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**MULTIFUNCTIONAL GRAPHENE OXIDE-TiO₂ MEMBRANE
FOR WASTEWATER PURIFICATION AND OIL-WATER
SEPARATION**

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SUMMARY

The severe scarcity of clean water is arousing concern worldwide. The development of clean water production heavily relies on membrane technology, although the performances of current membranes are significantly restricted by their monotonous function and membrane fouling. In this study, a novel multifunctional GO-TiO₂ based membrane was delicately designed and fabricated for the first time to solve the drawbacks of current membranes. The novel membranes fabricated in this work exhibit the promising activities for wastewater purification and oil-water separation: (1) excellent mechanical flexibility because of the cross-linkers existed in the membranes; (2) eliminating organic fouling due to the strong photodegradation property; (3) withstanding various wastewater conditions (such as acidic and basic conditions); and (4) high oil-water separation efficiency towards oil-water mixtures, especially surfactant stabilized oil-water emulsions, due to the superhydrophilic and underwater superoleophobic properties.

This study initiated from finding out the optimal TiO₂ nanostructure for fabrication of the membranes. Various TiO₂ nanostructures have been successfully synthesized, including one-dimensional (1D) TiO₂ nanotube, 1D TiO₂ nanowire, three-dimensional (3D) TiO₂ sphere assembled by nanoparticles (TiO₂ sphere-P) and 3D TiO₂ sphere assembled by nanosheets (TiO₂ sphere-S). The results of photodegradation activity indicate that the photodegradation efficiency of TiO₂ sphere-S is the highest among the investigated TiO₂ nanostructures. The best photodegradation activity of TiO₂ sphere-S can be attributed to the highest light harvesting capacity resulted from multiple reflections of light, and hierarchical mesoporous structure. In addition, the combination of TiO₂ sphere-S with graphene oxide (GO) sheets can further enhance the photodegradation and disinfection activities under solar light, which is more energy efficient. The promising photocatalytic activity of GO-TiO₂ composites is originated from the enhanced light absorption and efficient charge separation.

In the following work, GO-TiO₂ membrane was fabricated through assembling as-synthesized GO-TiO₂ composites on the surface of a polymer filtration membrane. This kind of membrane possesses the multifunction of concurrent water filtration and degradation of pollutants. GO sheets play double roles in GO-TiO₂ membrane, including (1) cross linker for individual TiO₂ microspheres; and (2) electron acceptor to enhance photocatalytic activity. Hence, this novel membrane shows sustainably high permeate flux due to the hierarchical membrane structure, high photodegradation activity and no membrane fouling. In order to further treat wastewater with different pH conditions, a novel GO-SO₃H/TiO₂ membrane was fabricated by chemical modification of synthesized GO sheets for the first time. This membrane shows enhanced strength and flexibility compared with pure inorganic membrane due to the special GO-SO₃H/TiO₂ heterojunctions. In addition, the strong coordination bonds between sulfonic group (-SO₃H) of GO-SO₃H and Ti⁴⁺ center of TiO₂ endow this membrane with excellent adaptability in various wastewater conditions. This membrane possesses high efficiency for concurrent photodegradation and water filtration without organic fouling problem.

Finally, considering the increasingly amount of oily wastewater, the fabricated multifunctional GO-SO₃H/TiO₂ (SGO-TiO₂) membrane also exhibited high efficiency of oil-water separation. The SGO-TiO₂ membrane was applied for the separation of a variety of oil-water mixtures, including free oil-water mixtures and surfactant stabilized oil-water emulsions. This is the first time to efficiently separate surfactant stabilized oil-water emulsions using a pressure driven SGO-TiO₂ membrane, the separation of which remains a great challenge by conventional approaches. During the oil-water separation process, this membrane shows the combined advantages of high oil rejection rate and ultralow membrane fouling, thanks to its interconnected nanoscale network, superhydrophilic and underwater superoleophobic interface, and self-cleaning function. The results of this study indicated that this multifunctional membrane could be a good candidate for practical wastewater purification and oil-water separation.

LIST OF PUBLICATIONS

Journal

1. **Peng Gao**, Anran Li, Darren D. Sun and Wun Jern Ng. Effects of various TiO₂ nanostructures and graphene oxide on photocatalytic activity of TiO₂. *Journal of Hazardous Materials*, 2014, 279, 96-104.
2. **Peng Gao**, Zhaoyang Liu, Darren D. Sun and Wun Jern Ng. The efficient separation of surfactant-stabilized oil–water emulsions with a flexible and superhydrophilic graphene–TiO₂ composite membrane. *Journal of Materials Chemistry A*, 2014, In press.
3. Darren D. Sun, You Wu and **Peng Gao**. Effects of TiO₂ nanostructure and operating parameters on optimized water disinfection processes: A comparative study. *Chemical Engineering Journal*, 2014, 249, 160-166.
4. **Peng Gao**, Zhaoyang Liu, Minghang Tai, Darren D. Sun and Wunjern Ng. Multifunctional graphene oxide-TiO₂ microsphere hierarchical membrane for clean water production. *Applied Catalysis B: Environmental*, 2013, 138–139, 17-25.
5. **Peng Gao**, Darren D. Sun and Wunjern Ng. Multifunctional nanostructured membrane for clean water reclamation from wastewater with various pH conditions. *RSC Advances*, 2013, 3, 15202-15210.
6. **Peng Gao**, Jincheng Liu, Darren D. Sun and Wunjern Ng. Graphene oxide-CdS composite with high photocatalytic degradation and disinfection activities under visible light irradiation. *Journal of Hazardous Materials*, 2013, 250–251, 412-420.
7. **Peng Gao**, Jincheng Liu, Tong Zhang, Darren D. Sun and Wunjern Ng. Hierarchical TiO₂/CdS “spindle-like” composite with high photodegradation and antibacterial capability under visible light irradiation. *Journal of Hazardous Materials*, 2012, 229–230, 209-216.

Conference

1. **Peng Gao**, Anran Li, Minghang Tai, Zhaoyang Liu and Darren D. Sun. A

hierarchical carbon nanofiber-In₂S₃ photocatalyst with well controlled nanostructures for highly efficient hydrogen production under visible light. The World Innovation Conference, Washington, USA, June 15-19, 2014.

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LIST OF ABBREVIATIONS AND SYMBOLS

1D:	one-dimensional
2D:	two-dimensional
3D:	three-dimensional
Ag:	silver
Al ₂ O ₃ :	alumina
AO7:	acid orange 7
AFM:	atomic force microscopy
BET:	Brunauer-Emmet-Teller
CA:	cellulose acetate
CB:	conduction band
CdS:	cadmium sulfide
cfu/mL:	colony forming units per milliliter
ClCH ₂ CH ₂ SO ₃ H:	sodium 2-chloroethanesulfonate
ClO ₂ :	chlorine dioxide
CNTs:	carbon nanotubes
COD:	chemical oxygen demand
CVD:	chemical vapor deposition
DBPs:	disinfection by-products
DCM:	dichloromethane
DLS:	dynamic light scattering
DMF:	dimethyl formamide
DI:	deionized
DSSC:	dye sensitized solar cells
FESEM:	field emission scanning electron microscopy
FTIR:	fourier transform infrared
GO:	graphene oxide
GO-SO ₃ H:	sulfonated graphene oxide
HA:	humic acid

HAc: acetic acid
HCl: hydrochloric acid
HRTEM: high-resolution transmission electron microscopy
H₂O₂: hydrogen peroxide
H₂SO₄: sulfuric acid
In₂S₃: indium sulfide
IPA: isopropyl alcohol
KMnO₄: potassium permanganate
LB: Luria-Bertani nutrient
LBL: layer-by-layer
MB: methylene blue
MF: microfiltration
MnO₂: manganese oxide
NaCl: sodium chloride
NaNO₃: sodium nitrate
NaOH: sodium hydroxide
NF: nanofiltration
NOMs: natural organic matters
¹O₂: singlet oxygen
O₂⁻: superoxide radicals
•OH: hydroxyl radicals
PAM: polyacrylamide
PAN: polyacrylonitrile
PEG: poly(ethylene glycol)
PEGDA: poly(ethylene glycol) diacrylate
PEMs: polyelectrolyte multilayers
PES: polyethersulfone
PL: photoluminescence
PP: polypropylene
PSF: polysulfone

PVDF: polyvinylidene fluoride

PVP: polyvinyl pyrrolidone

QDSSCs: quantum dot-sensitized solar cells

RGO: reduced graphene oxide

RhB: rhodamine B

RO: reverse osmosis

ROSs: reactive oxygen species

SEM: scanning electron microscopy

SGO: sulfonated graphene oxide

SiO₂: silica

TBT: tetrabutyl titanate

TCO: transparent conducting oxide

TEM: transmission electron microscopy

TGA: thermal gravimetric analysis

TiO₂: titanium dioxide

TMP: trans-membrane pressure

TOC: total organic carbon

UF: ultrafiltration

USEPA: The United States Environmental Protection Agency

UV: ultraviolet

UV-Vis: ultraviolet-visible

VB: valance band

WHO: World Health Organization

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

ZnO: zinc oxide

ZrO₂: zirconia

CHAPTER 1: INTRODUCTION

1.1 Background

The development of the world economy heavily relies on clean water. With the exponentially expanding global population and industrialization, the demand for higher quality clean water is increasing rapidly. The scarcity of drinking water has become one of the most severe worldwide problems (Elimelech and Phillip, 2011). Moreover, in both developing and industrialized nations, the challenge of supplying adequate safe drinking water is further complicated by contamination of already-scarce freshwater resources (Shannon et al., 2008; Elimelech and Phillip, 2011). With the lack of clean water supplies, many social problems arise from the usage or consumption of contaminated water, which commonly contains dangerous pathogens (Shannon et al., 2008). It is reported that 2.6 billion people lack access to proper sanitation, 1.2 billion people drink unsafe water, and millions of people die annually from waterborne infectious disease, including 3900 children a day (Montgomery and Elimelech, 2007). In the past few decades, various contaminants are discharged into water, including heavy metals, natural organic matters (NOMs), microorganisms, oil and etc., which pose a serious threat to human health. Over the years, tremendous efforts have been dedicated in water treatment researches to alleviate the deterioration of water body qualities around the world.

Traditional methods including coagulation/flocculation, granular media filter, sedimentation and disinfection can address many of these problems. However, these treatment methods are based on large systems and usually require huge amount of chemicals and energy, which are less sustainable in the long run. In addition, most of current available water treatment technologies do not eliminate the contaminants, but only transfer them to other phases (Padmanabhan et al., 2006). Chemical based treatments generate large amount of secondary pollutants, such as sludge and brines, which have become huge concerns globally (Shannon et al., 2008; Chong et al., 2010).

Furthermore, some conventional approaches could not be easily implemented in some developing countries and regions due to lack of suitable and enough chemicals as well as poor infrastructure. Hence, affordable, safe, sustainable and robust methods to purify water are urgently needed in the near future.

Recently, nanomaterials have shown great potential in water treatment fields than the conventional techniques due to the strong oxidation, adsorption and catalytic activities (Khin et al., 2012). The surface area of nanomaterials is significantly larger than the bulk materials due to the nanoscale size, which provides more reactive sites in the water treatment. Until now, numerous nanomaterials have been applied in the fields of environmental remediation, including silver nanoparticles (Ag), manganese oxides (MnO_2), chitosan, photocatalysts (such as TiO_2 , ZnO and etc.). Ag nanoparticles are active in killing bacteria through a contact inhibition mode, which cause an increase in cell permeability if they attach on the bacteria cells and then results of osmotic collapse and death of bacteria (Panáček et al., 2006). MnO_2 nanostructures such as nanowires and microspheres are strong oxidants for the detoxification of organic and inorganic water contaminants, such as bisphenol A and arsenic (Zhang et al., 2011; Zhang and Sun, 2013). The photocatalysts have the excellent photocatalytic activities to degrade environmental pollutants including organics and bacteria.

Among the reported photocatalysts, TiO_2 is the most active and stable photocatalyst, which is expected to solve serious environmental pollution problems, including water and air purification. In the past two decades, TiO_2 based photocatalytic oxidation has been intensively studied, including photocatalytic decomposition of various organic matters and inactivating of bacteria and viruses (Chong et al., 2010). However, the wide application of TiO_2 is still restricted by its intrinsic drawbacks including the rapid charge recombination and limited light absorption. Hence, controlling the nanostructures of TiO_2 and combining with carbon materials are two effective approaches to improve the photocatalytic activity of TiO_2 .

However, the separation of TiO_2 nanomaterials is a worldwide challenge. To solve this problem, various TiO_2 based membranes were fabricated by the researchers. However, the photocatalytic efficiency of pure TiO_2 membrane is low. In addition, there are no cross-linkers within pure TiO_2 membrane. Furthermore, most of reported TiO_2 membranes were used to remove organic pollutants (such as NOMs and bacteria) from wastewater, while few reports discussed the oil removal activity of TiO_2 membrane. It should be noted that the fabrication of a novel membrane for oily wastewater treatment is also a big challenge due to the membrane fouling caused by viscous oil.

Hence, in this work, the photocatalytic activity of TiO_2 was firstly optimized by manipulating the nanostructures of TiO_2 . Subsequently, TiO_2 nanostructure with the best photocatalytic efficiency was combined with graphene oxide (GO) to further enhance the photocatalytic activity. Finally, the multifunctional GO- TiO_2 based membrane was fabricated for wastewater purification and oil-water separation.

1.2 Research Objectives and Significances

The overall objective of this study is to design and fabricate multifunctional GO- TiO_2 based membranes for wastewater purification and oil-water separation. TiO_2 nanomaterials and GO sheets have been chosen as the basic materials. The detailed objectives of this study are:

(1) To synthesize different TiO_2 nanostructures including 1D TiO_2 nanotubes, 1D TiO_2 nanowires and two kinds of 3D TiO_2 spheres with different building blocks. Investigate the influences of morphology and nanostructure of TiO_2 on the photocatalytic activity to find out the best TiO_2 nanostructure. The photocatalytic mechanisms of different TiO_2 nanostructures were proposed.

(2) To investigate influence of GO sheets on the photocatalytic degradation and disinfection activities of TiO_2 by synthesizing GO- TiO_2 composites. The

photocatalytic mechanism of GO-TiO₂ composites was illustrated.

(3) To fabricate GO-TiO₂ membrane and investigate the wastewater purification activity of this membrane by treating humic acid (HA) solution.

(4) To fabricate sulfonated GO-TiO₂ membrane by modification of GO sheets. The sulfonated functional groups were introduced through a simple chemical reaction. The wastewater purification activity of this membrane was investigated under different wastewater conditions (such as acidic and basic). The working mechanisms of the sulfonated GO-TiO₂ membrane under different conditions were illustrated.

(5) To investigate the oil-water separation performances of the sulfonated GO-TiO₂ membrane. A variety of oil-water mixtures including free oil-water mixtures and surfactant stabilized oil-water emulsions were studied. The mechanism of oil-water separation by the sulfonated GO-TiO₂ membrane was proposed.

Significances and benefits of this study are as follows:

The significance of this research is to fabricate a multifunctional membrane for wastewater purification and oil-water separation without fouling problem. This is because the removal of NOMs and oil, especially oil with small droplets, remains as a global challenge, while the commercial membranes suffer from serious fouling problems. This multifunctional membrane can be a promising candidate for municipal and industrial wastewater treatment. In addition, it also can be used for the treatment of accidental marine oil spill.

In particular, the main innovations of this research include:

(1) The photocatalytic activities of various TiO₂ nanostructures (nanotubes, nanowires, spheres) were compared for the first time and concluded that hierarchical TiO₂ spheres with nanosheets blocks acquired the best photocatalytic efficiency.

(2) GO-TiO₂ composites were synthesized by combination of GO sheets with TiO₂ spheres for photocatalytic degradation and disinfection.

(3) Hierarchical GO-TiO₂ membranes were fabricated for the first time for wastewater purification.

(4) Sulfonated GO sheets were synthesized by introducing sulfonated groups into GO sheets by a chemical reaction.

(5) Multifunctional sulfonated GO-TiO₂ membranes were fabricated for the first time for wastewater purification under different pH conditions.

(6) Multifunctional sulfonated GO-TiO₂ membranes were used for the separation of surfactant stabilized oil-water emulsions for the first time.

These innovations have not been reported by other researchers so far.

1.3 Thesis overview

This thesis contains 8 chapters.

Chapter 1 is the introduction, which gives a brief introduction of the research background, research objectives and significances of this study.

Chapter 2 presents a comprehensive literature review, which covers traditional wastewater purification technology, photocatalytic technology, TiO₂ photocatalyst, GO, graphene/GO-TiO₂ composites, membrane technology and oil-water separation technology.

Chapter 3 introduces the materials and methodology used in this thesis. This section includes the chemicals, materials, the synthetic procedures, and the material characterization techniques. In addition, the photocatalytic degradation and

disinfection process, wastewater purification process, and oil-water separation process were also illustrated in detail.

Chapter 4 investigates the effects of various TiO_2 nanostructures and GO sheets on the photocatalytic activity of TiO_2 . The photocatalytic degradation and disinfection activities of GO- TiO_2 composites were also investigated.

Chapter 5 reports the fabrication of the hierarchical GO- TiO_2 membrane by using the synthesized GO- TiO_2 composites of **Chapter 4**. The wastewater purification activity and anti-fouling property of GO- TiO_2 membrane were investigated thoroughly by choosing HA solution as a standard wastewater.

Chapter 6 further reports the fabrication of sulfonated GO- TiO_2 multifunctional membrane by introducing sulfonated groups into GO sheets. This is because the GO- TiO_2 membrane fabricated in **Chapter 5** cannot withstand the alkaline condition. In addition, the wastewater purification activity of sulfonated GO- TiO_2 membrane under different pH condition was evaluated.

Chapter 7 investigates the oil-water separation performance of sulfonated GO- TiO_2 multifunctional membrane fabricated in **Chapter 6**.

Chapter 8 is a summary of this research, and some recommendations.

Data and information presented in this thesis may have been published or in the preparation for publication as listed in the section “List of Publications”.

CHAPTER 2: LITERATURE REVIEW

2.1 Traditional wastewater purification technology

Nowadays, scarcity of drinking water has become one of the most severe worldwide problems (Elimelech and Phillip, 2011). However, water quality has been compromised by pollution from municipal and industrial waste discharges. Expanding global population and global warming further worsen the problem of water contamination (Elimelech and Phillip, 2011). Traditionally, the wastewater was treated by multi-steps, including coagulation/flocculation, granular media filter, sedimentation and disinfection. Generally, the wastewater purification processes usually include two aspects: decontamination and disinfection.

2.1.1 Decontamination

The wastewater decontamination process is to remove toxic substances, including NOMs, heavy metals, synthetic organic matters, arsenic, nitrates, and so on (Shannon et al., 2008). These toxic substances are harmful and even carcinogenic to humans and other living beings. This section mainly focuses on the wastewater decontamination of organic matters.

NOMs widely exist in natural waters, including ground water, surface water and soil water. NOMs cover a wide range of organic materials, including but not limit to humic substances, aminosugars, proteins, polysaccharides, peptides, lipids and small hydrophilic acids (Van Geluwe et al., 2011). The water quality can be destroyed by NOMs. Firstly, water has strange color and odor. Secondly, the presence of NOMs increases the amount of chemicals used in coagulation/flocculation process. In addition, NOMs cause severe membrane fouling during membrane filtration. Most importantly, NOMs are precursors of toxic and carcinogenic disinfection by-products (DBPs) (Chong et al., 2010; Matilainen et al., 2010). Typically, NOMs are divided into two categories: autochthonous and allochthonous NOMs. Autochthonous NOMs include carbon fixation by algae and aquatic plants as well as extracellular

macromolecules of microorganisms. Allochthonous NOMs contain animal residues and decay of plants in water (Van Geluwe et al., 2011). Humic substances contribute to a major fraction of allochthonous NOMs in aquatic environment (Hong and Elimelech, 1997). In the current research, humic acid (HA) is chosen as a standard NOM. The traditional and economical method of NOMs removal is adsorption, coagulation/flocculation, followed by sedimentation and sand filtration (Matilainen et al., 2010). However, chemical based treatments generate large amount of secondary pollutants, such as sludge and brines (Shannon et al., 2008; Chong et al., 2010). In addition, the traditional technologies do not eliminate the NOMs, but only transfer them to other phases (Padmanabhan et al., 2006). As a result, less energy and chemical intensive methods are the only option.

2.1.2 Disinfection

Waterborne bacteria, enteric viruses and pathogens significantly affect the health of humans. The diseases caused by waterborne bacteria are serious especially in the developing countries, which lack access to safe and clean drinking water, and suitable sanitation facilities (Shannon et al., 2008). The goal for disinfection process is to effectively and economically remove or eliminate the bacteria, viruses and pathogens from water, while avoiding the secondary problems caused by disinfection process. The conventional disinfection techniques include chlorination, UV irradiation, and ozonation.

As a standard practice, free chlorine has been widely used to inactivate bacteria, viruses and pathogens in traditional disinfection process due to its low cost and high efficiency. In addition, chloramines and chlorine dioxide (ClO_2) are also widely adopted to control biological growth despite chlorine. However, some challenges impede further usage of chlorine related disinfectants. This is because although free chlorine is effective in controlling most of bacterial pathogens and protozoan parasites, a few waterborne pathogens including *Cryptosporidium parvum* and *Mycobacterium avium* can survive even at high pH and low temperature in the presence of free

chlorine (Shannon et al., 2008). Particularly, *M. avium* is commonly existed in biofilms, which poses a threat to membrane system (Shannon et al., 2008). In addition, chlorine related disinfection approaches generate toxic and carcinogenic DBPs such as haloacetic acids and trihalomethanes (Chong et al., 2010). These disadvantages force some drinking water utilities to give up chlorine related disinfection technologies and look for alternative techniques.

