 2015; Eleonora et al., 2013; Nan, Yu, Ma, Geng, & Zhang, 2015). In this work, Fe_2O_3 was chosen to provide a crosslinking network between TiO_2 nanowires in order to promote efficient bonding. As shown in Figure 6.2d, it is interesting to note the mechanical flexibility behaviour of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ membrane, and it can be bent freely due to the crosslinking effects provided by the Fe_2O_3 nanoneedles. With the possession of such excellent flexibility, this novel membrane can be allowed to be fitted in various configuration of membrane modules which broaden its practical application. Figure 6.2e and 1f show the FESEM images of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites and the surface morphology of the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane respectively. As shown in Figure 6.2e, Fe_2O_3 nanoneedles are grown uniformly along the surface of the TiO_2 nanowire. Owing to the formation of such hierarchical nanostructure, the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites are closely packed together, resulting in a compact formation (shown in Figure 6.2f). As compared to the pure TiO_2 membrane in Figure 6.2c, the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane portrays a much denser membrane. From Figure 6.2f, it suggests that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ membrane is built with pore sizes less than 120 nm, which is crucial for separating small oil droplets present in the oil-water mixtures. TEM was employed to study the microstructure of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane in thorough. A small section of the membrane was initially dispersed in ethanol through an ultrasonication process, and subsequently applied dropwise onto the copper grid for TEM characterisation. Figure 6.3 presents the TEM image of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites, and it could be clearly visualised that the Fe_2O_3 nanoneedles provide binding effects which effectively connect the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical composites together.

Figure 6-2: Morphology study; (a) Photograph illustrating the effect of TiO_2 nanowire membrane after bending; (b) FESEM image of pure TiO_2 nanowire; (c) FESEM image of the pure TiO_2 nanowire membrane; (d) photograph illustrating the mechanical flexibility of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane; (e) FESEM image of the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites, showing the uniform growth of Fe_2O_3 nanoneedles along the surface of TiO_2 nanowire; and (f) FESEM image of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane.

Figure 6-3: TEM analysis; TEM image of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite showing the clinching effects between the nanostructures.

6.2. Surface roughness and wetting behaviour

Geometric structure such as surface roughness and chemical composition are important factors that determine a membrane wetting property (Kou & Gao, 2011; X. Liu et al., 2012; L. Zhang et al., 2013a). Based on the equation: $\cos \theta_a = r \cos \theta$, where θ_a represents the apparent water CA on rough surface, r is the surface roughness factor and θ is the water CA on smooth surface, the hydrophilicity of a solid surface can be enhanced with the present of high surface roughness (Du, Liu, Chen, & He, 2009; Kou & Gao, 2011; M.OJHA, G.Dalakos, S.Panchamgam, Jr, & J.L.Plawsky, 2008). Figure 6.4a illustrates the 2D AFM images of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. The results reveal that the membrane comprises of a dense formation with minimum gap space. Moreover, it also suggests the detection of rough surface with approximately a 31 - 45 nm undulation range (Figure 6.4b), which will effectively improve the membrane hydrophilic property (Xue et al., 2011a).

Figure 6-4: Surface roughness study; (a) 2D and (b) 3D AFM scan images showing the sharp and random peaks for characterising the surface geometry of a $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane.

The water CA and underwater oil CA are illustrated in Figure 6.5a and 6.5b respectively. The outcomes of this characterization test confirm that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane is built with a superhydrophillic and underwater superoleophobic surface, in which a nearly zero (0°) water CA and approximately 150° underwater oil CA are acquired. Figure 6.5c shows the images captured by a high-speed camera system which demonstrate the wetting behaviour of a water droplet on the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. During the analysis, 3 μL of water droplet was quickly spread out within less than 0.9 s when contacted with the membrane surface, which illustrated the superior membrane's water wetting property. Owing to such surface properties, oil can be rejected by the membrane easily as only water is allow to pass through.

Figure 6-5: Water contact angle analysis; (a) Snapshot of a water droplet displaces onto the surface of the membrane with a close to zero contact angle; (b) snapshot of an underwater oil droplet (DCM) displaces onto the surface of the membrane with a contact angle of approximately 150°; and (c) Snapshots illustrating the process of the spreading of a water droplets onto the membrane surface in air, which requires a period of 0.863s.