The use of ultraviolet (UV) to inactivate bacteria has attracted considerable attentions recently. UV is considered as an efficient and cost-effective technique in controlling growth of bacteria. It has been reported that UV light destroys the bacterial DNA genetic code and inhibits their growth as well as propagation (Matin et al., 2011). In addition, this technique does not generate any DBPs and does not need the usage of chemicals in the treatment process. Furthermore, UV treatment not only effectively inactivates bacteria but also decomposes the organic compounds, which serve as nutrients for bacterial growth. However, UV treatment does not have the residual effects throughout distribution system, which cannot guarantee biological safety of treated water. In addition, UV is not efficient to disinfect some viruses.

Ozone is a powerful oxidant which has been widely used in wastewater treatment. Comparing with chlorination, ozonation is effective in inactivation of bacteria, but produces fewer toxic DBPs. It should be note that the most obvious advantage of ozonation is highly efficient in inactivating *C. parvum* oocysts, which typically shows resistance to chlorine (Shannon et al., 2008). The main drawbacks of ozonation include high costs for ozone generation and producing carcinogenic bromine compounds.

2.2 Photocatalytic technology for wastewater treatment

2.2.1 Introduction of photocatalytic technology

In the last several decades, the photocatalytic technology has shown its great potential in wastewater purification fields because of its strong ability to degrade water

contaminants, including organic pollutants, bacteria and water pathogens (Tang et al., 2004; Serpone and Emeline, 2012; Singh et al., 2013). The fundamental of the photocatalytic process is the generation of various reactive oxygen species (ROSs), including hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\cdot-}$), singlet oxygen ($^1\text{O}_2$) and hydrogen peroxide (H_2O_2) (Chong et al., 2010; Teoh et al., 2012). Among them, hydroxyl radicals are considered to be the most effective ROSs, which are widely used to evaluate the photocatalytic efficiency (Hou et al., 2012). Most of water contaminants, especially the NOMs, bacteria and other microorganisms, can react with these ROSs. The contaminants can be finally mineralized to carbon dioxide and water, without producing the secondary sludge and other pollutants, which overcomes the drawbacks of traditional wastewater purification methods. In addition, no chemical is needed in photocatalytic technology, which is environmental friendly and cost effective. In the whole photocatalytic process, the photocatalysts play indispensable roles which determine the photocatalytic efficiency and performances.

2.2.2 Introduction of photocatalyst

Ever since the first discovery of photocatalytic water splitting by n-type TiO_2 photo-electrodes in 1972 by Fujishima and Honda (Fujishima and Honda, 1972), the photocatalysts had attracted significant amount of research interests in the last several decades (Asahi et al., 2001; Lin et al., 2008; Chen et al., 2011; Qian et al., 2011). Generally, the working mechanism of the photocatalyst has been described in Figure 2.1. Firstly, the electron-hole pairs of the photocatalyst are generated under light irradiation. Secondly, the photo-generated electrons transfer from the valance band (VB) to the conduction band (CB), while leaving the photo-generated holes in VB. Thirdly, the photo-generated electrons and holes migrate to the surface of the photocatalyst. Finally, the photo-generated electrons and holes react with electron donors (D) and electron acceptors (A), respectively. During these processes, the electrons in CB can recombine with the holes in VB, which reduces the photocatalytic activity (Hoffmann et al., 1995; Tong et al., 2012).

Figure 2.1 Schematic illustration of working mechanism of a photocatalyst (Tong et al., 2012).

Until now, various photocatalysts have been developed, including single photocatalysts and coupled photocatalysts. In addition, the photocatalysts have been applied in the fields of wastewater treatment, hydrogen production, fuel cells, solar cells and so on (Kubacka et al., 2012). Single photocatalysts include titanium dioxide (TiO_2) (Albu et al., 2007; Gao et al., 2013; Wang et al., 2013; Gu et al., 2014), zinc oxide (ZnO) (Lu et al., 2008; Wang et al., 2012; Gao et al., 2013; Hong et al., 2013), cadmium sulfide (CdS) (Xiong et al., 2010; Huang et al., 2011; Huo et al., 2011; Xiang et al., 2013), indium sulfide (In_2S_3) (Chai et al., 2012; An et al., 2013; Zhang et al., 2013) and etc. (Zhang et al., 2009; Yu et al., 2011; Liu et al., 2013). The single photocatalysts have been widely used because of their facile preparation process and low cost. However, their performance and further development have been restricted by low photocatalytic efficiency which is resulted from the rapid recombination of electron-hole pairs. Hence, many research attentions have been switched to coupled photocatalysts in recent years (Hu et al., 2007; Agarwal et al., 2010; Li et al., 2010; Dong et al., 2012; Mei et al., 2013). Figure 2.2 shows that photo-generated electrons and holes of the photocatalysts can be efficiently separated if the CB and VB of two photocatalysts match with each other well. The photo-generated electrons transfer to

the photocatalyst with more positive CB level, while the photo-generated holes transfer to the photocatalyst with more negative VB level, as shown in Figure 2.2. To date, many coupled photocatalysts have been synthesized, including TiO_2/CdS , TiO_2/ZnO , TiO_2/WO_3 and so on (Zhang et al., 2009). These coupled photocatalysts show enhanced photocatalytic activity than the individual photocatalyst.

Figure 2.2 The separation of electrons and holes in the coupled photocatalyst (Zhang et al., 2009).

2.3 TiO_2 photocatalyst

2.3.1 Introduction of TiO_2

Among the reported photocatalysts, TiO_2 is the most intensively investigated material on account of its chemical stability, self-cleaning, antibacterial property and high photocatalytic activity in removing pollutants from water (Herrmann, 1999; Fujishima et al., 2000; Ardo and Meyer, 2009; Hwang et al., 2011). Generally, TiO_2 has three bulk crystalline forms, including anatase, rutile and brookite (Thompson and Yates Jr, 2006). The brookite is less investigated than rutile and anatase possibly due to its less stability. Figure 2.3 shows the bulk crystalline structure of rutile and anatase, respectively. For rutile, there is a slight distortion from orthorhombic structure, while there is a significant distortion of cubic lattice for anatase (Thompson and Yates Jr, 2006). In addition, anatase is a stable phase at low temperature and it will be

converted to rutile phase at high temperature.

Figure 2.3 Bulk crystal structure of rutile and anatase (Thompson and Yates Jr, 2006).

Table 2.1 Lattice parameters of anatase TiO₂ crystal structure.

Sample name	Anatase TiO ₂
Crystal system	Tetragonal
Space group	I41/amdZ
a	0.373 nm
c	0.296 nm

Table 2.1 shows the lattice parameters of anatase TiO₂ crystal structure. The bandgap of TiO₂ is 3.2 eV for anatase and 3.0 eV for rutile. TiO₂ will be excited when the incident photon energy is greater than the bandgap energy of TiO₂. Figure 2.4 shows the charge separation process and formation of ROSs in the TiO₂ photocatalytic system. The whole processes can be explained by the following equations (2.1-2.11) (Chong et al., 2010):

During the whole photocatalytic processes, the organic pollutants are degraded by TiO_2 to the intermediates firstly, and mineralized to innocuous carbon dioxide and water finally. Hence, the equations 2.1-2.11 can be summarized as equation 2.12:

Figure 2.4 The charge separation and formation of ROSs in the TiO_2 system (Chong et al., 2010).

Compared with rutile TiO_2 , anatase TiO_2 are preferred in photocatalytic wastewater purification fields due to its higher photocatalytic activity (Ding et al., 2000). Hence, in current work, anatase TiO_2 was synthesized for further applications.

2.3.2 Nanostructures of TiO_2

It has been reported that the photocatalytic activity of TiO₂ is strongly depended on its nanostructure and morphology (Ng et al., 2011; Zeng, 2011). In the last decade, TiO₂ with various nanostructures had been synthesized, including tubes (Yuan and Su, 2004; Roy et al., 2011; Yuan et al., 2013), wires (Yuan and Su, 2004; Feng et al., 2008; Zhang et al., 2008), fibers (Yang et al., 2009; Cavaliere et al., 2011; Zhang et al., 2013), cubes (Lai et al., 2012), spheres (Tian et al., 2011; Zhuang et al., 2012; Gao and Sun, 2014) and etc. (Ng et al., 2011; Xu et al., 2012; Zhu et al., 2012).

2.3.2.1 1D TiO₂ nanotubes

1D TiO₂ nanotubes have been widely synthesized by electrochemical anodization method and hydrothermal method (Yuan and Su, 2004; Bavykin et al., 2006; Mor et al., 2006; He et al., 2011; Jia et al., 2011; Roy et al., 2011; Xu et al., 2011). TiO₂ nanotubes show great potential for use in photocatalysis, electronic devices, and solar cells, because TiO₂ nanotubes provide the direct channel for electrons to transport and separate (Huang et al., 1997; Mor et al., 2006). Mor et al. (2006) reviewed the fabrication processes, properties and formation mechanism of TiO₂ nanotubes prepared by anodization method, and the setup of anodization was schematically shown in Figure 2.5. In this review article, two important features were discussed. Firstly, the fluoride-based electrolytes played significant roles in the anodization process because the etching process happened gradually in the presence of fluoride. Secondly, the structure properties and morphology of these TiO₂ nanotube arrays, including length, wall thickness, pore size and shape, were well controlled by adjusting the anodization parameters. Schmuki's group reported that highly ordered arrays of TiO₂ nanotubes were synthesized *via* a simple electrochemical anodization approach, as shown in Figure 2.6, and concluded that these 1D TiO₂ nanotubes possessed excellent photocatalytic activity due to its specific properties, including high surface area, high electron mobility and quantum confinement effects (Albu et al., 2007; Roy et al., 2011). Our group also constructed self-organized free-standing TiO₂ nanotube arrays through the typical anodization method, which exhibited high

efficiency in disinfection of drinking water (Ng et al., 2010).

Figure 2.5 Scheme of anodization setup (Mor et al., 2006).

Figure 2.6 SEM images of 1D TiO₂ nanotube arrays synthesized by anodization (Albu et al., 2007).

Bavykin et al. (2004) investigated the influence of hydrothermal parameters, such as hydrothermal temperature and reaction time, on the morphology of TiO₂ nanotubes in an alkali hydrothermal method. This report concluded: (1) the diameter of TiO₂ nanotubes was increased by increasing the hydrothermal temperature; (2) the surface area was decreased and the diameter was increased by increasing the molar ratio of

TiO₂: NaOH; and (3) the inner diameters were ranged from 2 nm to 10 nm. Lee et al. (2014) prepared TiO₂ nanotubes *via* the hydrothermal approach by using the precursors of commercial P25 powder and NaOH solution. In addition, TiO₂ nanotubes synthesized at different hydrothermal temperature exhibited different photocatalytic activity towards degradation of methylene blue (MB). Furthermore, TiO₂ nanotubes synthesized at 180 °C achieved the highest photodegradation efficiency due to the well-developed mesoporous structure. Xu et al. (2011) synthesized mesoporous TiO₂ nanotubes by the typical hydrothermal method, as shown in Figure 2.7, and the TiO₂ nanotubes acquired much better adsorption and photodegradation activities towards acid orange 7 (AO7), compared with commercial P25. Prado and co-workers prepared TiO₂ nanotubes by the hydrothermal approach and the effect of pH on the photocatalytic activity was investigated (Costa and Prado, 2009). TiO₂ nanotubes remained high removal efficiency of indigo carmine dye even after 10 cycles, and the highest photodegradation efficiency was achieved at pH 2.

Figure 2.7 TEM image of 1D TiO₂ nanotubes synthesized by hydrothermal method (Xu et al., 2011).

2.3.2.2 1D TiO₂ nanowires

1D TiO₂ nanowires are usually prepared by the hydrothermal method (Chen et al., 2012; Yu et al., 2013). Two kinds of TiO₂ nanowires have been synthesized, including free standing TiO₂ nanowires and TiO₂ nanowire arrays grown on the substrates.

These TiO₂ nanowires have been widely applied in solar cells and photodegradation of water pollutants. Liu et al. (2011) synthesized a cross-linked TiO₂ nanowire anode, which was comprised of anatase and rutile phase, for efficient water photolysis. This photoanode acquired high energy conversion efficiency, which could be attributed to the large surface area and long optical path length. Grimes and co-worker prepared TiO₂ nanowire arrays which were assembled by pure single rutile phase on transparent conducting oxide (TCO) glass *via* a low temperature hydrothermal reaction, as shown in Figure 2.8 (Feng et al., 2008). The TiO₂ nanowire arrays were grown vertically on TCO glass and a power conversion efficiency of 5.02% was obtained by using these TiO₂ nanowire arrays as photoanodes in a dye sensitized solar cells (DSSC). Kuang's group reported the successful preparation of hierarchical anatase TiO₂ nanowire arrays which contained long TiO₂ nanowires as trunks and short TiO₂ nanorods as branches on Ti-foil substrate through a two-step hydrothermal method (Liao et al., 2012). A high power conversion efficiency of 4.51% was achieved, which was owed to the excellent light reflection and scattering capacity, and superior dye adsorption ability. In addition, a flexible DSSC was assembled by adopting hierarchical TiO₂ nanowire arrays as photoanodes and PEDOT/ITO-PET as counter electrodes. Xiao et al. (2010) synthesized TiO₂ nanowire arrays with the mixed phases of anatase and rutile through calcination of TiO₂ nanotubes. The TiO₂ nanowire arrays exhibited higher photodegradation efficiency of methyl orange dye, compared with commercial P25 powder. Zhang et al. (2009) prepared two kinds of TiO₂ nanowires with different diameters (10 nm and 20-100 nm) by using different precursors. It was found that TiO₂ nanowires with diameter of 10 nm possessed the highest photodegradation efficiency towards degradation of HA. In addition, TiO₂ nanowires were easily recycled by membrane filtration after photodegradation processes compared with P25. It should be noted that the separation of the photocatalysts is a big challenge because the photocatalysts can be secondary pollutants. Su and co-workers prepared 1D TiO₂ nanotubes, TiO₂ nanowires and TiO₂ nanofibers *via* a facile hydrothermal method (Yuan and Su, 2004). They reported that the nanostructures of 1D TiO₂ materials could be controlled by adjusting the

hydrothermal temperature, reaction time, the source of alkaline solution, and the concentration of alkaline solution. Song et al. (2010) investigated the influence of morphology of 1D TiO₂ materials (nanotube, nanorod and nanowire) on the catalytic ozonation of phenol. They concluded that the higher rutile phase ratio and larger surface area contributed to the higher catalytic ozonation efficiency of phenol, while the morphology had limited influence.

Figure 2.8 SEM images of vertically aligned TiO₂ nanowire arrays on TCO glass (Feng et al., 2008).

2.3.2.3 3D TiO₂ spheres

Recently, 3D TiO₂ spheres have gained intensive research interests due to their outstanding properties, including efficient light absorption, large surface area and easy separation (Chen et al., 2009; Guo et al., 2009; Zhu et al., 2011; Pan et al., 2012; Pang et al., 2012; Xiang et al., 2012; Rui et al., 2013). To date, 3D TiO₂ spheres have been synthesized through various methodologies, including solvothermal and hydrothermal reaction (Liao et al., 2011; Sun et al., 2011; Gao and Sun, 2013; Gao and Sun, 2014), electrochemical process (Tang et al., 2012) and template assisted calcination method (Bai et al., 2012). Cai et al. (2013) reported the fabrication of hierarchical TiO₂ hollow microspheres by a rapid hydrothermal reaction. It was reported that these TiO₂ microspheres were constructed by TiO₂ hollow nanoparticles and the as-synthesized

TiO₂ microspheres exhibited high photodegradation rate of brilliant red X-3B dye. They attributed the excellent photodegradation activity to the lower recombination rates of charge carriers and higher light utilization rate, which were resulted from the special structural features.

Polshettiwar and co-workers synthesized hierarchical anatase TiO₂ with various nanostructures *via* a microwave irradiation reaction (Rahal et al., 2012). They concluded that both of the surface area and the nanostructures of TiO₂ have significant influences on the photocatalytic activity. Fu's group synthesized 3D hierarchical flower-like TiO₂ nanostructures by a facile solvothermal approach (Tian et al., 2011). They reported that these 3D TiO₂ nanostructures exhibited enhanced photodegradation activity of phenol due to their high light harvesting capacity, porous structure and more reactive sites. Liao et al. (2011) fabricated the hierarchical TiO₂ spheres which were assembled by anatase nanorods and nanoparticles through a simple solvothermal reaction. A high power conversion efficiency of 10.34% was achieved by applying these TiO₂ spheres in the DSSC, which were attributed to the high light scattering capacity, large surface area and fast electron transport rate. Tang and co-workers prepared the rutile TiO₂ microspheres which were constructed by 100% exposed reactive (111) facets by a simple hydrothermal method (Sun et al., 2011). They reported that these TiO₂ microspheres with reactive facets exhibited high photocatalytic antibacterial activity to *Staphylococcus aureus* because of efficient charge separation. Sun et al. (2011) synthesized 3D dendritic TiO₂ nanostructures with controlled shape and size through a hydrothermal reaction. It was reported that the primary units of these 3D dendritic TiO₂ nanostructures were adjusted to be nanorods, nanowires and nanoribbons by controlling the surfactant and hydrolysis rate, as shown in Figure 2.9. Zhao and co-workers fabricated mesoporous F-TiO₂ spheres by a step-wise solvothermal method (Pan et al., 2011). The mesoporous F-TiO₂ spheres exhibited high photodegradation efficiency due to the large surface area, mesoporous structure and surface fluorination. Ming et al. (2011) synthesized nanoporous TiO₂ spheres by hydrolysis of tetra-n-butyl titanate (TBT) in ethanol with the help of water

vapors. The results indicated that the nanoporous TiO_2 spheres had narrow pore size distribution and showed promising photodegradation of rhodamine B (RhB) and benzene under visible light irradiation.

Our group reported the fabrication of the large-scale production of TiO_2 nanorod spheres by a template-assisted calcination method (Bai et al., 2013). These hierarchical TiO_2 nanorods spheres exhibited excellent photodegradation efficiency of RhB and AO7 dyes, as well as high antibacterial activity towards *E. coli* due to their unique nanostructure.

Figure 2.9 SEM images of 3D TiO_2 spheres (Sun et al., 2011).

2.4 Graphene oxide (GO)

2.4.1 Introduction of graphene and GO

Graphene, a single layer carbon sheet with perfect sp^2 -hybridized two dimensional structure (Figure 2.10), has attracted tremendous research attention since it is first discovered by Novoselov et al. (2004), due to its unique properties, including large specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), good optical transparency ($\sim 97.7\%$), excellent thermal conductivity ($3000\text{-}5000 \text{ W m}^{-1} \text{ K}^{-1}$) and high Young's modulus ($\sim 1 \text{ TPa}$)

(Wang et al., 2007; Allen et al., 2009; Chen et al., 2010; Huang et al., 2012). Graphene is a fundamental building block for other carbon materials, including C_{60} , carbon nanotubes (CNTs) and graphite (Geim and Novoselov, 2007). In addition, many approaches have been developed to synthesize graphene, such as chemical vapor deposition (CVD), epitaxial growth of graphene on silicon carbide, arc discharge method, substrate-free gas-phase synthesis of graphene, chemical reduction of GO, electrochemical synthesis of graphene, unzipping CNTs for graphene nanoribbon, and so on (Guo and Dong, 2011). Furthermore, graphene based films with desirable thickness and compositions have been applied in various research fields, including fuel cells, supercapacitor, hydrogen storage, lithium ion (Li-ion) battery, solar cells, electrochemical sensors, fluorescent sensors, and etc. (Guo and Dong, 2011). Pure graphene is rarely used in water and wastewater purification fields due to its hydrophobic property.

Figure 2.10 Schematic illustration of the structures of graphene, C_{60} , CNT and graphite (Geim and Novoselov, 2007).

GO is the one of the most important derivatives of graphene, which produced through chemical oxidation of natural graphite (Huang et al., 2012; Feng et al., 2013; Xu et al.,

2013). The most widely adopted method for the production of GO is Hummers' method, which is a strong oxidation process by mixing flake graphite, potassium permanganate (KMnO_4) and concentrated sulfuric acid (H_2SO_4) (Dreyer et al., 2010; Luo et al., 2010). A large number of oxygen containing functional groups present in GO structure (Figure 2.11), including hydroxyl and carboxyl groups, which make GO very hydrophilic and excellent supporter of inorganic nanoparticles (Dikin et al., 2007; Park and Ruoff, 2009).

Figure 2.11 Schematic illustration of the structure of GO (Park and Ruoff, 2009).

2.4.2 Graphene and GO (G/GO) based composites

Until now, a great amount of G/GO based materials have been synthesized, including G/GO-metal composites, G/GO-metal oxide composites, G/GO-polymer composites and etc. (Stankovich et al., 2006; Bai et al., 2011; Huang et al., 2012; Zhu et al., 2012). The synthetic methods of G/GO based composites can be classified as ex-situ hybridization and in-situ crystallization. In addition, in-situ crystallization method includes chemical reduction, electroless deposition, sol-gel, hydrothermal, electrochemical deposition, thermal evaporation, and so on (Huang et al., 2012).

G/GO sheets have been combined with various metals, such as Ag, Au, Pt, Pd, Ni, Cu and etc., to further enhance the electrochemical and analytical properties of pure metals, as shown in Figure 2.12 (Liu et al., 2010; Chen et al., 2011; Guo and Dong, 2011; Zhang et al., 2011). For example, Liu and co-workers combined graphene sheets with Pt nanoparticles to prepared graphene-Pt composites (Kou et al., 2009). The composites showed enhanced oxygen reduction activity due to the higher electrochemical surface area, compared with the commercial catalyst. Graphene-gold

composites were synthesized by deposition of gold nanoparticles on RGO sheets through in-situ chemical reduction of chloroauric acid (Xiong et al., 2010). In addition, graphene-gold composites exhibited excellent photodegradation ability of RhB dye under visible light due to the unique properties, including high adsorption capacity for organic dyes, slow charge recombination rate and strong interaction with dye chromophores.

Figure 2.12 TEM images of G/GO-metal composites (Liu et al., 2010).

G/GO-metal oxide composites are significant categories of G/GO based composites due to the special properties of metal oxides. Recently, metal oxides including TiO_2 , ZnO , SnO_2 , MnO_2 , Fe_3O_4 , NiO , SiO_2 and etc., have been successfully grown on G/GO sheets (Wang et al., 2010; Zhu et al., 2010; Li and Cao, 2011; Agegnehu et al., 2012; Huang et al., 2012; Wang et al., 2012; Zhang et al., 2012). For instance, Zhu et al. (2011) prepared transition metal oxide (Fe_2O_3 and CoO) nanoparticles/reduced GO (RGO) composites by an environmental friendly method. The results demonstrated that $\text{Fe}_2\text{O}_3/\text{RGO}$ and CoO/RGO exhibited high specific capacities and stable cyclabilities, which attained 881 and 600 mA h g^{-1} at a 0.3 C rate, respectively. The excellent performances of these Li-ion battery anodes can be attributed to the outstanding electrical conductivity and large surface area of RGO sheets, which keep

the good electrical contact with nanoparticles and the current collectors. NiO/graphene composites were synthesized by Yang et al. (2011) as a p-type photoelectrode in DSSC. Compared with pristine NiO film, the short circuit photocurrent and open circuit photovoltage were increased by using NiO/graphene composites due to efficient charge separation. Cao and co-workers reported the preparation of Cu₂O@RGO composites *via* a facile solution-phase approach (Li et al., 2011). The results indicated that Cu₂O@RGO composites exhibited high adsorption ability of RhB and MB dyes. In addition, these composites possessed excellent performances in supercapacitors. ZnO/graphene composites were synthesized by coating ZnO nanoparticles on GO sheets, followed by reduction of GO to graphene, as shown in Figure 2.13 (Xu et al., 2011). ZnO/graphene composites showed high photodegradation efficiency of MB dye with an apparent reaction rate constant k of 0.098 min⁻¹. The outstanding photocatalytic activity of ZnO/graphene composites was attributed to the retarded electron-hole recombination rate and high transfer rate of photo-generated electrons because of the interaction between ZnO nanoparticles and graphene sheets. Despite combining G/GO sheets with metal oxide nanoparticles, G/GO sheets were also good supporters for metal oxide with other morphology. RGO-hierarchical ZnO hollow sphere composites were prepared by a facile ultrasonic reaction (Luo et al., 2012). The photocurrent and photodegradation ability of RGO-ZnO composites were remarkably enhanced, which could be attributed to reduced electron-hole recombination rate because of the strong interaction between RGO sheets and ZnO spheres.

Figure 2.13 TEM images of ZnO/graphene composites (Xu et al., 2011).

In another aspect, various G/GO-polymer composites were prepared, including graphene-filled polymer composites, layered graphene-polymer films and layer graphene-polymer films, which were classified according to the different interaction between polymers and graphene sheets (Vickery et al., 2009; Huang et al., 2012). For example, GO sheets were deposited on polyelectrolyte multilayers (PEMs) layer-by-layer (LBL) by Langmuir-Blodgett method, as shown in Figure 2.14 (Kulkarni et al., 2010). The results showed that the mechanical properties of the GO-polyelectrolyte membranes were increased greatly. In addition, the elastic modulus of 8 vol% GO sheets incorporated composite membrane was about 20 GPa, which was more than ten times higher than that of pure LBL membrane (1.5 GPa).

Figure 2.14 Schematic illustration of fabrication of GO-polyelectrolyte membranes (Kulkarni et al., 2010).

2.5 G/GO-TiO₂ composites

2.5.1 The fabrication methods and applications of G/GO-TiO₂ composites

Among a variety of G/GO-metal oxide composites, G/GO-TiO₂ composites have attracted the most widely research attentions. As discussed in the previous section, the performances of pure TiO₂ were significantly restricted by its rapid recombination of electron-hole pairs. Coupling TiO₂ with G/GO sheets can greatly enhance its charge

separation efficiency due to the outstanding electron mobility and conductivity of G/GO sheets.

G/GO-TiO₂ composites have been synthesized by in-situ direct growth method, solution mixing method, hydrothermal method, solvothermal method and etc. (Xiang et al., 2012). In addition, G/GO-TiO₂ composites have been applied in the fields of solar cells, Li-batteries, supercapacitors, hydrogen production, photocatalytic wastewater purification and so on (Zhao et al., 2012). Zhu et al. (2011) synthesized graphene-TiO₂ composites by directly mixing P25 nanoparticles with graphene sheets and applied these graphene-TiO₂ composites as the photoanodes for CdS quantum dot-sensitized solar cells (QDSSCs). The power conversion efficiency of graphene-TiO₂ composites photoanodes was 56% higher than pure TiO₂ photoanodes, which could be attributed to the reduced charge recombination rate, enhanced electron transfer rate, and the increased CdS adsorption. TiO₂ nanosheets/graphene composites were prepared by mixing hydrothermally synthesized TiO₂ nanosheets with GO sheets (Fan et al., 2012). The results indicated that TiO₂ nanosheets/graphene composites acquired high DSSC efficiency because graphene sheets improved the light harvesting ability, and reduced the electron-hole recombination rate and interfacial resistance.

Wang et al. (2009) reported in-situ self-assembly of TiO₂ nanoparticles on graphene sheets which were stabilized by anionic sulfate surfactants. They concluded that TiO₂-graphene hybrids were good candidates for Li-ion battery, the specific capacity of which was twice higher than the battery fabricated by pure TiO₂, because the graphene enhanced the conductivity of the electrode. Ultrathin TiO₂ nanosheets with exposed (001) facets were successfully grown on graphene sheets by Lou and co-workers (Ding et al., 2011). The results showed that the synergetic effects of (001) high energy facets of TiO₂ and the excellent conductivity of graphene contributed to the high and fast lithium storage activity.

Xiang et al. (2011) prepared graphene/TiO₂ composites through a microwave

hydrothermal method and the hydrogen production activity was investigated thoroughly. Figure 2.15 shows the SEM and TEM images of graphene/TiO₂ composites. It was reported the mass ratio of graphene/TiO₂ had a great influence on the hydrogen production activity and the optimal amount of graphene was about 1 wt%. The hydrogen production rate was decreased by further increasing graphene content. The highest hydrogen production rate of graphene/TiO₂ composites (1 wt% graphene) was attributed to the efficient charge separation, which was schematically illustrated in Figure 2.16.

Figure 2.15 SEM and TEM images of graphene/TiO₂ composites (Xiang et al., 2011).

Figure 2.16 Schematic illustration of charge separation process in the photocatalytic hydrogen production system of graphene/TiO₂ composites (Xiang et al., 2011).

In the following work, they further investigated the synergetic effects of MoS₂ and graphene sheets on the hydrogen production activity of TiO₂ (Xiang et al., 2012). High hydrogen production rate (165.3 $\mu\text{mol h}^{-1}$) and apparent quantum efficiency (9.7%) were achieved because of the positive effects between MoS₂ and graphene, which acted as sources of active adsorption sites and electron collectors. A recent research indicated that TiO₂/graphene composites had multifunctional activities (Li et al., 2011). Li and co-workers used a template-free self-assembly method to prepare TiO₂/graphene composites, in which mesoporous TiO₂ nanospheres were directly grown on graphene sheets (Li et al., 2011). The results demonstrated that TiO₂ nanospheres/graphene composites possessed excellent Li-ion battery performance and photocatalytic activities, including photodegradation of RhB dye and photocatalytic hydrogen production. Liang et al. (2011) demonstrated that graphene sheets with fewer defects were good candidates for graphene-TiO₂ composites. The less defective graphene sheets were prepared by solvent-exfoliation. The results indicated that the as-synthesized graphene-TiO₂ composites exhibited higher efficiency in reduction of CO₂ due to the prominent electrical mobility of less defective graphene. Zou's group adopted the LBL approach to synthesize graphene-TiO₂ hollow spheres which contained modified titania nanosheets and graphene sheets (Tu et al., 2012). In addition, the polymer beads were used as sacrificial templates, which were removed in the subsequent microwave irradiation process. These composites showed high photocatalytic efficiency for CO₂ conversion, which was more than 9 times higher than that of P25 powders.

2.5.2 G/GO-TiO₂ composites for photocatalytic degradation and disinfection

G/GO-TiO₂ composites have been widely used in wastewater purification fields, including photocatalytic degradation and disinfection. The first report of graphene-TiO₂ composites for photodegradation was published by Li and co-workers (Zhang et al., 2010). They reported that P25-graphene composites were synthesized

by hydrothermally treating the mixture of GO sheets and P25 nanoparticles. In addition, P25-graphene composites exhibited better photodegradation activity towards MB dye, compared with P25 powder and P25-CNTs composites, which was ascribed to the efficient charge separation, enhanced light absorption and high adsorption capacity of MB dye. TiO_2 with exposed (001) facets were deposited on graphene sheets to prepare graphene/ TiO_2 composites in a simple solvothermal reaction (Jiang et al., 2011). The photodegradation activity and charge transfer mechanism were investigated in detail. The results showed that graphene/ TiO_2 composites degraded 85.2% of MB dye within 60 min, which is significantly higher than that of P25 (40.8%) and TiO_2 (65.5%), because the electron-hole recombination rates were reduced by the efficient electron transfer from TiO_2 to graphene. Wang et al. (2012) reported the fabrication of hierarchical macro/mesoporous TiO_2 -graphene composites by hydrothermally treating the GO sheets and TBT in the solution of water and ethanol. The as-synthesized TiO_2 -graphene composites showed high photocatalytic efficiency for photodegradation of acetone in air. TiO_2 nanorod-graphene composites were prepared by deposition of TiO_2 nanorods on graphene sheets *via* a non-hydrolytic sol-gel method (Lee et al., 2012). Figure 2.17 shows the TEM images of TiO_2 nanorod-graphene composites. TiO_2 nanorods are well dispersed on graphene sheets without aggregation, as shown in Figure 2.17. Compared with pure TiO_2 nanorods and P25, TiO_2 nanorod-graphene composites exhibited higher photocatalytic efficiency towards degradation of MB dye under visible light irradiation because of the larger surface area and improved charge separation. Liu et al. (2011) investigated the role of graphene in graphene-semiconductor photocatalysts by preparation of RGO- TiO_2 composites, in which TiO_2 nanoparticles were wrapped by RGO sheets. During the photodegradation process, RGO sheets adsorbed organic dyes and captured photo-generated electrons from TiO_2 , as schematically illustrated in Figure 2.18. Hence, the enhanced adsorption of dyes and efficient electron transfer contributed to the prominent photodegradation activity.

Figure 2.17 TEM images of TiO_2 nanorod-graphene composites (Lee et al., 2012).

Figure 2.18 Schematic illustration of RGO sheets as capturers of organic dyes and photo-generated electrons (Liu et al., 2011).

The photocatalytic disinfection activity of GO-TiO_2 composites was firstly investigated by Akhavan and co-workers (Akhavan and Ghaderi, 2009). GO-TiO_2 composites were prepared by spreading GO solution on the TiO_2 thin films, followed

by calcination (Akhavan and Ghaderi, 2009). The results indicated that GO sheets were gradually reduced when GO-TiO₂ composites were put under UV light. In addition, GO-TiO₂ composites after 4 h of UV light irradiation obtained the highest photocatalytic disinfection efficiency, which was about 7.5 times higher than that of pure TiO₂ thin film. Cao et al. (2013) used a direct redox reaction method to synthesize TiO₂/graphene composites which were composed of ultrafine TiO₂ nanoparticles and graphene sheets. The antibacterial activity against *E. coli* cells of TiO₂/graphene photocatalysts was higher than that of pure TiO₂ under visible light irradiation due to the enhanced light absorption. Liu and co-workers reported gram-scale production of GO-TiO₂ nanorod composites and demonstrated GO-TiO₂ composites possessed the enhanced antibacterial activity (Liu et al., 2011). This work proposed a promising idea for mass production of GO based composites at a low cost, which accelerated their commercialization. Very recently, Liu et al. (2013) delicately synthesized GO-TiO₂-Ag composites to investigate the synergetic effects of GO sheets and Ag nanoparticles on the photocatalytic disinfection activity of TiO₂ nanorods. GO-TiO₂-Ag composites exhibited high antibacterial activity under both dark condition and solar irradiation. The intrinsic disinfection activity was attributed to the presence of Ag nanoparticles, while the excellent photocatalytic disinfection activity under solar irradiation was ascribed to the efficient charge separation between GO sheets and Ag nanoparticles.

2.6 Membrane technology

2.6.1 Introduction of membrane technology

In recent years, there is a trend in the use of membrane technology for water treatment due to no chemical additives, regeneration of used media or thermal inputs (Pendergast and Hoek, 2011). Currently, pressure-driven membranes have attracted considerable research interests and been widely applied in industries. The structure of membranes can be classified according to their pore size or intended application (Table 1) (Mathias, 2006). Typically, microfiltration (MF) is adopted to remove suspended solids, bacteria and protozoa; ultrafiltration (UF) is available for virus and

colloid removal; nanofiltration (NF) is commonly used for hardness, heavy metals and NOMs removal; and reverse osmosis (RO) is commercialized for desalination and ultrapure water production (Pendergast and Hoek, 2011). Generally, the membranes can be classified to polymeric (organic) membranes and ceramic (inorganic) membranes according to the different raw materials.

Table 2.2 Membrane characterization by pore size and target species (Pendergast and Hoek, 2011)

Pore type (size range/nm)	Membrane type (pore size/nm)	Species	Dimensions /nm
Macropores (>50)	Microfiltration (50-500)	Yeasts & fungi	1000-10000
		Bacteria	300-10000
		Oil emulsions	100-10000
Mesopores (2-50)	Ultrafiltration (2-50)	Colloidal solids	100-1000
		Viruses	30-300
		Proteins/polysaccharides	3-10
		Humics/nucleic acids	<3
Micropores (0.2-2)	Nanofiltration (≤ 2)	Common antibiotics	0.6-1.2
	Reverse osmosis (0.3-0.6)	Organic antibiotics	0.3-0.8
	Forward osmosis (0.3-0.6)	Inorganic ions	0.2-0.4
		Water	0.2

2.6.2 Polymeric membranes

Polymeric membranes have been commercialized for a long time, and widely applied in industrial and municipal wastewater treatment. Until now, various polymers have been used to fabricate polymeric membranes, including cellulose acetate (CA), polyacrylonitrile (PAN), polyethersulfone (PES), polypropylene (PP), polyvinylidene fluoride (PVDF), polysulfone (PSF) and so on (Pendergast and Hoek, 2011). Some techniques are adopted to fabricate polymeric membranes, such as phase inversion, interfacial polymerization, track-etching and stretching (Lalia et al., 2013). According

to the different structures, polymeric membranes can be classified to integrally skinned membranes and thin film composite membranes. The advantages of polymeric membranes are the relatively low cost and facile fabrication process. The drawbacks of polymeric membranes include low flux, limited temperature range, low chlorine tolerance and short lifetime.

Although the current polymeric membranes meet the requirements of many applications, the performance of polymeric membranes can be further improved by manipulating the morphology and structures of membranes. It was reported that adding the additives was an effective method to adjust the membrane properties. The additives include inorganic materials such as LiCl, and organic materials such as polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) (Lalia et al., 2013). For example, Fontananova and co-workers used PVDF to fabricate porous asymmetric membranes through the traditional phase inversion method (Fontananova et al., 2006). They found that adding PVP increased membrane permeability. In addition, the mechanical stability of PVDF membranes was enhanced by adding LiCl.

Recently, fabrication of nanofibrous membranes by electrospinning approach has show great potential because of the scaffold structure of the nanofibers, which reduces the membrane resistance and increases the water flux (Kaur et al., 2008). In addition, the average pore size, porosity, and surface wettability of the membranes can be easily controlled by adjusting the concentration of electrospinning solution, applied electric potential and flow rate of the solution (Lalia et al., 2013). For instance, Kaur et al. (2012) fabricated electrospun nanofibrous membrane to investigate the influence of electrospun fiber size on water flux and separation efficiency. They concluded that the pore size and water flux were decreased with the decreasing of fiber size, while the separation efficiency was increased.

However, membrane fouling poses a major obstacle that restricts the further development of polymeric membrane. Membrane fouling is caused by the

accumulation of organic or inorganic solutes on the membrane surface or within the pores of the membrane (Matin et al., 2011). Fouling contributes to flux decline and worsens the quality of permeate, ultimately resulting in a huge amount of energy being required for the extra operating pressure (Mulder, 1991; Bai et al., 2010). Various constituents can lead to fouling, including soluble inorganic compounds, colloidal and suspended solids, dissolved NOMs and microorganisms. Although colloidal and suspended solids can be nearly removed by pretreatment, such as coagulation/flocculation and media filtration, thorough removal of NOMs and bacteria remains a challenge in membrane treatment process. Membrane fouling requires intensive chemical cleaning, which shortens membrane life. In addition, the membrane performance cannot be totally recovered after cleaning. Chemical cleaning also cuts down profits of water producing company by imposing a large economic burden on membrane system operation. Therefore, there is an urgent need to develop a novel membrane which can solve the above mentioned problems.

2.6.3 Ceramic membranes

Recently, ceramic membranes have attracted intensive research interests due to their excellent properties as compared to polymeric membranes: (1) higher chemical stability contributing to longer membrane lifetime, (2) higher mechanical stability allowing higher operating pressure, (3) higher thermal stability resulting higher working temperature, and (4) higher hydrophilicity leading to lower fouling problems (Van Der Bruggen et al., 2003; Choi et al., 2006; Oh et al., 2007).

Typically, ceramic membranes include a dense upper layer on the surface and porous support layer on the bottom, which form the asymmetric structures. Until now, many kinds of inorganic materials are found to be suitable for assembling ceramic membranes, including alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), titania (TiO_2), sintered metals, and etc. (Mansoor, 2010; Pendergast and Hoek, 2011). The fabrication of ceramic membranes usually includes two processes: sol-gel and high temperature calcination. Hofs et al. (2011) compared the permeability and fouling

problems of four ceramic membranes (Al_2O_3 , ZrO_2 , TiO_2 , SiC) with the PES/PVP polymeric membrane. The results indicated that the trans-membrane pressure (TMP) of the PES/PVP membrane increased more obviously due to the membrane fouling compared with the ceramic membranes. In addition, the ceramic membranes exhibited high removal rate of non purgeable organic carbon. Currently, there are two obstacles which restrict the wide application of ceramic membranes. Firstly, the commercial ceramic membranes are MF and UF membranes, while NF and RO ceramic membranes are not available. In practical view, it is more meaningful to fabricate NF and RO ceramic membranes due to the strong mechanical stability of ceramic membranes which can withstand high pressure. Secondly, the membrane fouling caused by organic pollutants still affects the permeate flux and water quality.

With the development of nanotechnology, nanostructured ceramic membranes have been fabricated to overcome these drawbacks. It was reported that coating zeolite on the surface of ceramic membrane was an effective approach to fabricate RO ceramic membrane. MFI-type zeolite membranes were fabricated by adjusting the Si/Al ratios *via* the method of seeding and secondary growth (Li et al., 2007). It was demonstrated that the water flux and salt rejection rate increased significantly with the increment of aluminum content when the membrane was used to separate 0.01 M NaCl solution. Liu et al. (2013) fabricated two kinds of RO membranes using two different zeolite including hydrophilic FAU and hydrophobic MFI for seawater desalination. They reported that both of these RO membranes had high salt rejection rates (nearly 100%). In addition, the permeability of zeolite membranes was about 100 times higher than that of commercial RO membranes when the thickness of fabricated zeolite membrane was smaller than 3.5 nm. On the other hand, photocatalytic materials (such as TiO_2 , ZnO and etc.) assembled membranes have been used to solve the problems of membrane fouling because this kind membrane can degrade organic water pollutants efficiently under light. Among all of them, TiO_2 based membranes have received countless attentions since the commercialization of TiO_2 powders in the early twentieth century.

2.6.4 TiO₂ based membranes

There are two categories of TiO₂ based membranes. The first kind is using TiO₂ nanoparticles to modify the surface of commercial polymeric membranes. Another category is TiO₂ based ceramic membranes.

Kim et al. (2003) combined TiO₂ nanoparticles with a commercial RO membrane and demonstrated that modified membrane showed enhanced sterilization effects under UV light. Moreover, the water flux of hybrid membrane decreased much slower than bare membrane under UV irradiation. Damodar et al. (2009) synthesized TiO₂ entrapped PVDF membranes by adding different amount of TiO₂ nanoparticles. The results showed that TiO₂ nanoparticles greatly influenced the hydrophilicity and pore size of the modified membranes. In addition, the composite PVDF/TiO₂ membrane with 4 wt% of TiO₂ nanoparticles exhibited the highest antibacterial activity. Furthermore, membrane flux and TMP could be recovered to its initial value by UV irradiation when membrane bio-fouling happened. A self-cleaning membrane by coating RO membrane surface with TiO₂ nanoparticles was fabricated by Madaeni et al. (2007). They concluded that the flux of coated membrane had been improved significantly under UV irradiation.