6.3. Separation of surfactant-stabilized oil-in-water emulsions

Several types of oil-in-water emulsions with nanometer-sized and micrometer-sized droplets were prepared using cooking oil, olive oil and lubricant oil to investigate the oil-water separation ability of the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. Figure 6.6 displays the schematic diagram of the separation mechanism, showing the ability of the novel membrane in separating oil and water as a result of the underwater superoleophobic interface. The separation process of the olive oil-in-water emulsion is demonstrated in Figure 6.7a. At the beginning of the process, the olive oil-in-water emulsion was discharged into the filtration cup (top section of the filtration system). Subsequently, the vacuum was turned on which allowed the water (the orange colour

originates from the AO7 indicator) to permeate through the membrane, concurrently repelling the olive oil due to the membrane's superhydrophilic and underwater superoleophobic properties. Ultimately, the separation efficiencies of this novel membrane in separating the mentioned oil-in-water emulsions were compiled in Figure 6.7b. The results showed the outstanding oil-water separation ability of the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane, by achieving extreme high separation efficiency of $>99.8\%$ for all the prepared oil-in-water emulsions as mentioned (99.90% for olive oil-in-water emulsion, 99.87% for cooking oil-in-water emulsion and 99.89% for lubricant-in-water emulsion). Moreover, the oil droplets present in the feed and the permeate of the cooking oil-in-water emulsion were examined using an optical microscopy to further ensure the effectiveness of this novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane in separating surfactant-stabilized oil-in-water emulsions. Typically, surfactant (Triton X-100) has been recognised as an essential component for preparing oil-in-water emulsion. Figure 6.8 shows that the size of the oil droplets is between 1 – 140 μm in the absence of surfactant. On the other hand, the oil droplets were significantly reduced in size with the addition of surfactant, resulting in the formation of smaller oil droplets with an average size of approximately 200 nm, as shown in Figure 6.7c (left). Dynamic light scattering (DLS) measurements were employed to further validate this findings through droplet size distribution (Figure 6.8). As shown in the microscopy images presented on the right of Figure 6.7c, a clear permeate was collected after the separation process. Hence, this has highlighted that the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ membrane is effective in separating surfactant-stabilized oil-in-water emulsions with oil droplets sizes of less than 400 nm. Moreover, this membrane is able to withstand a relatively high flux of $81 \text{ L m}^{-2} \text{ h}^{-1}$ while performing the oil-water separation process.

Figure 6-6: Oil-water separation analogy; A schematic diagram illustrating the formation of the novel TiO₂/Fe₂O₃ composite membrane performing an oil-water separation process, in which only water is allowed to pass through while rejecting oil.

Figure 6-7: Oil-water separation study; (a) Photograph illustrating the filtration setup for the separating olive-oil-in-water separation process using novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$

composite membrane (left) before separation and (right) after separation (the orange colour originates from the AO7 indicator which represent water); (b) Separation efficiencies of different surfactant-stabilised oil-in-water emulsions in term of oil rejection rates; and (c) optical microscopy images showing the oil droplets present in the olive oil-in-water emulsion before and after oil-water separation process. Left: Oil droplet present in the emulsion before separation (approximate oil droplet size is 200 nm). Middle: Photograph of the olive oil-in-water emulsion's feed and permeate. Right: Optical microscopy image showing a clear permeate after separation process with no sign of oil droplet.

Figure 6-8: Oil droplets measurement; a) Optical microscopy image of olive oil-in-water emulsions without the addition of surfactant. Size of oil droplets appear to be between 1 to 140 μm . (b) DLS data of olive oil-in-water emulsions without the addition of surfactant affirming the oil droplet size to be in the range of 1 to 140 μm .

Figure 6-9: Effect of surfactant; DLS data of surfactant-stabilized olive oil-in-water emulsions showing the reduction in the size of oil droplet to approximately 200 nm.

Figure 6-10: TGA & TOC analysis; TGA graph of olive oil-in-water emulsions permeate and TOC results of olive oil-in-water emulsions feed and permeate. Explanation of oil-water separation efficiency: During the TGA experiment, the sample

was heated at 110°C for 30 min. After heating, 99.90% of water in the permeate was evaporated, which explained the high oil removal efficiency portrayed by the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. Furthermore, total organic carbon (TOC) was also employed to study the membrane separation efficiency, as shown in the inset of Figure 6.1. The results showed that permeate obtained a TOC reading of 5.1 mg/L while the initial TOC reading of the emulsion was 8201 mg/L. From this study, it can be explained that the olive oil present in the feed was efficiently segregated from the olive oil-in-water emulsions. Hence, the combination of the TGA and TOC results justified that the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane displayed an outstanding oil-water separation capability.