A great amount of studies have been carried out to fabricate TiO₂ based ceramic membranes and test their performance. Choi et al. (2007) prepared nanostructured crystalline TiO₂ thin films and TiO₂/Al₂O₃ composite membranes through a simple sol-gel route and demonstrated that the photocatalytic TiO₂ membrane displayed excellent performances, including high water permeability, sharp polyethylene glycol retention, high efficient in inactivation of *E. coli* and less fouling tendency. TiO₂ nanotubular membrane was fabricated by Albu et al. (2007) through a facile electrochemical method. This membrane allowed effective direct, size-selective and flow-through photocatalytic reactions. Ciston et al. (2009) coated a reactive TiO₂ membrane on the surface of a ceramic ultrafiltration membrane (ZrO₂) and concluded that photo-reactive coating of TiO₂ membrane was highly efficient in controlling the

bio-fouling under UV irradiation.

Meanwhile, our group has already done a large number of studies about TiO_2 membrane in the past few years. Liquid-phase deposition method was adopted to graft TiO_2 nanotubes in alumina membrane to prepare TiO_2 nanotube membranes, and the procedures were schematically shown in Figure 2.19 (Zhang et al., 2008). The results of wastewater purification indicated that the membrane fouling was significantly reduced under UV irradiation when the TiO_2 nanotube membrane was used to purify HA solution. Zhang et al. (2008) fabricated a novel TiO_2 nanowire free standing membrane by hydrothermal synthesis-filtration method, as shown in Figure 2.20. This membrane was composed of nanowires, which typically were of 20-100 nm in diameter. In addition, the pore size of this membrane was around 0.05 μm , which could be attributed to MF membrane. Furthermore, this TiO_2 nanowire membrane removed nearly 100% HA through a concurrent filtration and photocatalytic oxidation without fouling problems under UV light. In a following work, Zhang et al. (2009) fabricated a TiO_2 nanowire UF membrane with a layered hierarchical structure. This novel membrane was consisted of two layers—selective layer (TiO_2 nanowire of 10 nm in diameter) and supporting layer (TiO_2 nanowire of 20-100nm in diameter), as shown in Figure 2.21. In addition, the as-fabricated UF membrane offered three major advantages, including high permeability and selectivity, concurrent photocatalytic oxidation and separation, and antifouling as well as antibacterial capacity. Liu et al. (2012) prepared Ag/ TiO_2 nanofiber membrane through deposition of Ag nanoparticles on electrospun TiO_2 nanofibers and concluded that this membrane killed nearly 99.9% bacteria and decomposed 80.0% dye under solar irradiation during 30 min.

However, several problems related to TiO_2 membranes still remain as obstacles in the membrane field. Firstly, the efficiency of pure TiO_2 membranes is not high due to the intrinsic rapid recombination of charge carriers. In addition, there are no cross-linkers within pure TiO_2 membrane, which results in the low mechanical strength.

Figure 2.19 Schematic illustration of fabrication processes of TiO₂ nanotube membrane (Zhang et al., 2008).

Figure 2.20 Free standing TiO₂ nanowire MF membrane (Zhang et al., 2008).

Figure 2.21 TiO₂ nanowire UF membrane with TiO₂ nanowire (diameter: 10 nm) as selective layer and TiO₂ nanowire (diameter: 20-100 nm) as supporting layer (Zhang et al., 2009)

2.7 Oil-water separation technology

2.7.1 Introduction of oil-water separation

The increase

ing oil-water mixtures discharged from frequent oil spill accidents, emerging shale oil fracking process and traditional petroleum industry are posing unprecedented threat on the already vulnerable environmental system (Asatekin and Mayes, 2009; Kintisch, 2010; Cheng et al., 2011; Hayase et al., 2013; Li et al., 2013). In addition, the rapid development of hydrocarbon processing industry also produces a great amount of oily wastewater which usually contains many kinds of oils, such as crude oil, grease, diesel, lubricant, gasoline, kerosene and so on. Oily wastewater cannot be directly discharged because the oil is extremely stable in water, which has severe environmental, biological, economic and social influences. For example, oil is toxic to the living things in sea and fresh water. The oil-water mixtures can be classified into several categories according to the diameter (d) of the dispersed oil, including free oil-water mixtures if $d > 150\ \mu\text{m}$, oil-water dispersions if $20\ \mu\text{m} < d < 150\ \mu\text{m}$, and oil-water emulsions if $d < 20\ \mu\text{m}$ (Kota et al., 2012). It should be noted that the diameter of oil droplets can be reduced significantly in the presence of surfactants (such as detergents) which are widely used in family and industry. It is more difficult to remove the small oil droplets which can be stable in water for a long time and need more time to demulsify. Many techniques have been applied in the oil-water separation field, including traditional gravity separation and skimming, adsorption, air floating and etc. (Cheryan and Rajagopalan, 1998; Yuan et al., 2008; Bi et al., 2012; Kota et al., 2012; Wu et al., 2012). However, these techniques suffer either from low efficiency or high cost of energy and materials. Significant attentions have been paid to membrane technology in oil-water separation field due to its high efficiency, small footprint, and easy scale-up (Yuan et al., 2008; Kwon et al., 2012; Li et al., 2012; McCloskey et al., 2012; Zhang et al., 2012; Gao et al., 2013; Maphutha et al., 2013).

2.7.2 Membrane technology for oil-water separation

Membrane technologies, including MF, UF, NF and RO, have been applied for

oil-water separation. Membrane process is highly efficient to separate oil-water emulsions which are difficult to be treated by conventional methods (Yang et al., 2011; Yang et al., 2012; Maphutha et al., 2013). Figure 2.22 shows the membrane based system for oil-water separation. During the oil-water separation process, no chemicals are needed which makes the membrane process environmental friendly. In addition, no post treatment is needed. Furthermore, membrane processes are efficient to remove both of oil and other pollutants (such as suspended solids) which are widely existed in oily wastewater. Typically, there are two kinds of membranes including hydrophobic and hydrophilic membranes, and both of them have been used to separate oil-water mixture (Kota et al., 2012).

Marchese et al. (2000) used cross-flow pilot-scale ultrafiltration to treat emulsified oily wastewater. The results indicated that the UF membrane achieved high removal rates of COD (90.1%) and hydrocarbon concentration (99.7%). However, the emulsified oil was easily adsorbed on the membrane, which caused a fouling layer on the top of UF membrane. Ju and co-workers fabricated a fouling resistant membrane for oil-water separation by coating poly(ethylene glycol) diacrylate (PEGDA) on the surface of PSF membrane (Ju et al., 2008). This membrane exhibited low fouling potential and achieved a high water flux which was about 4 times higher than that of uncoated membrane, even after 24 h. Ceramic mullite and mullite-alumina MF membranes were fabricated by Abbasi et al. (2010) to investigate their activity of treating oily wastewater. They found that the ceramic mullite membranes acquired the lowest fouling resistance and the highest rejection rate.

Generally, hydrophilic membranes are advantageous over hydrophobic membranes in oil-water separation field because: (1) they allow water to permeate, which prevents membrane fouling and clogging by viscous oil; (2) they avoid the formation of water barrier layer between the membranes and the oil phase, in contrast to the issue with hydrophobic and oleophilic membranes that water naturally settles below oil and form a barrier layer to prevents oil permeation (Gao et al., 2013; Shi et al., 2013; Zhang et

al., 2013; Zhang et al., 2013). In this sense, ceramic porous membranes are good choices for oil-water separation, due to their relatively hydrophilic property (Wen et al., 2013).

Figure 2.22 Schematic illustration of membrane system for oil-water separation (Cheryan and Rajagopalan, 1998).

2.7.3 Superhydrophilic membranes for oil-water separation

It is impracticable to adopt the well-established traditional phase inversion method, which has been widely used in porous hydrophobic membranes, for the fabrication of a porous hydrophilic membranes (Zhang et al., 2013). Therefore, people circumvented to fabricate porous hydrophilic membranes by coating hydrophilic materials on the surfaces of porous matrix (metal or polyester meshes). For example, Kota et al. (2012) coated hydro-responsive polymers on stainless steel meshes, and these superhydrophilic and superoleophobic membranes achieved 99.9% separation efficiency towards surfactant free oil-water emulsions, as well as free oil-water mixtures. Jiang and co-workers coated polyacrylamide (PAM) hydrogel on stainless steel meshes by a photo-initiated polymerization process, and these superhydrophilic and underwater superoleophobic membranes were used for the separation of oil-water mixtures (Xue et al., 2011). It was reported that this hydrogel coated mesh could effectively separate many oil-water mixtures under gravity, including crude oil-water, vegetable oil-water, diesel-water and gasoline-water mixtures. Very recently, Jin's group grew inorganic nanowires on copper mesh through a simple chemical oxidation

approach for effectively separating both immiscible oil-water mixtures and oil-in-water emulsions (Zhang et al., 2013). The as-fabricated membranes had anti-oil fouling property for a long time due to superhydrophilic and underwater superoleophobic surface properties. Wen et al. (2013) fabricated a superhydrophilic zeolite-coated mesh films by growing silica zeolite silicalite-1 crystals on stainless steel mesh for oil-water separation under gravity. This mesh was demonstrated to be an excellent filter for oil-water separation without fouling problem due to the underwater superoleophobic interface with low affinity for oil droplets. In addition, this mesh could withstand harsh environment which broadened its applications.

2.8 Summary

In summary, the literature review indicated that TiO_2 based photocatalysts and TiO_2 based membranes attracted a significant amount of research interests. Many related researches have been carried out. They include:

- (1) TiO_2 photocatalysts with various nanostructures were synthesized for photocatalytic degradation and disinfection, including 1D TiO_2 nanotubes, 1D TiO_2 nanowires, 3D TiO_2 spheres and etc.
- (2) Various GO- TiO_2 composites were prepared for photocatalytic degradation and disinfection, including GO-P25 composites, GO- TiO_2 nanotubes composites, GO- TiO_2 nanorods composites and etc.
- (3) A variety of TiO_2 based membranes were fabricated for wastewater purification, including free-standing TiO_2 nanotube membranes, TiO_2 nanowire membranes and etc.
- (4) Membrane technology was applied in oil-water separation field for oily wastewater treatment besides the conventional techniques. Both hydrophobic and hydrophilic membranes were used for the separation of the oil-water mixtures.

By careful analyses of current literatures, the research gaps are listed:

- (1) Although various TiO_2 nanostructures were synthesized, limited researches compared the photocatalytic activity between different TiO_2 nanostructures, especially

1D TiO₂ nanostructures and 3D TiO₂ nanostructures.

(2) The reported GO-TiO₂ composites were mainly focused on deposition TiO₂ nanoparticles or other low dimensional TiO₂ nanostructures on GO sheets.

(3) The fabricated TiO₂ membranes suffered from low efficiency and lacked cross-linkers among the membranes during the wastewater purification process.

(4) Current membranes for oil-water separation had significant membrane fouling problems. In addition, they could not separate oil-water emulsions with small oil droplets.

Hence, in this study, the above mentioned research gaps were solved one by one using the following approaches.

Firstly, four TiO₂ nanostructures were synthesized to investigate the influence of nanostructures on the photocatalytic activity, including 1D TiO₂ nanotubes, 1D TiO₂ nanowires and two kinds of 3D TiO₂ spheres with different primary building units. The results indicated 3D TiO₂ sphere with hierarchical nanosheet structures exhibited the highest photocatalytic efficiency.

Secondly, a novel ultrasonic method was used to combine 3D TiO₂ spheres with GO sheets to further enhance the photocatalytic activity of TiO₂ spheres.

Thirdly, a novel GO-TiO₂ membrane was fabricated by using as-synthesized hierarchical GO-TiO₂ composites for wastewater purification. However, this membrane cannot be used under alkaline condition.

Subsequently, the sulfonated functional groups were introduced into GO sheets to synthesize sulfonated GO sheets through a chemical method. The sulfonated GO-TiO₂ membrane was fabricated for wastewater purification under different wastewater conditions, even slight alkaline condition.

Finally, the as-fabricated sulfonated GO-TiO₂ membrane had multifunctional properties, which were also applied for oil-water separation in the oily wastewater treatment field. The superhydrophilic and underwater superoleophobic sulfonated GO-TiO₂ membranes could efficiently separate surfactant stabilized oil-water emulsions without fouling problems.

CHAPTER 3: MATERIALS & METHODOLOGY

3.1 Materials

Degussa P25-a commercial TiO₂ powder (80% anatase and 20% rutile) was obtained from Evonik Degussa (Germany). Sodium hydroxide (NaOH, 99%), sodium nitrate (NaNO₃, 99%), tetrabutyl titanate (TBT, 97%), acetic acid (HAc, ≥99%), sodium chloride (NaCl, 99%), hydrogen peroxide (H₂O₂, 35%), potassium permanganate (KMnO₄, 99%), sodium 2-chloroethanesulfonate (ClCH₂CH₂SO₃H, 98%), concentrated sulfuric acid (H₂SO₄, 98%), hydrochloric acid (HCl, 36.5%), acid orange 7 (AO7), rhodamine B (RhB) and technical grade humic acid (HA) were purchased from Sigma-Aldrich. In addition, Isopropyl alcohol (IPA), toluene (99.8%), dimethyl formamide (DMF, 99.8%) and absolute ethanol were bought from Merck Ltd (Singapore). Natural graphite (SP1) was purchased from Bay Carbon Company (USA). *Escherichia coli* (*E. coli*, K12 ER2925) was purchased from New England Biolab. Crude oil and diesel were obtained from Shell Oil Company (Singapore). Vegetable oil was bought from the supermarket. All chemicals were used as received without further purification. The deionized (DI) water (18.3 MΩ-cm resistivity) was produced from Millipore Milli-Q water purification system.

3.2 Materials synthesis

3.2.1 Synthesis of TiO₂ nanotube

(For Chapter 4)

TiO₂ nanotube was fabricated by a previous reported hydrothermal method (Xu et al., 2011). In a typical process, 3 g of P25 was mixed with 100 mL of 10 M NaOH aqueous solution and the mixture was stirred thoroughly for 6 h. Then, the mixture was transferred to a Teflon-lined stainless-steel autoclave (125 mL) at 150 °C for 48 h, as shown in Figure 3.1. Subsequently, the precipitate was washed with 0.1 M HCl aqueous solution and DI water for three times, respectively, until the resulting pH was neutral. Finally, the synthesized product was annealed at 450 °C for 2 h to obtain TiO₂

nanotube.

Figure 3.1 The process of hydrothermal/solvothermal reaction.

3.2.2 Synthesis of TiO₂ nanowire

(For Chapter 4)

TiO₂ nanowire was synthesized *via* a conventional hydrothermal approach (Zhang et al., 2009). Typically, 3 g of P25 was mixed with 100 mL of 10 M NaOH aqueous solution thoroughly, and the suspension was hydrothermally reacted at 180 °C for 3 days. Then, the white product was washed with 0.1 M HCl aqueous solution and DI water for three times, respectively, until the resulting pH was neutral. Finally, the prepared product was annealed at 650 °C for 2 h to obtain TiO₂ nanowire.

3.2.3 Synthesis of TiO₂ particles assembled sphere (TiO₂ sphere-P)

(For Chapter 4)

TiO₂ sphere-P was prepared by solvothermal method. The mixture of 1 mL of TBT and 90 mL of IPA were treated at 200 °C for 20 h. The product was washed with absolute ethanol for three times before drying in an oven at 80 °C.

3.2.4 Synthesis of TiO₂ sheets assembled sphere (TiO₂ sphere-S)

(For **Chapter 4 & 5**)

TiO₂ sphere-S was synthesized by the reported solvothermal method with slight modification (Ye et al., 2011). Typically, 1 mL of TBT was added to 75 mL of HAc with continuous stirring for 10 min. Thereafter, the obtained white suspension was transferred to a 125 mL Teflon-lined stainless-steel autoclave, which was then heated to 180 °C and kept for 6 h. The product was collected by centrifugation after the autoclave cooled to room temperature and followed by ethanol washing. Finally, the material was dried at 60 °C for 24 h and annealed at 500 °C for 2 h to obtain TiO₂ sphere-S.

3.2.5 Synthesis of graphene oxide (GO)

(For **Chapter 4, 5, 6 & 7**)

GO was prepared according to the modification of Hummer's method (Hummers and Offeman, 1958), and the procedure was described previously (Liu et al., 2010; Gao et al., 2012). In a typical procedure, 500 mg of graphite powder and 2.0 g of NaNO₃ were put into cold (below 5 °C) concentrated H₂SO₄ (18 mL). This mixture was stirred continuously for 1 h and the temperature was kept below 5 °C by cooling in an ice bath. Then, 3 g of KMnO₄ was added gradually and reaction was continued for another 2 h at a temperature below 5 °C. Subsequently, the mixture was heated to 35 °C for 30 min, and then 40 mL of DI water was added slowly while the temperature was increased and kept at 100 °C for 15 min. The mixture was diluted with 70 mL of DI water when it was cooled to room temperature. The color of the suspension changed to bright yellow after adding 10 mL of H₂O₂. For thorough purification, the suspension was filtered and washed with 400 mL of 5% HCl twice followed by further washing with 200 mL of DI water for 3 times. Finally, the as-obtained precipitate was dried in the vacuum drier for at least 5 days for further use.

3.2.6 Synthesis of graphene oxide-TiO₂ sphere-S composites (GO-TiO₂)

(For **Chapter 4 & 5**)

In a typical process, firstly, 3 mg of as-synthesized GO was well dissolved in 100 mL

of DI water. Then, 100 mg of as-prepared TiO₂ sphere-S was added to GO solution. The mixtures were put under ultrasonic condition for 30 min and then kept stirring for 2 h. Finally, the mixtures were centrifuged and put into vacuum drier for further usage, and the as-prepared sample was labeled as GO-TiO₂ composites.

3.2.7 Synthesis of sulfonated graphene oxide (GO-SO₃H or SGO)

(For **Chapter 6 & 7**)

GO-SO₃H was prepared by a similar process of synthesizing GO-COOH (Sun et al., 2008). In a typical process, 200 mg of GO, 3 g of ClCH₂CH₂SO₃H and 1.6 g of NaOH were added into 500 mL DI water. The mixture was put under ultrasonic condition for 3 h and then 2 mL of HCl was added into the mixture. Finally, the precipitate was washed with ethanol for three times and put into vacuum drier for 2 days.

3.2.8 Synthesis of hierarchical TiO₂ spheres

(For **Chapter 6 & 7**)

Hierarchical TiO₂ spheres were prepared according to the slight modification of reported method (Wu et al., 2012). In a typical procedure, 1 mL of TBT was added the mixture of 15 mL of DMF and 15 mL of IPA drop by drop. Then, the mixture was transferred to a Teflon-lined stainless-steel autoclave (45 mL), which was then heated to 200 °C and kept for 20 h. The product was collected by centrifugation after the autoclave cooled to room temperature and followed by ethanol washing. Finally, the material was dried at 60 °C for 24 h and annealed at 450 °C for 2 h with a ramping rate of 5 °C min⁻¹.

3.2.9 Synthesis of sulfonated graphene oxide-TiO₂ composites (GO-SO₃H/TiO₂ or SGO-TiO₂)

(For **Chapter 6 & 7**)

GO-SO₃H/TiO₂ composites were prepared by mixing GO-SO₃H and TiO₂ under ultrasonic condition. 5 mg of as synthesized GO-SO₃H was well dissolved in 100 mL of DI water. Then, 100 mg of as prepared hierarchical TiO₂ sphere was added to GO-SO₃H solution. The mixture was ultrasonicated for 30 min and then kept stirring for 2 h. Finally, the mixture was centrifuged and the precipitate was put into vacuum

drier for further usage.

3.2.10 Assembly of graphene oxide-TiO₂ microsphere (sphere-S) (GO-TiO₂) membrane

(For **Chapter 5**)

200 mg of as synthesized GO-TiO₂ was dissolved into 100 mL of DI water to form uniform suspension. Subsequently, the suspension was injected into the filtration cup with one piece of commercial cellulose acetate (CA) membrane (Φ 47 mm, 0.45 μ m, Millipore, USA) on the bottom of the cup. GO-TiO₂ membrane was uniformly assembled on the surface of CA membrane after switching on the nitrogen gas for 30 min. For comparison, P25 membrane and TiO₂ microsphere membrane were also fabricated using 200 mg of P25 and TiO₂ microsphere as raw materials, respectively.

3.2.11 Assembly of sulfonated graphene oxide-TiO₂ (GO-SO₃H/TiO₂ or SGO-TiO₂) membrane

(For **Chapter 6 & 7**)

100 mg of as synthesized GO-SO₃H/TiO₂ was dissolved into 100 mL of DI water to form uniform suspension. Then, the suspension was injected into the filtration cup with one piece of commercial CA membrane (Φ 47 mm, 0.2 μ m, Millipore, USA) on the bottom of the cup. A GO-SO₃H/TiO₂ membrane was uniformly assembled on the surface of CA membrane after switching on the nitrogen gas for 30 min. The GO-SO₃H/TiO₂ membrane was further compressed under 5 bar at 100 °C on a hot press to enhance the connection and mechanical strength. As references, pure TiO₂ membrane and GO-TiO₂ membrane were also fabricated *via* an identical process to the fabrication of GO-SO₃H/TiO₂ membrane. It should be noted that GO-SO₃H/TiO₂ membrane (**Chapter 6**) is the same with SGO-TiO₂ membrane (**Chapter 7**).