6.4. Self-cleaning property

Membrane applications employed in oil-water separation and water purification fields have been frequently restricted by membrane fouling. This phenomenon can be mainly attributed to the deposition of water soluble or insoluble organic matters on the membrane surface, which tends to reduce the water flux eventually (Gao, Tai, & Sun, 2013). Under the provision of UV irradiation, TiO_2 photocatalyst is widely recognised for its ability in generating strong reactive species such as hydroxyl radicals and superoxide anions (P. Gao, J. Liu, T. Zhang, D. Sun, & W. Ng, 2012; Gao, Sun, & Ng, 2013). Furthermore, the incorporation of Fe_2O_3 nanoneedles can introduce a narrower band gap, as well as exhibiting lower recombination rate, which are advantageous for efficient photocatalytic processes (S. Zhang, Zheng, Wang, & Chen, 2006). In theory, the foulants (organic matter) accumulated on the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane can be potentially decomposed and eliminated owing to the generation and presence of reactive species. In this study, the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane was investigated for its capability in regaining its properties once contaminated. This was carried out by firstly immersing the membrane into an oleic acid/acetone solution. Figure 6.11a illustrates the result of this study by showing the transformation of CA before and after UV irradiation in a period of 6 cycles. After contaminating the membrane with oleic acid, its superhydrophilic property was destroyed. As shown in Figure 6.11b, the membrane exhibits a hydrophobic property with an approximate water CA of 100° upon contamination. After UV irradiation, the water CA was found to be approximately less than 10° which indicated the recovery of the membrane's superhydrophilic property, as shown in Figure 6.11c. This occurrence can be explained

by the photocatalytic ability and excellent photodegradation efficiency portrayed by the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites, which significantly alleviates the fouling phenomenon. With the above results, they show that this novel membrane has the capability to be employed in practical oil-water separation processes.

Figure 6-11: Study on self-cleaning function; (a) Transformation of water contact for 6 cycles under the exposure of UV light; (b) Snapshot of a water droplet displaced on the contaminated membrane surface with a water contact angle of approximately 100°; and (c) Snapshot of a water droplet displaced on the membrane surface with a water contact angle of approximately 9°, which was significantly reduced from 100° after UV irradiation.

6.5. Practical oil-water separation

This novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane was investigated for its ability to be employed in practical oil-water separation process through the separation of lubricant oil-in-water emulsions at various temperature and ionic concentrations. As shown in Figure 6.12a, the performance of the novel membrane was slightly affected in the event when the temperature of lubricant oil-in-water mixture was raised. This outcome could be attributed to the alteration in oil-in-water solubility, in which it has been reported that the solubility of oil increases with the raise in temperature (Shiu et al., 1990). Nonetheless, the decrease in separation efficiency at 40°C is not significant (from 99.89% to 99.87%), and this indicates that this membrane is feasible to be applied in different temperature medims. Furthermore, NaCl solutions of various concentration were added into the lubricant oil-in-water emulsion to investigate the separation efficiency of this membrane operating under different ionic conditions. Figure 6.12b shows that the concentration of NaCl has no vital effect on the membrane's performance, and it is able to achieve a separation efficiency of as high as 99.91%. Ultimately, the above experimental results suggest that this novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane has huge potential to be employed in practical oil-water separation operations, such as treating industrial oily wastewater and cleaning up oil spill incidents.

Figure 6-12: Oil-water separation efficiency; separation efficiency of lubricant oil-in-water emulsions using novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane performed at different (a) temperature and (b) ionic strength.

Thus far, we have successfully developed and introduced a novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane built with superhydrophilic, underwater superoleophobic, self-cleaning and mechanically flexible characteristics. Owing to these properties, this novel membrane achieved outstanding oil rejection rates while performing oil-water separation for surfactant-stabilised oil-in-water emulsions. Notably, the membrane also displays its outstanding anti-oil fouling and self-cleaning property. In the following sections, the membrane will be further evaluated for its tolerance condition for environmental application.

6.6. Energy-dispersive X-ray spectroscopy (EDS) and x-ray diffraction (XRD) analysis

The energy-dispersive X-ray spectroscopy (EDS) image shown in Figure 6.13a confirms that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructures were surrounded by needle-like nanostructures. The corresponding EDS spectrum in Figure 6.13b affirms the presence of Ti and Fe elements in the composite hierarchical nanostructures. As shown in Figure 6.13c-e, the mapping images further justify the co-existence of Ti, Fe and O elements. Furthermore, these images also depict the well dispersity of the mentioned elements. Essentially, having a good elemental dispersion would boost the elemental contact between TiO_2 and Fe_2O_3 , which immensely enhance their photocatalytic reactions via migration of electrons between conduction bands (Siew Siang, Hongwei, Zhaoyang, & Darren Delai, 2013; Yoong, Chong, & Dutta, 2009).

Figure 6-13: Surface composition of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure; (a) High magnification dark field FESEM image of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure;

(b) EDX spectrum of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure; and elemental mapping images for (c) Ti, (d) Fe and (e) O.