3.3 Materials Characterization

3.3.1 Atomic force microscopy (AFM)

The surface topography of GO and GO-SO₃H (SGO) sheets was characterized by AFM using a non-contact mode on a PSIA XE-150 scanning probe microscope (Park SE-100). The AFM samples were prepared by dropping GO and GO-SO₃H

suspensions on the clean mica followed by drying at 50 °C for 1 h.

3.3.2 Field emission scanning electron microscopy (FESEM)

The morphology of synthesized samples was investigated by FESEM (JSM-7600F) microscope operating at 5 kV. The FESEM samples were prepared by depositing a few samples on the carbon tape which was attached on the holder, followed by platinum sputtering.

3.3.3 Transmission electron microscopy (TEM)

The microstructures and morphology of synthesized samples were evaluated by TEM (JEOL 2010-H) microscope operating at 200 kV. TEM samples were prepared by dropping the sample suspensions on the copper grids followed by drying at 50 °C for 1h

3.3.4 X-ray diffraction (XRD)

The structure and crystal phase of synthesized samples were examined by XRD (Shimadzu XRD-6000) with monochromated high-intensity Cu K α radiation ($\lambda=1.5418$ Å) operated at 40 kV and 30 mA. The scanning rate of XRD measurements was 2 °/min.

3.3.5 X-ray photoelectron spectroscopy (XPS)

XPS spectra of synthesized samples were acquired by using a Kratos Axis Ultra Spectrometer with a monochromic Al K α source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. The binding energy (BE) values were calibrated by using carbonaceous C 1s line (284.8 eV) as a reference.

3.3.6 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of synthesized samples were recorded on a Perkin Elmer GX FTIR system by using compressed KBr disc technique.

3.3.7 Ultraviolet-visible spectroscopy (UV-Vis)

UV-Vis spectra of synthesized samples were measured by a UV-Vis spectrometer (UV-visible resource 3000).

3.3.8 Photoluminescence spectroscopy (PL)

PL spectra of synthesized samples were recorded on the spectrofluorophotometer (Shimadzu RF-5301).

3.3.9 Brunauer-Emmet-Teller (BET) specific surface area

BET specific surface area of synthesized samples was determined at liquid nitrogen temperature (77K) using the Micromeritics ASAP 2040 system. The pore size distribution is calculated from the desorption branch of the isotherm according to the BJH model.

3.4 Photocatalytic degradation (photodegradation) experiments

(For **Chapter 4**)

The photodegradation of AO7 dyes by TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P, TiO₂ sphere-S and GO-TiO₂ composites under UV light was carried out, respectively. Typically, 30 mg of obtained samples was added into 50 mL of 50 mg L⁻¹ AO7 in a 100 mL glass beaker. The solution was put under a UVP Pen-Ray mercury lamp (254 nm, 5.4 mW · cm⁻², USA) in the black box (shown in Figure 3.2) while all other light sources were closed, after the mixture was stirred for 1 h to reach the adsorption equilibrium. During the given time intervals, the photoreacted solution (2 mL) was extracted by a 3 mL syringe and then was analyzed by recording variations of the absorption band maximum (485 nm) with a UV-visible spectrometer to determine the degradation efficiency (C/C₀) (Xu et al., 2011).

The photodegradation activity of GO-TiO₂ composite was investigated under solar light irradiation. The photodegradation process is similar with photodegradation of TiO₂ nanostructures, except changing the UV light to the solar light simulator (Xenon arc lamp, Newport Oriel, 100 mW · cm⁻²), as shown in Figure 3.3.

Figure 3.2 The black box for photodegradation under UV light irradiation.

Figure 3.3 The solar simulator (Xenon arc lamp, Newport Oriel, $100 \text{ mW} \cdot \text{cm}^{-2}$).

3.5 Photocatalytic disinfection experiments

(For **Chapter 4**)

In this work, *E. coli* was chosen as a standard microorganism sample for photocatalytic disinfection experiments. Normally, *E. coli* was cultivated in Luria-Bertani nutrient solution and followed by incubating for 24 h at 37°C in incubator to obtain the desired concentration. Thereafter, pure *E. coli* was centrifuged and re-suspended in a saline solution (0.9% NaCl) to maintain the concentration around 10^8 colony forming units (CFU mL^{-1}). TiO_2 sphere-S and GO-TiO_2

composites with the same mass of 5 mg were added to 50 mL of 10^8 CFU mL⁻¹ *E. coli* saline solution in 100 mL glass beaker to investigate their antibacterial ability, respectively. Typically, each material was put into two 100 mL glass beakers since one was placed under dark condition and the other one was put under solar light. 100 μ L of solution was taken out from each Petri dish at a given reaction time and daubed on solidified agar nutrient plates uniformly. The colony forming units were counted after these plates were incubated at 37 °C for another 24 h. As a comparison, the blank control experiments without any disinfectants were also conducted under dark condition and solar light irradiation, respectively. In principle, all solution and apparatuses used in these disinfection experiments were autoclaved at 121 °C for 20 min to ensure sterility.

3.6 Water purification experiments of GO-TiO₂ membrane

(For Chapter 5)

3.6.1 Investigation of GO-TiO₂ membrane flux

The flux performance of GO-TiO₂ membrane was tested in a dead-end membrane system setup without UV light irradiation, which had been reported by our group, as shown in Figure 3.4 (Bai et al., 2010). As contrasts, P25 membrane and TiO₂ microsphere membrane were also investigated under the same condition. In addition, the flux of CA membrane was recorded as control. This bench-scale system comprises of a membrane cell with a filtration cup volume of 60 mL and the effective membrane area is 11.94 cm². Working pressure was provided by N₂ gas cylinder, which was connected to the filtration cup. The weight of permeate was measured continuously over time using a balance, which was connected to the data logger. Furthermore, data was collected every ten second and then averaged each ten minute. Permeate flux was calculated on the basis of permeate mass divided by effective surface area and filtration time, unit is L/(m² h). The membrane flux was investigated under different trans-membrane pressure (TMP). In addition, these membranes were pre-compressed under pressure of 2 bar for 6 h to exclude the interference of membrane swelling.

3.6.2 Photodegradation activity of GO-TiO₂ membrane

The photodegradation activity of GO-TiO₂ membrane was evaluated using RhB and AO7 as model pollutants. The same dead-end membrane filtration setup was used with UV light irradiation (254 nm, 40 mW/cm²), as shown in Figure 3.4. For the photodegradation of RhB, 50 mL of RhB solution with concentration of 50 mg/L (50 ppm) was filled into the filtration cup. UV light was turned on after the solution was kept in dark for 60 min to reach adsorption equilibrium. The TMP was maintained about 0.5 bar within the whole process. 2 mL permeate were collected to measure the UV adsorption at an interval of 5 min within 30 min. In addition, 50 mL of AO7 with concentration of 50 mg/L was also investigated under the same condition. As references, CA membrane, P25 membrane and TiO₂ microsphere membrane were investigated under the same processes.

Figure 3.4 Schematic diagram of lab-scale dead end water filtration setup.

3.6.3 Anti-fouling property of GO-TiO₂ membrane

HA feed water with concentration of 20 mg/L was permeated through GO-TiO₂ membrane under pressure (2 bar) provided by N₂ gas, with or without UV irradiation. The permeate flux was calculated and TOC of permeate was measured within certain time. In comparison with GO-TiO₂ membrane, anti-fouling activities of CA

membrane, P25 membrane and TiO₂ microsphere membrane were also investigated under the same condition.

3.7 Water purification experiments of GO-SO₃H/TiO₂ membrane under different pH conditions

(For Chapter 6)

3.7.1 Water purification experiments of GO-SO₃H/TiO₂ membrane under neutral condition (pH=7)

Water purification experiments of GO-SO₃H/TiO₂ membrane under neutral pH were carried out similarly with that of GO-TiO₂ membrane (**Chapter 3.6**).

3.7.2 Water purification experiments of GO-SO₃H/TiO₂ membrane under acidic condition (pH=4) and alkaline condition (pH=11)

The stability and practical applicability of GO/TiO₂ and GO-SO₃H/TiO₂ membrane were investigated under different pH conditions. The pH of HA solution was adjusted to 4 and 11 by adding HCl and NaOH, respectively, without changing other operating parameters.

3.8 Oil-water separation experiments of SGO-TiO₂ membrane

(For Chapter 7)

3.8.1 Preparation of oil-water mixtures

In this work, two categories of oil-water mixtures were prepared. The first category is free oil-water mixture. For free oil-water mixture, crude oil and water with the volume ratio of 3:7 were simply mixed together without stirring or ultrasonication. The second category is surfactant stabilized oil-in-water emulsions. Surfactant stabilized oil-in-water emulsions were prepared by mixing surfactant (Triton, X-100), water and oil (namely toluene, crude oil, vegetable oil and diesel) in a ratio of 2:100:1 v/v/v and sonicated under a power of 1kW for 1 h to produce a white and milky solution. The droplet sizes of toluene-in-water emulsion are around 200 nm measured by dynamic light scattering (DLS) by using Mastersizer-2000. The surfactant stabilized oil-in-water emulsions were stable for several weeks and no

de-emulsification was observed.

3.8.2 Surface wettability of SGO-TiO₂ membrane

The surface wettability of SGO-TiO₂ membrane was characterized by contact angle measurements. Contact angles were measured on an machine (VCA Optima, USA). The water droplets (about 3 μ L) were dropped onto the surface of the membrane and the measurements were done at three different positions of each membrane. For underwater CA, the membrane was first immersed in water. A 5 μ L dichloromethane (DCM) droplet was dropped carefully on the membrane and the CA was measured. The average value of three measurements was adopted as the contact angle.

3.8.3 Oil-water separation

Oil-water separation performance of the membrane was investigated by a vacuum filtration setup, as shown in Figure 3.5.

Figure 3.5 (a) Schematic illustration of oil/water separation setup; and (b) Optical photo of oil-water separation setup.

The free oil-water mixture or the surfactant stabilized oil-in-water emulsions were poured into the filtration cup. When the vacuum pump was turned on, the water permeated through the membrane into the container, while the oil droplets were rejected on the membrane surface. The droplet size of oil-in-water emulsions was measured by DLS. In addition, the oil droplet size of the oil-in-water emulsions and

the permeate solution was investigated by the optical microscopy (Olympus TH4-200, Japan). The water content in the permeate solution was measured using a Perkin Elmer Thermogravimetric Analyzer TGA 7 with Thermal Analysis Controller TAC 7/DX. The sample was heated from room temperature to 110 °C at a rate of 5 °C min⁻¹ and kept at 110 °C for 30 min.

CHAPTER 4: EFFECTS OF VARIOUS TiO₂ NANOSTRUCTURES AND GRAPHENE OXIDE ON PHOTOCATALYTIC ACTIVITY OF TiO₂

4.1 Introduction

Recently, TiO₂ has been widely applied in photocatalytic wastewater purification fields. It has been reported that the photocatalytic activity of TiO₂ strongly depended on its nanostructures. To date, various TiO₂ nanostructures have been synthesized, including tubes, wires, fibers and spheres. However, it still lacks a comprehensive study which compares the photocatalytic activity of different TiO₂ nanostructures.

Despite manipulating the nanostructure of TiO₂, combining TiO₂ with carbon materials (such as carbon nanotube, graphene and graphene oxide) is another effective method to improve the photocatalytic activity of TiO₂ (Woan et al., 2009; Xiang et al., 2011; Gao and Sun, 2013). Graphene oxide (GO) is a chemically modified graphene with oxygen functional groups (Gao et al., 2012). In recent years, many groups and researchers have reported the combination of TiO₂ nanostructures with GO sheets (Xiang et al., 2012; Zhao et al., 2012). In addition, GO-TiO₂ composites have been widely applied in the fields of solar cells, hydrogen production and water purification. Hence, it is meaningful and practical to find out which kind of TiO₂ nanostructure is more efficient in photocatalytic process firstly. Then, the TiO₂ nanostructure with best photocatalytic activity will be coupled with GO sheets to further improve its photocatalytic performance.

In this study, initially, four kinds of TiO₂ nanostructures were synthesized, including 1D TiO₂ nanotube, 1D TiO₂ nanowire, 3D TiO₂ sphere constructed by nanoparticles (TiO₂ sphere-P) and 3D TiO₂ sphere constructed by nanosheets (TiO₂ sphere-S). The photocatalytic activities of these TiO₂ nanostructures were investigated thoroughly by photodegradation of AO7 dye. The results indicated that TiO₂ sphere-S exhibited the

best photodegradation efficiency, which degraded 100% of AO7 dye within 35 min under UV irradiation. The excellent photodegradation activity of TiO₂ sphere-S can be attributed to the hierarchical porous structure and efficient light harvesting originated from multi-reflection and scattering of incident light. Subsequently, GO sheets were introduced into the photocatalytic system by mixing GO with TiO₂ sphere-S under ultrasonication. GO-TiO₂ composites exhibited better photodegradation and disinfection activity than TiO₂ sphere-S under solar light irradiation, due to the enhanced light absorption and retarded charge recombination. Hence, this study shows that optimizing the nanostructures of photocatalysts and combining with GO sheets are two promising approaches to improve the performance of the photocatalysts.

4.2 Results and discussion

4.2.1 Characterization of various TiO₂ nanostructures

Figure 4.1 shows the representative FESEM images of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively. Figure 4.1a and b show that TiO₂ nanotube easily aggregates together and the morphology of individual nanotube cannot be observed clearly. The severe aggregation will affect the photocatalytic activity of TiO₂ nanotube. Figure 4.1c is the panorama of TiO₂ nanowire, which has the length from several to several tens micrometers. A closer observation of TiO₂ nanowire indicates that the diameter of individual nanowire ranges between 20 nm and 80 nm, and some nanowires tend to bind together to form a bundle, as shown in Figure 4.1d. Figure 4.1e is the FESEM image of TiO₂ sphere-P and it shows TiO₂ sphere-P has a wide size distribution from less than 1 μm to more than 5 μm. Figure 4.1f shows that the TiO₂ sphere-P is actually constructed by primary nanoparticles. Figure 4.1g shows the TiO₂ sphere-S has a relative narrow size distribution, which ranges between 2 μm and 3 μm. A typical TiO₂ sphere-S with the average diameter about 2.5 μm is exhibited in the inset of Figure 4.1g. In addition, a high magnification FESEM image (Figure 4.1h) shows that the TiO₂ sphere-S is well assembled by secondary nanorods and nanosheets, which grow along the radial direction. The

Figure 4.1 FESEM images of TiO_2 nanotube (a) and (b), TiO_2 nanowire (c) and (d), TiO_2 sphere-P (e) and (f), and TiO_2 sphere-S (g) and (h).

nanostructure of the secondary nanorods and nanosheets will be investigated thoroughly by TEM analyses, which will be discussed in the following section.

The crystalline phases of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by XRD patterns, as shown in Figure 4.2. The characteristic diffraction peaks at $2\theta=25.3^\circ$, 37.8° , 48° , 53.5° , 55.6° , 62.7° and 75° correspond well to the (101), (004), (200), (105), (211), (204) and (215) planes, respectively, of the anatase TiO₂ (JCPDS 21-1272). In addition, the XRD spectra of TiO₂ with different nanostructures show similar diffraction peaks, indicating that the synthesized TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S are all anatase phase. This demonstrates that the crystalline phases of four TiO₂ nanostructures do not affect the photocatalytic activity in current work. Furthermore, the sharp diffraction peaks of four XRD patterns demonstrate the good crystallinity of different synthesized TiO₂ nanostructures. The highly crystallized nanostructures can

Figure 4.2 XRD patterns of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively.

reduce the opportunity of charge recombination, which improves the photocatalytic

performance (Wu et al., 2012). The results of FESEM and XRD analyses confirm that TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S have been successfully prepared.

4.2.2 Photodegradation activity of various TiO₂ nanostructures under UV light

The photocatalytic activities of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by degradation of a commercial dye—AO7, which is a common pollutant from the textile industry. Figure 4.3a shows that TiO₂ nanotube exhibits strong adsorption ability towards AO7 within 30 min due to its large BET surface area and mesoporous structure, which has been investigated in our previous report (Xu et al., 2011). In addition, around 92% of AO7 can be degraded by TiO₂ nanotube during 35 min, while TiO₂ nanowire can only decompose less than 80% of AO7, as shown in Figure 4.3a. Although both TiO₂ sphere-P and TiO₂ sphere-S are 3D nanostructures, TiO₂ sphere-P exhibits much lower photodegradation efficiency towards AO7 than TiO₂ sphere-S which can almost degrade 100% of AO7. Figure 4.3b shows UV-Vis absorption spectra of AO7 degraded by TiO₂ sphere-S, which detailed illustrates the photodegradation process. In addition, Figure 4.3c vividly depicts the color changes of AO7 degraded by TiO₂ sphere-S within 35 min.

Figure 4.3 (a) Changes of AO7 concentration during photodegradation of AO7 dye by TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S, respectively; (b) UV-Vis absorption spectra of AO7 degraded by TiO_2 sphere-S during 35 min; and (c) color changes of AO7 degraded by TiO_2 sphere-S during 35 min.

Generally, the specific surface area and light absorption ability are two essential factors of the photocatalysts, which can significantly influence the photocatalytic activity of the photocatalysts. The specific surface area and pore size distribution of TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S were investigated by N_2 adsorption/desorption analyses, as shown in Figure 4.4a-d. The BET surface area of TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S are $106.12 \text{ m}^2 \text{ g}^{-1}$, $32.69 \text{ m}^2 \text{ g}^{-1}$, $64.24 \text{ m}^2 \text{ g}^{-1}$, and $87.63 \text{ m}^2 \text{ g}^{-1}$, respectively. Among them, the BET surface area of TiO_2 nanotube is the largest, which contributes to the excellent

adsorption capacity. In addition, the photodegradation efficiency of TiO₂ nanotube is higher than that of TiO₂ nanowire and TiO₂ sphere-P due to the larger surface area. The large surface area of the photocatalysts allows more surface to be reached by the incident light and provides more reactive sites during photodegradation process. However, the photodegradation efficiency of TiO₂ nanotube is lower than that of TiO₂ sphere-S, even though the surface area of TiO₂ nanotube is larger than that of TiO₂ sphere-S. This result indicates that the BET surface area is not the only role governing the photocatalytic activity.

Figure 4.4 N₂ adsorption/desorption isotherms of (a) TiO₂ nanotube, (b) TiO₂ nanowire, (c) TiO₂ sphere-P and (d) TiO₂ sphere-S, respectively (inset: pore size distribution calculated by the BJH method from the desorption branch).

The light absorption activities of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by measuring the UV-Vis spectra of them, as shown in Figure 4.5. The four TiO₂ nanostructures show similar absorption edges, locating in

the UV region (around 390 nm) due to the intrinsic band-gap absorption of TiO₂. All synthesized TiO₂ nanostructures have no absorbance in the visible light region because of the wide band-gap of anatase TiO₂ (Chai et al., 2011). It is interesting to note that the absorbance of TiO₂ sphere-S is stronger than the others within the light region from 300 nm to 380 nm (UV region), as shown in Figure 4.5. This can be explained by Scheme 4.1. The hierarchical nanostructure of TiO₂ sphere-S with secondary nanosheets and nanowires allows multiple reflection and scattering of incident light, which results in more efficient utilization of the light, compared with TiO₂ nanotube, TiO₂ nanowire and TiO₂ sphere-P, as shown in Scheme 4.1. Hence, the hierarchical morphology of TiO₂ sphere-S contributes to the large BET surface area and high light absorption capacity, which synergistically lead to the best photocatalytic performance.

Figure 4.5 UV-Vis spectra of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively.

Scheme 4.1 Schematic illustration of multi-reflections within TiO₂ sphere-S compared with TiO₂ sphere-P.

4.2.3 The detailed nanostructure of TiO₂ sphere-S

The detailed nanostructures of TiO₂ sphere-S before and after calcinations have been thoroughly investigated by TEM characterization. TEM images of Figure 4.6 exhibit the clear morphology and structure transformation between unannealed and annealed TiO₂ sphere-S. Figure 4.6b shows that the edges of unannealed TiO₂ sphere-S are assembled from nanorod and nanosheets like structure. Figure 4.6c is a TEM image of pure TiO₂ sphere-S after calcinations. The diameter of annealed TiO₂ sphere-S is around 2.5 μm, which is coordinated well with FESEM images. A higher magnification TEM image of Figure 4.6d clearly exhibits the hierarchical building blocks of nanorods and nanosheets. Further closer observation of the nanorods shows that the nanorods are in fact constructed by highly crystalline nanoparticles, as shown in Figure 4.6e. Figure 4.6f shows that the clear lattice-fringe with inter-plane spacing of 0.34 nm is attributed to the (101) crystal plane of the anatase TiO₂, which confirms that TiO₂ microsphere is composed of highly crystallized anatase (Liao et al., 2011). To our knowledge, high crystalline nanoparticle can improve the charge transfer and

Figure 4.6 (a) and (b) TEM images of TiO₂ sphere-S before calcinations; (c-e) TEM images of TiO₂ sphere-S after calcinations; and (f) HRTEM image of TiO₂.

separation (Chen et al., 2011; Wu et al., 2012), which will further enhance the

photocatalytic activity.

4.2.4 Characterization of GO sheets

The surface morphology of well synthesized GO sheets was characterized by AFM. Figure 4.7a shows single layered GO sheets with some overlap are successfully synthesized and the typical size of GO sheets is more than 2 μm . In addition, as shown in Figure 4.7b, the thickness of single layered GO sheets is around 0.9 nm from the two line scans and three 3D image of AFM, which is similar with the previous reports (Park and Ruoff, 2009; Kim et al., 2012).

Figure 4.7 (a) 2D AFM image of GO sheets; and (b) Two line scan and 3D AFM image of GO sheets.

4.2.5 Characterization of GO-TiO₂ composites

Figure 4.8a schematically illustrates the preparation process of GO-TiO₂ composites. GO sheets and TiO₂ sphere-S can uniformly disperse in water, and GO sheets anchored on TiO₂ sphere-S on micro-size scale under ultrasonic condition. Figure 4.8b and c are FESEM images of GO-TiO₂ composites. As shown in Figure 2b, GO sheets connected with TiO₂ sphere-S can be clearly identified, while some TiO₂ sphere-S are even wrapped mostly by GO sheets and GO sheets also can bind TiO₂ sphere-S together. Figure 4.8c shows that the edges of two TiO₂ sphere-S are

Figure 4.8 (a) Schematic preparation process of GO-TiO₂ composites; (b) and (c) FESEM image of GO-TiO₂; (d) and (e) TEM image of GO-TiO₂; and (f) HRTEM image of GO-TiO₂.

connected by GO sheets, in which GO act as “bridges” to chemically bond with TiO₂ (Zhu et al., 2011). TEM is a powerful technique to analyze GO based composites because GO sheets sometimes cannot be clearly observed under SEM. Hence, the nanostructure of GO-TiO₂ was further characterized by TEM. Figure 4.8d shows one TiO₂ sphere-S connected with GO sheets. The edge of GO-TiO₂ is blurry and nanorod structure cannot be seen clearly, which is different from that of pure TiO₂ sphere-S (inset of Figure 4.6c and d). This is because GO sheets are attached on the surface and edge of TiO₂ sphere-S. Figure 4.8e is the higher magnification TEM image of red frame in Figure 4.8d. As shown in Figure 4.8e, GO sheets bond with the edge of TiO₂ sphere-S can be clearly identified. HRTEM image of Figure 4.8f reveals that TiO₂ sphere-S is composed of high crystalline anatase ($d_{101}=0.34$ nm). In addition, the characterized wrinkles of GO sheets can also be observed in Figure 4.8f. Based on the results of FESEM and TEM analyses, GO sheets can be tightly anchored on TiO₂ sphere-S under ultrasonication, which is beneficial for interfacial electron transfer.

XRD was used to analyze the crystalline phases of GO, TiO₂ sphere-S and GO-TiO₂. Figure 4.9 shows that the diffraction peak at $2\theta=11.9^\circ$ can be attributed to the characteristic (001) plane of GO sheets, which corresponds to the interlayer spacing of 0.74 nm. The interlayer spacing of GO is significantly larger than that of native graphite ($d=0.34$ nm at $2\theta=26.3^\circ$) (Park et al., 2009; Zhang et al., 2009). GO-TiO₂ composite exhibits similar XRD pattern with TiO₂ sphere-S, indicating GO sheets do not change the crystalline phase of TiO₂ sphere-S. In addition, no peaks of GO can be observed in the XRD pattern of GO-TiO₂, indicating the regular stack of GO is destroyed (Liu et al., 2010). The results of FESEM, TEM and XRD analyses confirm the successful preparation of GO-TiO₂ composites.

Figure 4.9 XRD patterns of GO, TiO₂ sphere-S, and GO-TiO₂, respectively.

4.2.6 Photocatalytic activity of GO-TiO₂ composites under solar light

Photodegradation of AO7 was carried out to investigate and compare the photocatalytic activity of TiO₂ sphere-S and GO-TiO₂ composites. 20 mg of TiO₂ sphere-S and GO-TiO₂ were added into the 50 mL AO7 with the concentration of 30 mg L⁻¹, respectively, under solar light irradiation. Figure 4.10a shows the kinetic curves of photodegradation of AO7 within 60 min, which indicates that solar light itself has limited ability to degrade AO7. In addition, over 90% of AO7 can be degraded by GO-TiO₂ composites, the efficiency of which is higher than that of TiO₂ sphere-S. The disinfection activities of TiO₂ sphere-P and GO-TiO₂ towards *E. coli* cells were also investigated to further confirm their photocatalytic performance. Figure 4.10b shows that nearly 100% of *E. coli* cells are killed by GO-TiO₂ within 120 min under solar light irradiation, while less than 80% of *E. coli* cells can be inactivated by TiO₂ sphere-S. The high photocatalytic disinfection efficiency of GO-TiO₂ can be further demonstrated by the photos of agar plates at the different disinfection intervals, as shown in Figure 4.10c.

Figure 4.10 (a) Changes of AO7 concentration during photodegradation of AO7 dye without photocatalysts and with TiO₂ sphere-S and GO-TiO₂ under solar light; (b) Time course for disinfection activity towards *E. coli* by TiO₂ sphere-P and GO-TiO₂ under solar light within 120 min; and (c) the photos of agar plates at the different disinfection time.

The higher photodegradation and disinfection activity of GO-TiO₂ composites than

TiO₂ sphere-S can be attributed to the enhanced light absorption, and reduced charge recombination, which has been demonstrated by UV-Vis and PL spectra, respectively, as shown in Figure 4.11. Figure 4.11a shows the UV-Vis spectra of TiO₂ sphere-S and GO-TiO₂. GO-TiO₂ exhibits similar position at the absorption edge with that of TiO₂

Figure 4.11 (a) UV-Vis spectra of TiO₂ sphere-S and GO-TiO₂; and (b) PL spectra of TiO₂ sphere-S and GO-TiO₂.

sphere-S, indicating that GO sheets only modify the surface of TiO₂ sphere-S instead

of doping into the lattice of TiO_2 . Remarkably, the introduction of GO sheets results in the wide absorption in the visible light range from 400 nm to 800 nm. The enhancement of absorption in the visible light region significantly contributes to the excellent photocatalytic activity of GO- TiO_2 composite. The measurement of PL spectra has been widely adopted to characterize the charge recombination rate of photocatalysts because the PL emission is originated from the recombination of photo-generated electrons and holes (Yu et al., 2011). Figure 4.11b shows the PL spectra of TiO_2 sphere-S and GO- TiO_2 . The PL intensity of GO- TiO_2 is greatly lower than that of TiO_2 , indicating that the charge recombination rate has been efficiently reduced after combining TiO_2 sphere-S with GO sheets because GO sheets are excellent electron accumulators (Xiang et al., 2011). The high light absorption capacity and efficient charge separation cooperatively result in enhanced photodegradation and disinfection activity of GO- TiO_2 composite.

The tentative photocatalytic mechanism, including charge separation process and formation process of hydroxyl radicals ($\cdot\text{OH}$), has been schematically illustrated in Scheme 4.2. Initially, the electron-hole pairs of TiO_2 sphere-S are generated under solar light irradiation. The photo-generated electrons move from valance band (VB) to conduction band (CB) immediately under the excited state. Thereafter, the photo-generated electrons will transfer to GO sheets which closely contact on the surface of TiO_2 sphere-S, while photo-generated holes are left behind in the VB of TiO_2 sphere-S. Subsequently, the separated electrons and holes will react with dissolved oxygen and water molecules to form hydroxyl radicals ($\cdot\text{OH}$), which are strong oxidants towards degradation of AO7 dye and disinfection of *E. coli* cells.

Scheme 4.2 Schematic illustration of the charge separation process and the formation process of hydroxyl radicals ($\cdot\text{OH}$).

4.3 Conclusions

In summary, four TiO_2 nanostructures, including 1D TiO_2 nanotube, 1D TiO_2 nanowire, 3D TiO_2 sphere-P and 3D TiO_2 sphere-S, have been successfully prepared to investigate the influences of nanostructures on the photocatalytic activity of TiO_2 . The results show that the photodegradation efficiency of TiO_2 sphere-S is the highest among four TiO_2 nanostructures, which can degrade 100% of AO7 during 35 min. The high light utilization capacity and hierarchical mesoporous structure synergistically contribute to the best photodegradation activity of TiO_2 sphere-S. The further enhancement of the photocatalytic performance can be achieved by coupling TiO_2 sphere-S with GO sheets which can improve the light absorption and facilitate the separation of charge carriers. Consequently, optimization of nanostructure and combination of GO sheets are two efficient approaches to enhance the photocatalytic activity of TiO_2 , which can also be referenced for other photocatalysts in future.

CHAPTER 5: MULTIFUNCTIONAL GRAPHENE OXIDE-TiO₂ MEMBRANE FOR CLEAN WATER PRODUCTION

5.1 Introduction

Recently, there is a trend in the use of membrane technology for production of safe drinking water (Liang et al., 2011; Pendergast and Hoek, 2011; Liu et al., 2012). Although extant polymer membrane can perform efficient and selective separations in many water treatment fields including industrial waste water reclamation and desalination, some problems associated with membrane properties and membrane treatment processes, such as low flux, low selectivity and fouling still remain significant challenges. Among them, membrane fouling poses a major obstacle that requires further improvements in the membrane performance (Mansouri et al., 2010; Rana and Matsuura, 2010). In recent years, ceramic TiO₂ membranes have attracted intensive research interests in view of their higher mechanical strength, enhanced chemical stability and excellent performance in the removal of pollutants to eliminate fouling problems (Van Der Bruggen et al., 2003; Zhang et al., 2009). However, some problems related to these TiO₂ membranes still remain unresolved. Firstly, no connection was formed between the materials making the membrane easily broken. In addition, drying and calcination processes usually introduce the pinholes and cracks into the membrane (Ke et al., 2007). Furthermore, pure TiO₂ membrane is not efficient for photodegradation of pollutant due to the rapid charge recombination rate (Chen and Mao, 2007). Hence, there is an urgent need to develop a facile method to fabricate a novel membrane with anti-fouling property to overcome above drawbacks. Therefore, a practical way to conquer the problems of current TiO₂ membrane is adopting GO sheets as cross linkers to form joints between individual TiO₂ particle, wire or sphere.

In this study, we report a new type of GO-TiO₂ microsphere membrane for concurrent

water filtration and photodegradation. This novel membrane is consisted of as-synthesized GO-TiO₂ composites (**Chapter 4**), in which GO sheets serve as binders for individual TiO₂ microspheres. Compared with previous ceramic membranes, GO-TiO₂ microsphere membrane possesses two major advantages: (1) sustainably high water flux due to alleviation of membrane fouling by the hierarchically porous membrane structure; and (2) enhanced strength and flexibility from the cross-linking effect of GO sheets.

5.2 Results and discussion

5.2.1 Characterization of GO-TiO₂ membrane

Figure 5.1a is a digital photo of GO-TiO₂ membrane. It shows that GO-TiO₂ membrane is mechanically flexible due to the cross-linking function of GO sheets, which can be freely bent by hands. This flexible property will broaden the practical applications of this multifunctional membrane by fitting in various configurations of membrane modules. However, the mechanical strength of pure TiO₂ membrane is vulnerable, as shown in Figure 5.1b. The membrane is broken easily to several pieces, which is a common drawback for the pure ceramic membrane. The results demonstrate that GO sheets play significant roles in GO-TiO₂ membrane.

Figure 5.1 Digital photos of GO-TiO₂ membrane (a) and pure TiO₂ membrane (b).

Figure 5.2 shows the top surface (Figure 5.2a-c) and cross sectional morphology (Figure 5.2d-f) of GO-TiO₂ membrane at different magnifications. It should be noted that no cracks can be observed either from the surface or the cross section, indicating the high integrity of prepared GO-TiO₂ membrane because GO sheets act as polymer glue to cross-link individual TiO₂ sphere together.

Figure 5.2 (a-c) Surface FESEM images of GO-TiO₂ membrane at different magnifications; and (d-f) Cross sectional FESEM images of GO-TiO₂ membrane at different magnifications.

5.2.2 Water filtration property of GO-TiO₂ membrane

To demonstrate the engineering applicability of GO-TiO₂ membrane for water purification, the flux performance of GO-TiO₂ membrane was investigated in a lab-scale dead end setup, as shown in Figure 3.4. As contrasts, the water filtration activity of control CA membrane, P25 membrane and TiO₂ microsphere membrane were also tested. In addition, steady permeate flux was achieved by pre-compressing these membranes under pressure of 2 bar for 6 h to exclude the interference of membrane swelling (Tang et al., 2007). Figure 5.3a shows the pure water flux of control CA membrane, P25 membrane, TiO₂ microsphere membrane and GO-TiO₂ membrane, respectively, while the same mass of 200 mg of P25, TiO₂ microsphere and GO-TiO₂ are well deposited on CA membrane surface. As shown in Figure 5.3a, permeate flux of all these membranes increases linearly with TMP, indicating that these membranes are incompressible and only intrinsic membrane resistances (R_m) are present in these experiments (Yuan and Zydney, 1999). In addition, the flux of TiO₂ microsphere membrane and GO-TiO₂ membrane is significantly larger than that of P25 membrane, which can be explained by Figure 5.4. Figure 5.4 shows the schematic diagram (left side) and surface morphology (right side) of P25 membrane, TiO₂ microsphere membrane and GO-TiO₂ membrane, individually. As shown in Figure 5.4a, P25 nanoparticle with size around 20 nm prefer to form an extremely dense layer on the surface of polymer membrane and some particles are likely to block the pore of CA membrane, resulting of low flux even at high TMP (Pan et al., 2008). However, TiO₂ microsphere membrane and GO-TiO₂ membrane form more porous structure due to the large size of individual TiO₂ microsphere with porous property. In addition, as expected, the permeate flux of GO-TiO₂ membrane is slightly lower than that of TiO₂ microsphere membrane because the presence of GO sheets. GO sheets can reduce the both inter- and intra-pore of GO-TiO₂ membrane, which is beneficial for high separation efficiency (Zhang et al., 2012). It is well known that membrane with high flux and separation efficiency is ideal in water treatment fields, since more high quality water will be produced at a low cost. In this respect, GO-TiO₂ membrane shows bright future in water purification field. Furthermore, the thickness

of GO-TiO₂ membrane can be easily adjusted through changing the mass of GO-TiO₂ deposited on the surface of CA membrane, while the thickness has little influence on the permeate flux because the porous structure of GO-TiO₂ membrane, as shown in Figure 5.3b.

Figure 5.3 (a) Changes in permeate flux of control (CA membrane), P25, TiO₂ microsphere and GO-TiO₂ membrane with different TMP, respectively; and (b) Influence of thickness of GO-TiO₂ membrane on permeate flux under different TMP.

Figure 5.4 (a) Schematic diagram of P25 membrane (left side) and FESEM image of P25 membrane surface (right side); (b) Schematic diagram of TiO₂ microsphere membrane (left side) and FESEM image of TiO₂ microsphere membrane surface (right side); and (c) Schematic diagram of GO-TiO₂ membrane (left side) and FESEM image of GO-TiO₂ membrane surface (right side).

5.2.3 Photodegradation activity of GO-TiO₂ membrane

The photodegradation activity of GO-TiO₂ membrane was investigated by degradation of RhB and AO7, which are the major pollutants from textile industries.

CA membrane, P25 membrane and TiO_2 microsphere membrane were also tested as references under the same condition. Figure 5.5a and b show the removal rate of RhB and AO7 dye in the process of membrane filtration alone and UV light irradiation alone, respectively. As shown in Figure 5.5a, the GO- TiO_2 membrane itself has limited efficiency in removing dyes and less than 15% of RhB and AO7 can be removed by membrane filtration process without UV irradiation. This is because

Figure 5.5 Removal rate of RhB and AO7 dye in the process of membrane filtration alone (a) and UV light irradiation alone (b); (c) and (d) Photodegradation of RhB and AO7 in the presence of CA membrane, P25, TiO_2 microsphere and GO- TiO_2 membrane, respectively.

GO- TiO_2 membrane is only a common filter without UV light and the concentration reduction of dyes is attributed to the adsorption activity of GO- TiO_2 membrane. Figure 5.5b shows that UV light itself can only degrade less than 50% of RhB and AO7. GO- TiO_2 membrane shows higher photodegradation efficiency towards both

RhB and AO7 dyes than P25 and TiO₂ microsphere membrane, as shown in Figure 5.5a and b, RhB and AO7 dyes are totally degraded within 30 and 20 min by GO-TiO₂ membrane under UV irradiation, respectively. The efficient photocatalytic activity plays a significant role in eliminating membrane fouling, because less organics and macromolecules can be accumulated on the GO-TiO₂ membrane surface, which guarantees GO-TiO₂ membrane can maintain high permeate flux for longer time than traditional membranes.

5.2.4 Anti-fouling property of GO-TiO₂ membrane

Fabricating membrane with anti-fouling property is an urgent need for water purification industry due to the high cost for cleaning membrane fouling. The anti-fouling capacity of CA membrane, P25 membrane, TiO₂ microsphere membrane and GO-TiO₂ membrane were investigated by choosing HA as a standard pollutant, which is a typical NOMs in water and the precursor of carcinogenic DBPs (Wisniewski et al., 2002). Membranes used for anti-fouling test should be firstly pre-compacted under pressure of 2 bar for 6 h to eliminate the influence of initial flux decline and confirm that decrease of flux is solely caused by HA fouling (Tang et al., 2007). Figure 5.6a shows the time courses of permeate flux without UV light irradiation, in the presence of control CA membrane, P25 membrane, TiO₂ microsphere membrane and GO-TiO₂ membrane, respectively. Remarkably rapid drop of flux for all membranes can be observed in the first 30 min, as shown in Figure 5.6a. This can be attributed to the large HA particles or aggregates were rapidly deposited on the surface of membrane and blocked the pores at the initial stage of filtration (Yuan and Zydney, 1999). In addition, significant membrane fouling was occurred after 2 hour and stably small flux (ca. 7 L/(m² h)) was reached because thick HA cake layer was formed on the surface of membrane (Zularisam et al., 2006). Nevertheless, membrane fouling can be greatly reduced with UV irradiation. As shown in Figure 5.6b, the permeate flux of CA membrane still declines relatively fast, indicating the efficiency of UV irradiation itself is limited. Compared with Figure 5.6a, the permeate flux of both GO-TiO₂ membrane and TiO₂ microsphere membrane can keep at a high

Figure 5.6 (a) Changes of permeate flux of different membrane with time under pressure of 2 bar without UV irradiation; and (b) Changes of permeate flux of different membrane with time under pressure of 2 bar with UV irradiation.

value for a relative long time, while the flux of GO- TiO_2 membrane is higher than that of TiO_2 microsphere membrane. The permeate flux of GO- TiO_2 membrane (ca. $60 \text{ L}/(\text{m}^2 \text{ h})$) is around 9 times higher than that of CA and P25 membrane at the steady

state. In addition, no obvious decline of flux can be observed even within 15 h because most of HA was photodegraded into small molecules, including carbon dioxide and water (Zhang et al., 2008), by GO-TiO₂ under UV irradiation, which can be verified by the results of TOC analysis.

Figure 5.7 shows residual TOC rate of HA from the water permeated through CA, P25, TiO₂ microsphere and GO-TiO₂ membrane, individually. Combining CA membrane with UV irradiation exhibits limited efficiency in removing HA, while GO-TiO₂ membrane shows the highest efficiency and over 90% TOC has been eliminated, which contributes to high flux within a long time. This indicates that most of HA rejected on the membrane surface could be degraded under the current permeate flux (ca. 60 L/(m² h)) because the amount of HA did not exceed the maximal photocatalytic capacity of GO-TiO₂ membrane (Zhang et al., 2008). However, it should be noted that if higher concentration of HA or higher TMP were adopted, the HA might not be degraded effectively and would cause membrane fouling, which would be investigated and improved in the future study.

Figure 5.7 Residual TOC rate in permeate water filtrated through different membrane.

In this work, the enhanced TOC removal efficiency of GO-TiO₂ membrane than CA, P25 and TiO₂ microsphere membrane can be attributed to (1) high specific BET surface area and porous structure; and (2) good contact between GO sheets and TiO₂ microsphere improves the electron transfer from conduction band (CB) of TiO₂ to GO sheets, which reduces the charge recombination rate and enhances the photocatalytic activity. Figure 5.8 shows the N₂ adsorption/desorption isotherm of GO-TiO₂. The BET surface area of GO-TiO₂ is 107.57 m² g⁻¹, which is greatly larger than that of P25 (45 m² g⁻¹) and pure TiO₂ (87.63 m² g⁻¹) (shown in Figure 4.4d). Major pore size distribution of GO-TiO₂ is ranged from 10 to 40 nm with a peak around 20 nm, which is a typical mesoporous structure, as shown in the inset of Figure 5.8. The mesoporous structure with such big surface area provides more channels for water molecule to go through and enhances the photogenerated electrons and holes to participate in photocatalytic activity (Pan et al., 2008; Liao et al., 2011). In addition, the efficient charge separation process was confirmed by PL spectra, as shown in Figure 4.11b. PL emission is originated from the recombination of free charge carriers so the intensity of PL indicates the charge recombination and transfer efficiency in semiconductors (Liu et al., 2011; Xiang et al., 2011; Yu et al., 2011). The PL intensity of GO-TiO₂ is significant lower than that of TiO₂, demonstrating that charge recombination rate is reduced after combining TiO₂ with GO sheets (Xiang et al., 2011). This result indicates that photo-generated electrons of TiO₂ efficiently transfer to GO sheets, while photo-generated holes remain on TiO₂, which enhance the charge separation efficiency.