The crystalline phases of the as-synthesised primary TiO_2 nanowire and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure were confirmed by their XRD patterns. Figure 6.14 represents the XRD patterns of the as-prepared primary TiO_2 nanowire and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure. As communicated in previous reports, layered hydrogen titanates can be transformed into anatase TiO_2 through calcination process (B. Liu, Khare, & Aydil, 2011; Xiwang, Alan Jianhong, Peifung, Darren Delai, & James, 2008). In this study, a batch of highly crystalline anatase TiO_2 nanowire was achieved after heating at 700°C , and these XRD peaks can be indexed to anatase TiO_2 as communicated in literatures (JCPDS file No.21-1272)(Zhaoyang Liu, Sun, Guo, & Leckie, 2007; Z.-Y. Yuan & Su, 2004). As compared to the other phases of TiO_2 , anatase TiO_2 is widely reported for its outstanding photocatalytic properties which will greatly enhance the photodegradation ability of TiO_2 material (T. A. Arun et al., 2014; Xiuzhen, Guangfeng, Jinfeng, & Jinyuan, 2013). The XRD pattern of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure indicates the introduction of hematite $\alpha\text{-Fe}_2\text{O}_3$ into the composite sample (JCPDS file No.89-0597)(Chaudhari, Chan Kim, Son, & Yu, 2009). The sharp peaks suggest that the $\alpha\text{-Fe}_2\text{O}_3$ nanoneedles are highly crystalline. With the addition of hematite $\alpha\text{-Fe}_2\text{O}_3$, it will improve the membrane photocatalytic performance via fast interfacial charge-transfer process(Litter & Navío, 1996; Xia & Yin, 2013). These phenomenon will be discussed in the following sections.

Figure 6-14: Crystallinity studies; XRD spectrum of TiO₂ nanowire and TiO₂/Fe₂O₃ hierarchical nanostructure respectively.

6.7. BET and light adsorption analysis

The photocatalytic activity of a typical photocatalyst can be influenced by two essential components which encompass specific surface area and light absorption ability. As illustrates in Figure 6.15a and 6.15b, the specific surface area of the primary TiO₂ nanowire and TiO₂/Fe₂O₃ hierarchical nanostructure are investigated by N₂ adsorption/desorption analyses. TiO₂ nanowire and TiO₂/Fe₂O₃ hierarchical nanostructure obtained a BET surface area of 63.4 m²g⁻¹ and 288.1 m²g⁻¹ respectively. The analytical results show that the addition of Fe₂O₃ nanoneedles increase the overall BET surface area by 4.5 times, which will increase the adsorption capacity. Furthermore, the photodegradation efficiency of TiO₂/Fe₂O₃ hierarchical nanostructure will also be enhanced owing to its larger surface area. This can be attributed to two main factors: 1) more contact established between the incident light and nanostructure surfaces and 2) increase in active sites available for photodegradation.

Figure 6-15: N₂ adsorption/desorption isotherms; (a) TiO₂ nanowire; and (b) TiO₂/Fe₂O₃ hierarchical nanostructure.

The light absorption activities of primary TiO₂ nanowire and TiO₂/Fe₂O₃ hierarchical nanostructure were examined using UV-visible spectrometer. Figure 6.16 shows the UV-vis spectra obtained for both the materials. TiO₂ nanowire shows an absorption edge locating only within the UV region (approximately 350 nm) by virtue of its intrinsic wide band-gap formation. On the other hand, the TiO₂/Fe₂O₃ hierarchical nanostructure exhibits absorption edges locating within the UV region as well as the visible light region. This can be due to the incorporation of Fe₂O₃ which inevitably narrow the overall band gap structure, and improve its light adsorption activity (Yan, Wang, Yao, & Yao, 2013). In addition, the hierarchical nanostructure formed by TiO₂ nanowire and Fe₂O₃ nanoneedles encourages multiple reflection and scattering of incident light, which promotes efficient light utilization phenomenon as compared to primary TiO₂ nanowire (Scheme 2). Thus, the large BET surface area and high light absorption capacity inherent in the TiO₂/Fe₂O₃ hierarchical nanostructure synergistically lead to outstanding photocatalytic performance.

Figure 6-16: Light absorption analysis; (a) TiO_2 nanowire; and (b) $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure.

Scheme 2: Light reflection and scattering phenomenon of TiO_2 nanowire; and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure

6.8. Photocatalytic degradation analysis

TiO₂/Fe₂O₃ composite membrane was assembled by accumulating the TiO₂/Fe₂O₃ hierarchical nanostructure on a commercial cellulose acetate membrane. The membrane's ability for eliminating contaminants via photodegradation and filtration was investigated and discussed in this section. For comparison, TiO₂ nanowire membrane was prepared by the similar method to assess its photodegradation abilities. In these studies, three different representatives of industrial dyes were used, mainly methyl blue (MB), rhodamine B (RhB) and acid orange (AO7). As shown in Figure 7.8, MB was firstly selected to study the photodegradation process occurring on the surface of TiO₂/Fe₂O₃ composite membrane under UV irradiation. Figure 6.17a illustrates the absorption spectrum of MB solution after irradiated under UV light on the TiO₂/Fe₂O₃ composite membrane. The results show that 50 ppm of as-prepared MB solution is completely degraded after exposing to UV light for 30 min. As compared to TiO₂ nanowire membrane, the TiO₂/Fe₂O₃ composite membrane portrays better photodegradation capability under the same conditions (Figure 6.17b), and this can be attributed to the advantages contributed by the hierarchical formation of TiO₂/Fe₂O₃ nanostructure (Tan, Tai, Juay, Liu, & Sun, 2015). The filtration system as shown in Figure 3.1 was activated following the photodegradation process. As a result of the filtration process, MB was eliminated from the solution via the concurrent photodegradation and filtration through the as prepared membranes. After analysing the permeate collected from the TiO₂/Fe₂O₃ composite membranes, it was found that a complete removal of MB was achieved. On the other hand, the permeate obtained from the TiO₂ nanowire membranes still contain 38 % of MB.