Figure 5.8 N₂ adsorption/desorption isotherm of GO-TiO₂ (inset: pore size distribution).

Figure 5.9a and b show FESEM images of surface of GO-TiO₂ membrane after filtration in the absence and presence of UV irradiation, respectively. Undoubtedly, an extremely dense HA layer was formed on the surface of GO-TiO₂ membrane without UV irradiation, which resulted in low permeate flux in the later period of filtration process. The inset image of Figure 5.9a also shows that a brown layer is formed on the initial grey surface of GO-TiO₂ membrane (inset of Figure 5.9b), confirming the formation of serious fouling layer during the filtration of HA solution. In addition, the appearance of GO-TiO₂ membrane still can be identified under the HA layer. However, under UV irradiation condition, almost no HA layer can be found on the surface of GO-TiO₂ membrane, indicating that GO-TiO₂ membrane can effectively eliminate membrane fouling with the help of UV light. Consequently, based on the results of permeate flux, photocatalytic activity, fouling as well as the properties of membrane itself (strength and flexibility), GO-TiO₂ membrane shows superior properties and activities than other membranes in our experiments. Enhanced strength and flexibility of GO-TiO₂ membrane can be attributed to the fact that high strength and flexible GO sheets act as binders between TiO₂ microspheres to prevent membrane from rupture.

In addition, flexible membrane can be applied to more water filtration fields due to its better adaptability, so the GO sheets play an indispensable role in GO-TiO₂ membrane.

Figure 5.9 FESEM images of GO-TiO₂ membrane surface after filtration: (a) membrane surface without UV irradiation (inset: digital photo of GO-TiO₂ membrane); and (b) membrane surface with UV irradiation (inset: digital photo of GO-TiO₂ membrane).

5.3 Conclusions

In summary, a novel GO-TiO₂ membrane was uniformly assembled on the surface of polymer membrane through filtration of as-synthesized GO-TiO₂ composites. This novel membrane possesses enhanced strength and flexibility than traditional TiO₂ membrane. In addition, this membrane exhibits multifunctional properties for concurrent water filtration and photodegradation: (1) high photocatalytic activity towards both RhB and AO7 dyes; (2) high water flux; and (3) eliminating membrane fouling in a long time. All these excellent properties can be attributed to high specific surface area and porous structure of GO-TiO₂ membrane, in which GO acts as cross linker to combine individual TiO₂ microsphere. Furthermore, GO sheets are also good electron acceptors to facilitate charge transfer and enhance the photodegradation efficiency during water purification process. All these excellent properties indicate

that GO-TiO₂ membrane has a bright future in the clean water production field.

CHAPTER 6: MULTIFUNCTIONAL SULFONATED GRAPHENE OXIDE-TiO₂ MEMBRANE FOR CLEAN WATER RECLAMATION FROM WASTEWATER WITH VARIOUS PH CONDITIONS

6.1 Introduction

In the **Chapter 5**, multifunctional GO-TiO₂ membrane has been fabricated for wastewater purification. However, as-fabricated GO-TiO₂ membrane could only treat wastewater with pH lower than 7. Considering the diversity and complexity of municipal and industrial wastewater, the ideal membrane in wastewater purification field should possess the ability of withstanding various wastewater conditions. Hence, the fabricated GO-TiO₂ membrane should be further modified to achieve this objective.

In this study, a novel multifunctional sulfonated graphene oxide-TiO₂ (GO-SO₃H/TiO₂) membrane was delicately designed and fabricated for the first time. Initially, GO-SO₃H was synthesized by introducing -SO₃H groups into GO sheets in sulfonation reaction. Augmenting the universal merits of GO with novel -SO₃H groups presents a critical opportunity to solve the above mentioned challenges. In this membrane, GO-SO₃H sheets acts as linkages to combine individual hierarchical TiO₂ sphere by forming connections between -SO₃H and the center of Ti⁴⁺. The strong affinity between GO-SO₃H and TiO₂ enhances the strength and flexibility of this membrane. In addition, this novel membrane exhibits high water flux without membrane fouling. Furthermore, this membrane can work efficiently in different wastewater quality with a wide pH range because of the special coordination bond between GO-SO₃H sheets and TiO₂ spheres. Consequently, this novel multifunctional membrane can be a promising candidate for water purification under different wastewater conditions.

6.2 Results and discussion

6.2.1 Schematic fabrication process of GO-SO₃H/TiO₂ membrane

The process of design and fabrication of GO-SO₃H/TiO₂ membrane is illustrated in Scheme 6.1. Firstly, sulfonic acid groups were introduced into GO sample by reacting GO solution with ClCH₂CH₂SO₃H in a basic environment. During this process, epoxide and hydroxyl groups of GO were converted to sulfonic acid groups. Then, GO-SO₃H solution was mixed with hierarchical TiO₂ sphere under vigorous stirring condition. Finally, GO-SO₃H/TiO₂ membrane was fabricated by filtration of GO-SO₃H/TiO₂ solution and hot pressing.

Scheme 6.1 Schematic illustration for the fabrication of GO-SO₃H/TiO₂ multifunctional membrane.

6.2.2 Characterization of GO and GO-SO₃H sheets

The morphology of the synthesized GO and GO-SO₃H sheets was well characterized. Figure 6.1a and b show the AFM images of GO and GO-SO₃H sheets, respectively. As shown in Figure 6.1a, the typical size of GO sheets is larger than 2 μ m with a

Figure 6.1 (a) and (b) AFM images of GO and GO-SO₃H sheets, respectively; (c) and (d) TEM images of GO and GO-SO₃H sheets, respectively.

thickness of about 0.9 nm for a single layered GO sheet, which is similar with published results (Park and Ruoff, 2009). Whereas, the size of GO-SO₃H sheets ranges from 0.5 to 1 μm, which is much smaller than that of GO sheets, because GO sheets can be broken into pieces under ultrasonication. The reduction in the size of GO sheets was further confirmed by TEM image in Figure 6.1c and d. In addition, it should be noted that the thickness of single layered GO-SO₃H sheets was increased to 1.0 nm owing to the introduction of sulfonic acid groups, as characterized by two line

scans shown in Figure 6.1b. TEM images in Figure 6.1c and d illustrate the characterized wrinkles and folds of GO and GO-SO₃H sheets, respectively. Figure 6.2 shows the change in color from brown to black as the solution of GO underwent sulfonation reaction producing GO-SO₃H. This remarkable color change can be attributed to the partial reduction of GO sheets in strong basic environment (Zhang et al., 2010).

Figure 6.2 Digital photo of GO and GO-SO₃H solution.

6.2.3 Characterization of hierarchical TiO₂ sphere

Figure 6.3a and b are the FESEM images of unannealed TiO₂ spheres. Figure 6.3a shows that the size of these hierarchical TiO₂ spheres is uniform with the diameter of around 500 nm. In addition, a closer observation indicates that these TiO₂ spheres are actually assembled by thin 2D sheets with the thickness of ca. 10 nm, as seen in Figure 6.3b. After heat treatment in air at 450 °C for 2 h, the morphology of TiO₂ spheres has a remarkable change, as exhibited in Figure 6.3c and d. Figure 6.3c and d are FESEM images of TiO₂ sphere after calcinations at different magnification. The size of the annealed TiO₂ spheres has no obvious shrinkage, while the void-free 2D sheets of unannealed sphere change to the porous structures which are in fact constructed by crystallized TiO₂ nanoparticles, as shown in Figure 6.3d. The

formation of pores is because of the evaporation of the organic precursor.

Figure 6.3 (a) and (b) FESEM image of hierarchical TiO₂ sphere before calcinations; (c) and (d) FESEM image of hierarchical TiO₂ sphere after calcinations.

The detailed nanostructures of unannealed and annealed TiO₂ spheres were further investigated by TEM characterization, as shown in Figure 6.4. Figure 6.4a-b and c-d are TEM images of unannealed and annealed TiO₂ spheres at different magnification, respectively. Figure 6.4a and b show that the unannealed TiO₂ spheres are constructed by ultra-thin 2D sheets. However, the annealed TiO₂ spheres are composed of numerous nanoparticles, as shown in Figure 6.4c and d. The analyses of TEM characterization are in good agreement with the results of FESEM characterization. In addition, the HRTEM image is shown in Figure 6.4e. The clear d-spacing of 0.35 nm can be assigned to the (101) crystal plane of anatase TiO₂, indicating that these hierarchical TiO₂ spheres are highly crystallized (Gao et al., 2012). The high crystalline hierarchical TiO₂ structure is beneficial for light harvesting and charge

Figure 6.4 (a) and (b) TEM image of hierarchical TiO_2 sphere before calcinations; (c) and (d) TEM image of hierarchical TiO_2 sphere after calcinations; (e) HRTEM image of hierarchical TiO_2 sphere after calcinations; and (f) SAED pattern of hierarchical TiO_2 sphere after calcinations.

separation (Joo et al., 2012; Wu et al., 2013). Furthermore, Figure 6.4f is the SAED pattern of the annealed TiO₂ sphere and the diffuse ring pattern indicates that the TiO₂ spheres are polycrystalline structure.

6.2.4 Characterization of GO-SO₃H/TiO₂ composite

The GO-SO₃H/TiO₂ composites were synthesized by ultrasonic mixing GO-SO₃H sheets with TiO₂ spheres, as schematically illustrated in Figure 6.5a. Firstly, TiO₂ spheres and GO-SO₃H sheets are well dispersed in water. Then, TiO₂ spheres are combined with GO-SO₃H sheets to form GO-SO₃H/TiO₂ composites under ultrasonic condition. Ultrasonication process can hinder the aggregation of GO-SO₃H sheets, which is a common problem for other synthetic methods, such as hydrothermal reaction. To substantiate the formation of GO-SO₃H/TiO₂ composites, the morphology and nanostructure of GO-SO₃H/TiO₂ were well characterized by FESEM and TEM. Figure 6.5b shows FESEM image of GO-SO₃H/TiO₂ composites and it can be observed that TiO₂ spheres are linked together as compared with the images of pure hierarchical TiO₂ in Figure 6.3c. In addition, Figure 6.5c clearly shows GO-SO₃H sheets act as polymer glue which binds several TiO₂ spheres together. Figure 6.5d shows a low magnification TEM image, in which four TiO₂ spheres are cross-linked by GO-SO₃H sheets. The heterojunctions between TiO₂ and GO-SO₃H are marked with red circles. The right heterojunction in Figure 6.5d was further magnified and illustrated in Figure 6.5e. In addition, the characterized wrinkles of GO-SO₃H sheets and the highly crystallized anatase TiO₂ were indicated by white lines in the HRTEM image of Figure 6.5f. It should be noted that the mass ratio of GO-SO₃H sheets over TiO₂ spheres has a great influence on the following water filtration performance of GO-SO₃H/TiO₂ membrane. An increased number of GO-SO₃H sheets could significantly reduce the permeate flux because GO-SO₃H sheets are impermeable. In this work, the ratio was carefully controlled at 5%, demonstrated by TGA analysis in Figure 6.6. The above FESEM and TEM results indicate successful grafting of GO-SO₃H sheets onto hierarchical TiO₂ spheres with the formation of junctions due to the bonding between oxygen containing groups

Figure 6.5 (a) Schematic preparation process of GO-SO₃H/TiO₂ composite; (b) and (c) FESEM image of GO-SO₃H/TiO₂; (d) and (e) TEM image of GO-SO₃H/TiO₂; and (f) HRTEM image of GO-SO₃H/TiO₂.

(sulfonic and carboxylic acid groups) of GO-SO₃H sheets and Ti⁴⁺ centre of TiO₂ spheres.

Figure 6.6 TGA curves of TiO₂, GO-SO₃H and GO-SO₃H/TiO₂.

The crystallographic structures of GO, GO-SO₃H, TiO₂ and GO-SO₃H/TiO₂ were characterized by XRD, as shown in Figure 6.7. GO shows an obvious diffraction peak at 2θ of ca. 12° , corresponding to the d-spacing of about 0.74 nm (Liu et al., 2010; Zhu et al., 2010). However, the diffraction peak of GO-SO₃H slightly shifts to approximately 10.6° as compared with that of GO. This can be attributed to the introduction of sulfonic acid groups into the layers of GO, which enlarges the interlayer spacing of GO-SO₃H (Zhang et al., 2012). In addition, the diffraction peaks of TiO₂ and GO-SO₃H/TiO₂ at 2θ of 25.3 , 38.2 , 48.1 , 53.5 , 55.6 , 62.7 and 75.0° are unambiguously assigned to anatase TiO₂ (JCPDF 21-1272). A small peak at 2θ of ca. 31° (indicated by asterisk) might be due to the existence of trace amount of brookite.

Figure 6.7 XRD patterns of GO, GO-SO₃H, TiO₂ and GO-SO₃H/TiO₂, respectively.

Figure 6.8 shows the FTIR spectra of GO, GO-SO₃H, TiO₂ and GO-SO₃H/TiO₂, respectively. The phenolic and carboxylic groups of GO can be clearly identified in Figure 6.8, including 1230 cm⁻¹ (phenolic C-OH stretching), 1389 cm⁻¹ (carboxylic C-OH stretching), and 1726 cm⁻¹ (C=O stretching vibrations of carboxyl) (Xu et al., 2008; Li et al., 2011). In addition, the band at 1630 cm⁻¹ and the band ranging from 3200 cm⁻¹ to 3600 cm⁻¹ can be ascribed to H-O-H bending band of adsorbed water molecules (Liu et al., 2012). In comparison with GO, the band of GO-SO₃H at 1230 cm⁻¹ disappears, while a new band at 1167 cm⁻¹ can be observed. This appearance of a new band can be assigned to the S=O stretching vibration of the sulfonic acid groups (Zhang et al., 2010), as shown in the inset of Figure 6.8. This result indicates that sulfonic groups were successfully introduced into GO-SO₃H by replacing epoxide and hydroxyl groups, which further validates the schematic illustration in Scheme 6.1. For the FTIR spectra of TiO₂ and GO-SO₃H/TiO₂, the broad band ranging from 490 cm⁻¹ to 900 cm⁻¹ can be attributed to the characteristic vibrations of Ti-O band of TiO₂. Furthermore, a weak band at around 1400 cm⁻¹ can be assigned to the coordination between Ti and the carboxyl groups of GO-SO₃H (Liu et al., 2010), demonstrating that GO-SO₃H sheets are chemically linked with hierarchical TiO₂ spheres, which is

coordinated well with the results of FESEM, TEM and XRD.

Figure 6.8 FTIR spectra of GO, GO-SO₃H, TiO₂, GO-SO₃H/TiO₂, respectively (inset: FTIR spectra of GO and GO-SO₃H ranging from 1000 to 1300 cm⁻¹).

XPS spectra were measured to further confirm the preparation of GO-SO₃H/TiO₂. Figure 6.9a shows the full XPS spectra of GO, GO-SO₃H and GO-SO₃H/TiO₂, respectively. It can be clearly observed that only Ti, C, O and S exist in GO-SO₃H/TiO₂ without any impurities, as shown in Figure 6.9a. High resolution XPS spectrum of Ti 2p from GO-SO₃H/TiO₂ exhibits two characteristic peaks, including Ti 2p_{1/2} (463.5 eV) and Ti 2p_{3/2} (457.9 eV), seen in Figure 6.9b, indicating only Ti⁴⁺ exists in prepared samples. In addition, a clear S 2p peak of GO-SO₃H/TiO₂ at around 167 eV indicates that GO-SO₃H sheets have been successfully grafted onto TiO₂, (Wu et al., 2010) as shown in Figure 6.9c. Figure 6.9d-f are high resolution XPS spectra of C 1s from GO, GO-SO₃H and GO-SO₃H/TiO₂, respectively. It can be observed that C-OH and HO-C=O groups exist in all three spectra, while the intensity of C-OH peak is different within these spectra. The intensity of C-OH from GO-SO₃H and GO-SO₃H/TiO₂ decreases significantly compared with that of GO, demonstrating that most of C-OH groups in GO sheets have been converted into C-SO₃H groups during

the sulfonation reaction, as illustrated in the Scheme 6.1. The results of XPS spectra provide strong evidences that GO-SO₃H/TiO₂ composites have been successfully prepared.

Figure 6.9 (a) Full scan XPS spectra of GO, GO-SO₃H and GO-SO₃H/TiO₂; (b, c) High resolution XPS spectra of Ti 2p and S 2p, respectively, from GO-SO₃H/TiO₂; and (d, e, f) High resolution XPS spectra of C 1s from GO, GO-SO₃H and GO-SO₃H/TiO₂, individually.

6.2.5 Characterization of GO-SO₃H/TiO₂ membrane

Figure 6.10a and b show the surface and cross sectional FESEM images of GO-SO₃H/TiO₂ membrane, respectively. As exhibited in Figure 6.10a, no obvious cracks can be observed on the GO-SO₃H/TiO₂ membrane, indicating good membrane

Figure 6.10 (a) Low and high (inset) magnification FESEM images of GO-SO₃H/TiO₂ membrane surface; (b) Cross section FESEM image of GO-SO₃H/TiO₂ membrane; (c) digital photo of GO-SO₃H/TiO₂ membrane; and (d) digital photo of TiO₂ membrane.

integrity. Figure 6.10b shows that GO-SO₃H/TiO₂ membrane is compact after hot pressing with a thickness of about 30 μm. In addition, the thickness can be easily controlled by adjusting the mass of GO-SO₃H/TiO₂ composites. The tightly inter-connected structure of GO-SO₃H/TiO₂ membrane endows it with good flexibility, as shown in Figure 6.10c. Comparatively, pure TiO₂ membrane without GO-SO₃H

sheets was not able to remain intact after drying due to the lack of cross-linker, as shown in Figure 6.10d.

6.2.6 Water purification and anti-fouling performance of GO-SO₃H/TiO₂ membrane

HA was chosen as a standard pollutant to investigate the water filtration and anti-fouling performances of GO-SO₃H/TiO₂ membrane, because HA is commonly found in water and the precursor of carcinogenic DBPs. Figure 6.11a shows the permeate flux of TiO₂ membrane, GO/TiO₂ membrane and GO-SO₃H/TiO₂ membrane without UV light irradiation, respectively. The permeate flux declined to 6.5 L/m²h within 60 min for all tested membranes, which was caused by HA fouling. As shown in Figure 6.11c, a dense cake layer can be found on the surface of GO-SO₃H/TiO₂ membrane. However, the membrane fouling could be significantly alleviated when the membrane worked under the UV light. Figure 6.11b shows that the permeate flux of GO-SO₃H/TiO₂ membrane decline slightly from ca. 45 L/m²h to 36 L/m²h and the flux can remain at 36 L/m²h for a period of 6 to 7 h. The initial and steady permeate flux of GO/TiO₂ membrane are around 40 and 30 L/m²h, respectively, which is lower than that of GO-SO₃H/TiO₂ membrane. The reduction in flux can be attributed to the much larger size of GO sheets compared to GO-SO₃H, as shown in the AFM image of Figure 6.1a and b. The large GO sheets may block the pore of membrane and increase the intrinsic membrane resistance (R_m). On the other hand, the permeate flux of TiO₂ membrane drops rapidly and reaches a constant small value (ca. 12.5 L/m²h) indicating the limited efficiency of TiO₂ membrane, which will be discussed in the subsequent section. The FESEM image of Figure 6.11d clearly exhibits that no HA fouling layer can be found on GO-SO₃H/TiO₂ membrane surface due to the high photodegradation efficiency of GO-SO₃H/TiO₂ membrane.

a **b**

Figure 6.11 (a) and (b) Changes of permeate flux of different membrane without and with UV light irradiation, respectively; (c) and (d) FESEM images of GO-SO₃H/TiO₂ membrane surface after filtration without and with UV light irradiation, respectively.

6.2.7 Mechanism

The enhanced wastewater treatment performance of the GO/TiO₂ membrane and GO-SO₃H/TiO₂ membrane than TiO₂ membrane can be ascribed to the porous structure, large specific surface area and efficient charge separation, as explained in Figure 6.12a and b. Figure 6.12a shows the N₂ adsorption-desorption isotherms of GO-SO₃H/TiO₂ and the resulting BET surface area is 96.12 m²g⁻¹. In addition, the pore size distribution is valued between 1 and 100 nm with two peaks at around 3 nm and 35 nm, which can be assigned to mesoporous hierarchical nanostructure, as shown in the inset of Figure 6.12a. The materials with large surface area have a higher chance to contact and react with water pollutants, and the mesoporous nanostructure is beneficial for water to pass through because of its low resistance (Pan et al., 2008). The charge separation processes of TiO₂ and GO-SO₃H/TiO₂ were investigated by PL spectra, as shown in Figure 6.12b. The intensity of PL spectrum from GO-SO₃H/TiO₂ is much lower than that of pure TiO₂, indicating that the charge separation efficiency of GO-SO₃H/TiO₂ is significantly higher than that of TiO₂ because photogenerated electrons can quickly transfer to the GO-SO₃H sheets, which are good electron acceptors. Figure 6.12c illustrates the mechanism of concurrent water filtration and pollutant degradation. The electron-hole pairs of TiO₂ will be excited under UV irradiation and photogenerated electrons will transfer to GO-SO₃H sheets due to the close contact between TiO₂ and GO-SO₃H. The photogenerated electrons and holes further react with oxygen (O₂) and H₂O to form hydroxyl radicals (·OH), which are strong oxidants in water purification process.

Figure 6.12 (a) N_2 adsorption/desorption isotherm of $\text{GO-SO}_3\text{H}/\text{TiO}_2$ (inset: pore size distribution); (b) PL spectra of pure TiO_2 and $\text{GO-SO}_3\text{H}/\text{TiO}_2$; and (c) Schematic illustration of mechanism in concurrent water filtration and photodegradation process.