Figure 6-17: Photodegradation of MB; (a) Absorption spectrum of MB on the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ membrane under the irradiation of UV light; and (b) Change in MB

concentration with the presence of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane, pure TiO_2 nanowire membrane and photolysis process under the irradiation of UV light.

As presented in Figure 6.18, the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and TiO_2 nanowire membrane were employed to investigate the removal of RhB. The RhB solution was prepared with an initial concentration of 50 mg/L. After 60 min of photodegradation process under UV light, RhB was completely removed by the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes (Figure 6.18a). In contrast, TiO_2 nanowire membranes required a longer duration to achieve a similar result. Under the same conditions, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes portrayed better photodegradation capability as compared to its counterpart (Figure 6.18b). Based on the photocatalysis of RhB and membrane filtration process results, there was no presence of RhB detected in the permeate collected using $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes, while 50% of RhB was observed in the permeate of the TiO_2 nanowire membranes. The high presence of the RhB could be due to the low photodegradation of primary TiO_2 nanowire.

Figure 6-18: Photodegradation of Rhb; (a) Absorption spectrum of RhB on the TiO₂/Fe₂O₃ membrane under the irradiation of UV light; and (b) Change in RhB concentration with the presence of TiO₂/Fe₂O₃ composite membrane, pure TiO₂ nanowire membrane and photolysis process under the irradiation of UV light.

Figure 6.19 illustrates the removal of dye contaminant AO7 using $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and TiO_2 nanowire membrane. The physical change in AO7 concentration under the exposure of UV light on the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and TiO_2 nanowire membrane is presented in Figure 6.19. Based on this comparison, it is undoubtedly that $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane performed superior photodegradation activities than TiO_2 nanowire membrane. During the experiments, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane completely eliminated the AO7 dye contaminant within 60 min of UV irradiation, while TiO_2 nanowire membrane only manage to degrade 40% of it.

Figure 6-19: Photodegradation of AO7; Change in AO7 concentration with the presence of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane, pure TiO_2 nanowire membrane and photolysis process under the irradiation of UV light.

The overall degradation rates for the three dyes were illustrated in Figure 6.20. In general, the boost in photodegradation ability of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane could be attributed to the following considerations: 1) the significant increased in specific surface area of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure ($288.1 \text{ m}^2\text{g}^{-1}$) from primary TiO_2 nanowire ($63.4 \text{ m}^2\text{g}^{-1}$) enhanced the contaminant adsorption by catering more reaction sites for photocatalytic activity; 2) improved light utilisation rate as compared to primary

TiO₂ nanowire; and 3) the hierarchical formation of TiO₂/Fe₂O₃ nanostructure promotes light reflection and scattering phenomenon, in which primary TiO₂ nanowire is lacking due to their smooth surfaces. For a typical photocatalytic process, electrons and holes are formed, in which electrons will be captured by O₂ available on the surface to generate superoxide and hydroxyl radicals. Concurrently, the difference in band gap between TiO₂ and Fe₂O₃ expedite the transfer of photogenerated electrons from TiO₂ to Fe₂O₃, which impede the recombination of electrons and holes to a certain extent (Scheme 3) (Litter & Navío, 1996; Ranjit & Viswanathan, 1997; Roger, Teresita, Agustin, Guillermo, & Leonardo, 1994). Thus, enhancing the photocatalytic activity.

Figure 6-20: Overall photodegradation rate; Pseudo first-order reaction rate performed for degrading (a) methylblue, (b) rhodamine B and (c) acid orange by TiO₂/Fe₂O₃ composite membrane and TiO₂ nanowire membrane respectively.

Scheme 3: Schematic diagram of the photocatalytic reactions over the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructure illustrating the electron transfer and band position of TiO_2 and Fe_2O_3 .

6.9. Oil-water separation study

The superhydrophilic and underwater superoleophobic properties inherent in the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and TiO_2 nanowire membrane empowered them to perform oil-water separation process (Figure 6.5). For each experiment, the as-prepared membranes were used to segregate oil from water immediately after the filtration cycle. The benefit of employing a vacuum filtration approach includes its practicability of performing continuous separation procedures in a straightforward configuration. The oil-water emulsion used for this study was prepared by mixing lubricant oil with surfactant, which resulted in the formation of nanometer and micrometer-sized oil droplets. The separation mechanism of the membrane is shown in the schematic diagram illustrated in Figure 6.6, in which water can easily permeate through the membrane while oil droplets are rejected due to the underwater superoleophobic interface. Figure 6.21a illustrates the oil-water separation process using $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. Initially, the surfactant-stabilised oil-water emulsion was poured into the top glass funnel of the setup. The permeation of water occurs quickly when the vacuum pump was switched on, whereas the oil content was observed to be retained on the membrane surface owing to its superhydrophilic and underwater superoleophobic

characteristics. Figure 6.21b presents the separation efficiencies of the various $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes and TiO_2 nanowire membranes. Remarkably, the novel $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes exhibited extremely high separation efficiencies ($>99.5\%$), including 99.78% for MB photodegraded $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane, 99.77% RhB photodegraded $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and 99.56% AO7 photodegraded $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. Contrariwise, the various TiO_2 nanowire membrane only achieved an average separation efficiencies of 60% (66.22% for MB photodegraded TiO_2 membrane, 56.32% for RhB photodegraded TiO_2 membrane and 56.23% for AO7 photodegraded TiO_2 membrane). These outcomes could be explained by the following possible reasons: 1) As shown in Figure 6.22b, particle size mastersizer was used to investigate the size of oil droplets in the feed. From the analysis, it was observed that the addition of surfactant (Triton X-100) reduced the oil molecules from 1 – 50 μm to an average droplet size of 200 nm. According to the FESEM images, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane comprises of a smaller pore size formation as compared to TiO_2 nanowire membrane due to the incorporation of Fe_2O_3 nanoneedles. Hence, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane is capable of rejecting smaller oil droplets; and 2) The $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane achieved a water capture percentage of 838% while TiO_2 membrane only obtained 260%. This phenomenon can be attributed to the enlarged specific surface area of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructures. This study shows that $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane is capable of introducing more water layers by trapping more water molecules, which enhances the separation mechanism. From these experiments, it can be observed that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane portrays excellent capability in separating surfactant-stabilised oil-in-water emulsion with oil droplets as small as 200 nm. More importantly, it shows that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes were able to exhibit a superior oil-water separation ability even after the initial photodegradation process. In a nut shell, this novel membrane displays its competency in performing possible concurrent photodegradation, filtration and oil-water separation process.

Figure 6-21: Oil-water separation analysis; (a) Photograph of the oil-water separation setup for separating surfactant-stabilised oil-in water emulsion using TiO₂/Fe₂O₃ composite membrane. The membrane was pre-wetted and positioned in the vacuum

pump supported all glass-vacuum filter holder. (b) Separation efficiencies for both $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane and TiO_2 nanowire membrane after photodegrading methyblue, rhodamine B and acid orange respectively.

Figure 6-22: Permeate quality and oil droplet sizes; a) Photograph showing permeates obtained through the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane, pure TiO_2 nanowire respectively and b) DLS data of surfactant-stabilised lubricant oil-in-water emulsion verifying the reduction in oil droplet size to an average droplet size of 200 nm.

6.10. Conclusions

The flexible $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane has been successfully fabricated by depositing $\text{TiO}_2/\text{Fe}_2\text{O}_3$ hierarchical nanostructures on the surface of a commercial membrane through vacuum filtration process. This membrane exhibit superior photodegradation potential in degrading various dye contaminants such as MB, AO7 and RhB, under UV light irradiation. As compared to TiO_2 nanowire membrane, the enlarged specific surface area, improved light utilisation rate and retardation of electrons and holes recombination are the attributes that boost the photocatalytic activity of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane. Furthermore, the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes demonstrated excellent oil-water separation ability under vacuum filtration process even after photodegrading the various types of dye contaminant. This was attributed to the inherent superhydrophilic and underwater superoleophobic properties inherent within the membrane. In addition, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membranes were found to possess with a higher water capture percentage as compared to TiO_2 nanowire membrane, and this was due to the enlarged specific area resulted from the introduction of Fe_2O_3

nanoneedles. In sum, the discovery of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite membrane creates an opportunity to eliminate dye contaminants and carrying out oil-water separation process effectively, which can be considered as a promising candidate in numerous applications involving managing polluted surfactant stabilised oily wastewater.

7. Conclusions and Recommendations

7.1. Conclusions

The rapid growth of industrial activities and occurrences of environmental pollution such as contaminated oil spill evoke situations leading to water source contamination. Currently, burning, oil skimmers and employing oil-adsorbent are some common strategies that have been employed to handle the oily wastewater. However, most of these methods are not able to treat oil-water emulsions containing low oil concentration and finely dispersed oil droplets. Furthermore, severe membrane fouling caused by the effluent nature has limited the application of membrane filtration for oily wastewater treatment.

With the above considerations, TiO₂ based oil-water separation membranes have been fabricated and reported in this thesis. For the initial part of the research work, a preliminary study was conducted to investigate the feasibility of employing TiO₂ nanomaterial for an oil-water separation process. Furthermore, vacuum filtration was chosen due to its advantages as compared to gravity-driven filtration process. Therefore, a flexible self-cleaning TiO₂ nanowire/Cu microwire (TC) hierarchical membrane was fabricated, in which the interweaving Cu microwires were introduced to improve the flexibility and mechanical strength of the membrane. The TiO₂ nanowire had a consistent diameter of 80-90 nm, with a length of more than 10 μ m long, while the copper microwires had a distribution of diameters between 850 nm - 1000 nm, with a length range from several micrometers to several tens micrometers. The as-prepared membrane portray remarkable flexible characteristics, superhydrophilic and underwater superoleophobic properties. During the experiment, this membrane was capable of removing oil droplet > 600nm with an overall removal efficiency of $\geq 99.9\%$. Moreover, the TC membrane was also built with excellent self-cleaning properties.

Subsequently, the study focused on investigating the importance of modifying the photocatalysts nanostructures in order to improve both their oil-water separation performance and self-cleaning ability. In this study, three kinds of TiO₂ nanostructures membranes were examined, namely 1D TiO₂ nanotube (TNT) membrane, 1D TiO₂ nanowire (TNW) membrane and 3D nanosheet-decorated TiO₂ nanowire hierarchical structure (TSW) membrane. TSW membrane obtained the highest oil-water separation efficiency of 99.89% as compared to its counterparts. The FESEM analysis showed that

nanosheet-decorated TiO₂ nanowire hierarchical structure was formed through a two-step hydrothermal process, where the nanowire hosts were uniformly and densely covered by 200nm long and 150nm wide nanosheet structures. These single "heterostructure" increase the water intake of the membrane, in which the water capture percentage (WCP) for TNT, TNW and TSW membranes are 397%, 267% and 563% respectively. Thus, enhancing the oil-water separation ability. Furthermore, its large BET surface area, high light absorption capacity due to light scattering phenomenon and superior electron collection properties synergistically resulted the TSW membrane superior self-cleaning performance.

After identifying the optimum nanostructure required for the development of an efficient oil-water separation membrane, a TiO₂ composite nanostructure was synthesized by incorporating Fe₂O₃ nanomaterials. Iron oxide material has been reported for its high mechanical properties and flexible characteristic which can inevitably improve the strength of a material. Moreover, it also helps to improve the catalyst performance by narrowing the energy gap through introducing a new impurity energy level, which might effectively inhibit the fast electron-hole recombination rate. Hence, Fe₂O₃ was chosen to provide a crosslinking network between TiO₂ nanowires in order to promote efficient bonding. FESEM and TEM images showed that Fe₂O₃ nanoneedles are grown uniformly along the surface of the TiO₂ nanowire. Furthermore, the TiO₂/Fe₂O₃ composites are closely packed and clinched together, resulting in a compact formation, which enhanced its mechanical flexibility. With the possession of such excellent flexibility, this novel membrane can be allowed to be fitted in various configuration of membrane modules which broaden its practical application. The TiO₂/Fe₂O₃ multifunctional membrane possess a rough surface with approximately a 31 - 45 nm undulation range, which enhance the membrane's superhydrophilic and underwater superoleophobic properties. As a result, this membrane exhibited an outstanding oil-water separation efficiency rate of >99.87% for surfactant stabilised oil under vacuum driven condition. For this experiment, the oil droplets were reduced from 140 μ m to 400 nm with the addition of surfactant. Experimental results showed the impacts on the membrane's separation efficiency under various temperature and ionic strength condition are minimum. Hence, this highlighted that the TiO₂/Fe₂O₃ multifunctional membrane was capable of removing small oil droplet with a report high flux of 81 L m⁻² h⁻¹. Moreover, this membrane also

portray excellent self-cleaning phenomenon where the CA of a polluted membrane was reduced from 100° to less than 10° under UV light irradiation.

Consequently, the as-prepared $\text{TiO}_2/\text{Fe}_2\text{O}_3$ multifunctional membrane was examined for its capability of achieving a two-step photodegradation of dyes with oil-water separation process. The membrane was tested under three different types of dyes namely Methyl blue (MB), Rhodamine B (RhB) and acid orange (AO7). Basically, the oil-water separation study was conducted immediately after the photodegradation process using the photo-reacted membrane (namely MB treated membrane, AO7 treated membrane and RhB treated membrane). The experimental results showed that the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ multifunctional membranes were able to completely photodegrade the dyes and maintained a separation efficiency as high as 99.78%. In sum, the discovery of such membrane provide an opportunity to remove dyes and separating oil from water effectively, which could be potentially involved in numerous applications relating to polluted surfactant stabilised oily wastewater.

7.2. Recommendations for Future Work

The thesis has covered the works pertaining to the separation of oil-water emulsion using TiO_2 nanostructures and TiO_2 composite nanostructure ($\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite). However, further works are required to compliment the studies reported in the thesis. Thus, recommendations for the future work are summarised as follow

- i. In this thesis, the studies only focus on Ultra Violet light irradiation. As a result, there is an opportunity to explore the feasibility of utilising the multifunctional oil-water separation membrane under visible light condition. This is essential because solar visible light is a clean and renewable energy resources which is ideal for sustainable and environmental applications. Thus, it is meaningful to examine the performance of the multifunctional oil-water separation membrane under visible light exposure, especially focusing on its self-cleaning and photodegradation properties.
- ii. Seeking solutions in improving the mechanical strength of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ multifunctional membrane is essential for its future applications. For the current study, there is a limitation to the operating pressure, and one of the key to enhance the membrane's mechanical strength is to improve the bonding between the nanomaterials. Thus, allowing the membrane to be operated in a higher pressure

condition will expand its applicability in large scale oily wastewater treatment process.

- iii. Extensive study should be carried out to investigate the possible release of Fe ions from the synthesized nanomaterials. Ultimately, the outcome of this study will help to eliminate secondary pollution in the treated water.
- iv. Exploration of other functions for the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ multifunctional membrane such as Arsenic removal. Arsenic, a carcinogen, has been classified as a concern to the environment in many regions due to its toxic effect on human health (Nordstrom, 2002). Both TiO_2 and Fe_2O_3 had been reported for their ability in eliminating arsenic from water (Cui, Du, Yu, Jing, & Chan, 2014; S. Lin, Lu, & Liu, 2012). Hence, this will be a beneficial discovery in the water treatment process if $\text{TiO}_2/\text{Fe}_2\text{O}_3$ multifunctional membrane can separate oil from water, photodegrade contaminants and remove arsenic from water concurrently.

8. References

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Appendix A: Water Capture Measurement

The hydrophilic property of TC active layer is primarily due to the existence of TiO₂ nanowires and copper microwire. In order to prove the water affinity towards these nano/micro wires, water capture percentage (WCP) was determined using the following equations (1-3):

$$\text{Mass of dry TC deposit, } TC_{dry} = W_{2,dry} - W_{1,dry} \dots\dots\dots (\text{Equation 1})$$

$$\text{Mass of wet TC deposit, } TC_{wet} = W_{2,wet} - W_{1,wet} \dots\dots\dots (\text{Equation 2})$$

$$\begin{aligned} \text{Water capture percentage, } WCP(\%) \\ = \frac{TC_{wet} - TC_{dry}}{TC_{dry}} \times 100\% \dots\dots\dots (\text{Equation 3}) \end{aligned}$$

Where $W_{2, dry}$ and $W_{1, dry}$ represent the dry mass of TC membrane and pure glass fibre respectively. $W_{2, wet}$ and $W_{1, wet}$ represent the wet mass of TC membrane and pure glass fibre filter respectively. To minimise errors, WCP was measured three times for each membrane.

For comparison, WCP values of pure glass fibre filter was also measured. The results show that the existence of TiO₂ nanowires and copper microwire exhibited a significant increase in the amount of water uptake. This phenomenon could be attributed to the trapping of water molecules by the TC nano/micro wires when immersed in a water media. Ultimately, this enhanced WCP contributes greatly to the oil-water separation ability.

Appendix B: Self-cleaning Properties Kinetics

As shown in equation 4, Langmuir-Hinshelwood kinetics was employed to determine the UV photodegradation rate for methylene blue (MB) aqueous solution (X. Wang & Lim, 2010).

$$r = k_i \theta = k_i \left(\frac{KC}{1 + KC} \right) \dots \dots \dots (\text{Equation 4})$$

where (r) is a function of the degree of substrate coverage (θ), (C) is the concentration of MB, (K_i) is the intrinsic rate constant, and (K) is the Langmuir adsorption equilibrium constant. By assuming that the adsorption of MB in the dark is negligible, KC was suggested to be $\ll 1$. Hence, the simplified Langmuir-Hinshelwood kinetics and the derived pseudo-first-order reaction rate are shown in equation 5 and 6 respectively.

$$r = -\frac{dC}{dt} = kKC = kC \dots \dots \dots (\text{Equation 5})$$

$$\ln \frac{C_t}{C_o} = -kt \dots \dots \dots (\text{Equation 6})$$

Where (k) represent the rate kinetic constant, (C_t) is the MB concentration at time t, (C_o) is the initial MB concentration after 2 hours of dark adsorption. Moreover, it is apparent that the photodegradation trend plot follows the first order kinetics. As a result, the photodegradation rate was determined using the derived equations (Ng, Pan, & Sun, 2011)