6.2.8 Practical applicability of GO-SO₃H/TiO₂ membrane for clean water reclamation from wastewater with different pH

The water purification performances of GO/TiO₂ and GO-SO₃H/TiO₂ membrane were further investigated by filtrating HA solution under different pH conditions (acid and base), mimicking the diversity of actual wastewater condition. Figure 6.13a shows the permeate flux of GO/TiO₂ and GO-SO₃H/TiO₂ membrane under pH=4. The flux of GO/TiO₂ and GO-SO₃H/TiO₂ membrane slowly declines and reaches steady flux at approximately 32 and 36 L/m²h respectively, which are similar with that of neutral pH. In addition, Figure 6.13b shows that both of GO/TiO₂ and GO-SO₃H/TiO₂ membrane achieve high TOC removing rate (ca. 90%), indicating that most of HA has been degraded into water and carbon dioxide, which eliminates membrane fouling. However, GO/TiO₂ and GO-SO₃H/TiO₂ membrane exhibit totally different behavior under pH=11, as shown in Figure 6.13c. The permeate flux of GO-SO₃H/TiO₂ membrane still remains at a high value within 5 h, while the flux of GO/TiO₂ membrane drops significantly during wastewater filtration process. The flux of GO/TiO₂ membrane is around 10 L/m²h after 5 h, which is 3 times less than that of GO-SO₃H/TiO₂ membrane. The TOC removal efficiency of GO/TiO₂ membrane is also greatly reduced under basic condition, compared with that of GO-SO₃H/TiO₂ membrane, as shown in Figure 6.13d. Considering the stable performance of GO-SO₃H/TiO₂ membrane in various environment, GO-SO₃H/TiO₂ membrane can be applied in practical engineering industry.

a **b** **c**

Figure 6.13 (a) and (c) Permeate flux of GO/TiO₂ and GO-SO₃H/TiO₂ membrane with UV light irradiation under pH=4 and pH=11, respectively; (b) and (d) Residual TOC rate in permeate water under pH=4 and pH=11, respectively.

It is interesting for us to observe the different performance between the GO/TiO₂ and GO-SO₃H/TiO₂ membrane under alkaline condition. The GO/TiO₂ and GO-SO₃H/TiO₂ membrane after wastewater purification were characterized by TEM to investigate the reason behind this specific phenomenon. Based on our past investigations, we found that inorganic materials could detach from GO sheets in basic environment because of the reaction between GO sheets and alkali (Liu et al., 2010). Hence, we conjectured that GO could not connect TiO₂ spheres together and GO sheets would separate themselves from GO/TiO₂ membrane under basic condition. Figure 6.14c shows that one TiO₂ sphere loosely contacts on the edge of one GO sheet. In addition, one piece of GO sheet detached from the membrane can be observed in Figure 6.14d. Consequently, the charge separation rate of GO/TiO₂ membrane decreased significantly after GO sheets detached from the membrane, which reduced the photodegradation efficiency. The undegraded HA could form a fouling layer quickly on the membrane, reducing the permeate flux and quality. Moreover, dissociative GO sheets could also block the pore of GO/TiO₂ membrane and prevent the penetration of UV light as well as permeation of water molecules, which would further worsen the water purification performance. On the other hand, TiO₂ spheres

were still tightly linked together by GO-SO₃H sheets after working under alkaline wastewater condition, as explained by the TEM images of Figure 6.14a and b. The linkage between TiO₂ and GO-SO₃H can be clearly identified in Figure 6.14b, indicating that the coordination bond between the Ti center of TiO₂ and the sulfonic acid group of GO-SO₃H is strong enough to withstand the basic environment. Hence, the above reasons provide strong evidences that GO-SO₃H/TiO₂ membrane can be ideal candidate in the practical water purification industry.

Figure 6.14 (a) Low and (b) high magnification TEM images of GO-SO₃H/TiO₂ after water purification under pH=11; (c) Low and (d) high magnification TEM images of GO /TiO₂ after water purification under pH=11.

6.3 Conclusions

In summary, a new multifunctional GO-SO₃H/TiO₂ membrane was fabricated for wastewater purification. GO sheets were firstly functionalized by introduction of -SO₃H groups. GO-SO₃H sheets act as “polymer binders” to crosslink hierarchical TiO₂ spheres together. GO-SO₃H/TiO₂ membrane acquires better flexibility than pure inorganic membrane due to the existence of GO-SO₃H. In addition, this membrane shows excellent photodegradation activity towards water pollutants during water purification process. Particularly, this kind of membrane can tolerate different wastewater quality without damage, including strong acid and basic conditions, because of the special bonds between GO-SO₃H and TiO₂. The outstanding properties of GO-SO₃H/TiO₂ membrane endow it with high water flux and no membrane fouling. Successful fabrication of this novel membrane opens up a promising avenue for practical clean water production.

CHAPTER 7: A SUPERHYDROPHILIC SULFONATED GRAPHENE OXIDE-TiO₂ MEMBRANE FOR EFFICIENT OIL-WATER SEPARATION

7.1 Introduction

Ceramic porous membranes is a good choice for oil-water separation, due to their relatively hydrophilic property (Wen et al., 2013). However, all reported hydrophilic membranes are incapable of separating surfactant stabilized oil-in-water emulsions, mainly due to their intrinsic drawback of large pore sizes (usually more than one micrometre) in their selected porous matrix. In addition, another weakness caused by the large pore sizes in their membranes is that the low breakthrough value, which constrains their operations only under gravity rather than pressure (Kota et al., 2012). It is well known that, compared with pressure-driven processes, gravity-driven processes for oil-water separation needs an additional time for de-emulsification, which subsequently results in low productivity in comparable time. Therefore for practical oil-water separation, it makes more sense to fabricate a pressure-driven, instead of gravity-driven, hydrophilic membrane. In addition, the poor mechanical flexibility and prohibitively high cost severely limit the wide applications of these ceramic membranes. Flexibility property is critically important for membrane applications, because the majority of current industrial applications adopt the spiral-wound type of membrane modules, in which the membranes can be rolled up and subsequently the required footprint can be significantly reduced. Therefore, it has been strongly desired to develop a novel membrane with both flexible and highly hydrophilic properties for effectively separating surfactant stabilized oil-in-water emulsions, with the features of high oil rejection rate, high water permeate flux and low membrane fouling.

In this study, the membrane fabricated in **Chapter 6** was used for efficient separation of surfactant stabilized oil-in-water emulsions. This novel membrane is made of

sulfonated graphene oxide (SGO) nanosheets and hierarchically nanostructured TiO₂ spheres. The reason we chose these hierarchically nanostructured TiO₂ spheres as the building blocks of the membrane is because of their interconnected 3D nanoscale network, superhydrophilic interface, and photocatalytic self-cleaning function, as shown in our previous studies (Pan et al., 2008; Zhang et al., 2009; Bai et al., 2010). Wherein, the nanoscale pore structure will ensure them with high oil rejection rate, and superhydrophilic interface and photocatalytic self-cleaning function will collectively ensure them with ultralow membrane fouling. In this study, for the first time, we demonstrated a flexible and superhydrophilic SGO-TiO₂ membrane is capable for the effective separation of both free oil-water mixtures and surfactant stabilized oil-in-water emulsions.

7.2 Results and discussion

7.2.1 Surface roughness and wetting behaviour of SGO-TiO₂ membrane

Generally, the wettability of a membrane depends on both the chemical composition and the geometrical structure (surface roughness) (Kou and Gao, 2011; Liu et al., 2012; Wen et al., 2013). A high surface roughness enhances the hydrophilic property of the solid surface according to the equation: $\cos\theta_a = r\cos\theta$ (θ_a is the apparent water contact angle (CA) on a rough surface, θ is the CA on a smooth surface and r is the surface roughness factor) (Liu and He, 2008; Kou and Gao, 2011). The 2D AFM image in Figure 7.1a shows that the SGO-TiO₂ membrane surface is very dense without observable gaps. In addition, the 3D AFM image shows that the SGO-TiO₂ membrane surface is quite rough with about 250 nm undulation ranges, as shown in Figure 7.1b. The high roughness can enhance the hydrophilic property (Xue et al., 2011). Figure 7.1c and d show the water CA and underwater oil CA of this membrane, respectively. A nearly zero (0°) water CA and ~152° underwater oil CA are obtained, demonstrating the surface of this SGO-TiO₂ membrane is superhydrophilic and underwater superoleophobic. A high-speed camera system was used to record the

Figure 7.1 (a) 2D and (b) 3D AFM images of SGO-TiO₂ membrane, respectively; (c) Photograph of a water droplet on the membrane surface showing nearly zero contact angle; (d) Photograph of an underwater oil droplet (DCM) on the membrane surface showing contact angle of ~152°; and (e) Wetting values as a function of deposited time showing a water droplet spreading quickly on the membrane within 0.099 s.

spreading process of a water droplet to investigate the wetting behavior of water on the SGO-TiO₂ membrane, as shown in Figure 7.1e. A water droplet (3 μL) spreads out

very quickly when it contacts the membrane surface, and the whole process is completed less than 0.1 s, indicating a superior property of this membrane for water wetting. These specific surface properties are favorable for water permeation, while rejecting oil.

7.2.2 Separation of free crude oil-water mixture

The oil-water separation activity of SGO-TiO₂ membrane was firstly investigated by separation of free crude oil-water mixture. The crude oil-water separation process was carried out as shown in Figure 7.2. Firstly, the SGO-TiO₂ membrane was put between the filtration cup and bottle. Then, the crude oil-water mixture was put in the filtration cup. Water quickly permeated through the membrane when the vacuum pump was turned on, while the crude oil was rejected on the surface due to the superhydrophilic and underwater superoleophobic properties of this novel membrane, as shown in Figure 7.2.

Figure 7.2 Digital photos of separation process of free crude oil-water mixture.

7.2.3 Separation of surfactant stabilized oil-in-water emulsions

The oil-water separation performance of the novel SGO-TiO₂ membrane was further investigated by separating several kinds of surfactant stabilized oil-in-water emulsions with droplet sizes in the nanometer and micrometer scales, including toluene-in-water,

crude oil-in-water, and vegetable oil-in-water. The separation mechanism was schematically illustrated in Figure 7.3a, wherein, water can easily permeate through this novel membrane, while oil droplets are rejected due to the underwater superoleophobic interface and nanoscale pore size. Figure 7.3b shows the process for the separation of toluene-in-water emulsion. Initially, toluene-in-water emulsion was put in the filtration cup of the filtration system. The water (the red color is originated from RhB indicator) permeated through the membrane quickly when the vacuum pump was turned on, while toluene was repelled by the membrane, due to the superhydrophilic and underwater superoleophobic properties of this membrane. The separation efficiencies of this novel membrane with different oil-in-water emulsions are shown in Figure 7.3c. Remarkably, this membrane exhibits extremely high separation efficiency ($> 99.9\%$) with all investigated surfactant stabilized oil-in-water emulsions, including 99.92% for toluene-in-water, 99.94% for crude oil-in-water, and 99.91% for vegetable oil-in-water. In addition, optical microscopy was adopted to observe the droplets in the feed of toluene-in-water emulsion and the permeate to further confirm the high separation efficiency of this novel SGO-TiO₂ membrane towards surfactant stabilized oil-in-water emulsions. Typically, the surfactant (Triton) plays a vital role in the oil-in-water emulsions. The size of oil droplets is in the range of 1 to 50 μm without surfactant, as shown in Figure 7.3. However, the size of oil droplets was significantly reduced when the surfactant was added, and the average droplet size is about 200 nm, as shown in the left side of Fig. 3d. The droplet size distribution was confirmed by dynamic light scattering (DLS) measurements, as shown in Figure 7.5. After the separation process, no droplets are observed in the collected permeate (right side of Figure 7.3d), confirming this SGO-TiO₂ membrane is highly efficient to separate the surfactant stabilized oil-in-water emulsions with oil droplet sizes less than 1 μm .

Figure 7.3 (a) The schematic illustration of the structure of the novel SGO-TiO₂ membrane and the process of oil-water separation. It shows water can permeate

through the membrane while oil cannot; (b) Digital photos: (left) before separation of toluene-in-water emulsions and (right) after separation of toluene-in-water emulsions with the novel SGO-TiO₂ membrane; (c) separation efficiencies of different oil-in-water emulsions; (d) Optical microscopy images of toluene-in-water emulsions before and after oil-water separation with the novel SGO-TiO₂ membrane. Left side is the optical microscopy image of toluene-in-water emulsions before separation showing the size of oil droplets is around 200 nm; middle is digital photos of toluene-in-water emulsions before and after oil-water separation; right side is the optical microscopy image of toluene-in-water emulsions after oil-water separation showing no oil droplets can be observed.

Figure 7.4 (a) Optical microscopy images of toluene-in-water emulsions without surfactant showing the size of the oil droplets is in the range of 1-50 μm ; and (b) DLS data of toluene-in-water emulsions without surfactant confirming the size of the oil droplets is between 1 and 50 μm .

Figure 7.5 (a) DLS data of the feed emulsions for surfactant-stabilized emulsions of toluene-in-water showing the oil droplet size is around 200 nm; and (b) DLS data of the corresponding filtrate for surfactant-stabilized emulsions of toluene-in-water showing no oil droplets around these ranges are observed (the peak around 400 μm is an error signal caused by the machine).

7.2.4 Self-cleaning property of SGO-TiO₂ membrane

Membrane fouling significantly restricts the application of membrane in oil-water separation and water purification fields. In the presence of water soluble or unsoluble organic matters, they tend to deposit on the surface of membrane, which greatly reduces the water flux. TiO₂ is a well-known photocatalytic material which can generate strong reactive species, including hydroxyl radicals and superoxide anions, under UV irradiation. In addition, the photocatalytic activity can be enhanced due to the presence of SGO sheets which can facilitate the charge separation rate. Theoretically, the membrane fouling of this novel SGO-TiO₂ membrane can be eliminated because the organic matters can be decomposed by the reactive species. In this work, the capability of this novel SGO-TiO₂ membrane for separation of contaminant contained oil-in-water emulsions was investigated by immersing the membrane into the oleic acid/acetone solution, as shown in Figure 7.6a. After oil/water separation, the superhydrophilic property of the membrane was destroyed because the membrane was contaminated by oleic acid. The membrane showed a hydrophobic property with a water contact angle of $\sim 100^\circ$, as shown in Figure 7.6b. After UV irradiation, the membrane could totally restore its superhydrophilicity, with a water contact angle of $\sim 0^\circ$, as shown in Figure 7.6c. These results indicate that this

novel membrane can be applied in practical oil-water separation process.

Figure 7.6 (a) Changes of water CA before and after UV irradiation during 6 cycles; (b) Photograph of a water droplet on the membrane surface showing a water CA of $\sim 100^\circ$ because of oleic acid contamination before UV irradiation; and (c) Photograph of a water droplet on the membrane surface showing a water CA of $\sim 0^\circ$ after UV irradiation, indicating the membrane can restore its superhydrophilicity.

7.2.5 Practical oil-water separation activity of SGO-TiO₂ membrane

To investigate the practical oil-water separation ability, this novel SGO-TiO₂ membrane was adopted to separate the crude oil-in-water emulsions at different temperature and ionic concentration. Figure 7.7a shows that the separation efficiency of this novel membrane slightly decreases with increasing the temperatures of the

crude oil-water mixture, which is attributed to that the solubility of oil in water is higher at higher temperatures(Wan et al., 1990). The separation efficiency at 40 °C is slightly decreased from 99.94% to 99.91%, indicating the applicability of this membrane in a wide temperature range. Different concentrations of NaCl solutions were mixed with crude oil to investigate the effects of ionic concentrations on the separation efficiency of this membrane. Figure 7.7b shows that the concentration of NaCl has almost no influence on the separation efficiency, and the overall separation efficiency can reach as high as 99.94%. The above results demonstrate that this novel SGO-TiO₂ membrane can be applied in industrial oily wastewater treatment and marine oil spill cleanup.

Figure 7.7 (a) Separation efficiency of crude oil-in-water emulsions at different temperature; and (b) Separation efficiency of crude oil-in-water emulsions at different ionic concentration.

7.3 Conclusions

In conclusion, a mechanically flexible, superhydrophilic, underwater superoleophobic and self-cleaning SGO-TiO₂ membrane was successfully fabricated. We demonstrated that this novel membrane had the ability for separating both free oil-water mixture and surfactant stabilized oil-in-water emulsions with high separation efficiency in terms of oil rejection rate. More importantly, the membrane presents an excellent anti-oil fouling and self-cleaning property for long term operation. Therefore, this novel membrane is promising for numerous applications, such as for treating oily

wastewater from petroleum industry, bilge water and oil spills, especially those stabilized by surfactants.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This study aimed to design and fabricate a multifunctional GO-TiO₂ composite membrane for efficient wastewater purification and oil-water separation. Firstly, various TiO₂ nanostructures were synthesized to investigate the effects of morphology on the photocatalytic activity and find out the optimal TiO₂ nanostructure. Subsequently, GO-TiO₂ composites were prepared by combining GO with the optimal TiO₂ nanostructure to further enhance the photocatalytic performance of TiO₂ by facilitating the charge separation rate and increasing the light absorption ability. Thereafter, a novel hierarchical GO-TiO₂ membrane was fabricated by using as-synthesized GO-TiO₂ composites for wastewater purification. Finally, the GO-TiO₂ membrane was modified by introducing the sulfonated functional groups into GO sheets to overcome the limitations of the as-fabricated GO-TiO₂ membrane. Hence, the multifunctional SGO-TiO₂ membrane was delicately designed and fabricated for wastewater purification under different pH conditions and oil-water separation.

Various TiO₂ nanostructures were synthesized firstly, including 1D TiO₂ nanotube, 1D TiO₂ nanowire, 3D TiO₂ sphere-P and 3D TiO₂ sphere-S. The photocatalytic activities of these TiO₂ nanostructures were evaluated in detail by photodegradation of AO7 dye to investigate the influences of morphology and nanostructure on the photocatalytic activity. The results indicated that TiO₂ sphere-S possessed the best photodegradation efficiency, which degraded 100% of AO7 dye within 35 min under UV irradiation. The excellent photodegradation activity of TiO₂ sphere-S can be attributed to the hierarchical porous structure and efficient light harvesting originated from multi-reflection and scattering of incident light. Subsequently, GO-TiO₂ composites were synthesized by mixing GO sheets with TiO₂ sphere-S under ultrasonic condition. GO-TiO₂ composites exhibited outstanding photodegradation and disinfection

activities under solar light irradiation, which degraded more than 90% of AO7 dye and killed about 100% of *E. coli* cells during 60 min. The enhanced photocatalytic performances of GO-TiO₂ composites could be attributed to the enhanced light absorption and retarded charge recombination because of the strong interaction between GO sheets and TiO₂ sphere-S. Hence, this study shows that optimizing the nanostructures of TiO₂ and combining with GO sheets are two promising approaches to improve the photocatalytic efficiency of TiO₂. In addition, as-synthesized GO-TiO₂ composites can be excellent candidates in photocatalytic wastewater purification field.

The processes of separating and recycling of GO-TiO₂ composites after wastewater purification are tedious and not efficient. The residual GO-TiO₂ composites remain as secondary pollutants. Hence, in the following work, a novel hierarchical GO-TiO₂ membrane was fabricated by using as-synthesized GO-TiO₂ composites to eliminate the post separation process. The GO-TiO₂ membrane was uniformly assembled on the surface of polymer membrane through filtration of the GO-TiO₂ suspension. The results demonstrated that this novel membrane obtained enhanced strength and flexibility than traditional TiO₂ membrane because GO sheets acted as cross linkers to combine TiO₂ microspheres. In addition, this membrane showed multifunctional properties for concurrent water filtration and photodegradation during wastewater purification process: (1) high photocatalytic activity towards both RhB and AO7 dyes; (2) high water flux; and (3) eliminating membrane fouling in a long time. The excellent activities of GO-TiO₂ membrane can be attributed to high specific surface area and porous structure of GO-TiO₂ membrane, and highly efficient charge separation property. Hence, this study indicates that GO-TiO₂ membrane can be promising candidate in the membrane based wastewater purification field.

However, the as-fabricated GO-TiO₂ membrane can only treat wastewater with pH below 7. In order to meet the requirements of treating wastewater with different pH conditions, the membrane was further modified. In the next study, a novel multifunctional sulfonated GO-TiO₂ (GO-SO₃H/TiO₂) membrane was delicately

designed and fabricated for the first time. Firstly, GO-SO₃H sheets were synthesized by introducing -SO₃H groups into GO sheets in sulfonation reaction. It should be noted that GO-SO₃H sheets were stable under different conditions, which offers a critical opportunity to fabricate a pH tolerance membrane. In this novel membrane, GO-SO₃H sheets acts as linkages like “polymer binders” to combine TiO₂ spheres by forming connections between -SO₃H groups and TiO₂. The results indicated that the strong interactions between GO-SO₃H and TiO₂ enhanced the strength and flexibility of this membrane. In addition, this novel membrane showed high water flux without membrane fouling because of the high photodegradation efficiency in removing NOMs (HA). Most importantly, this membrane performed efficiently in different wastewater quality with a wide pH range because of the special coordination bond between GO-SO₃H sheets and TiO₂ spheres. Furthermore, GO-SO₃H/TiO₂ membrane kept a high water flux and anti-fouling activity even under pH=11, while the unmodified GO-TiO₂ membrane was destroyed under this condition. Consequently, this novel GO-SO₃H/TiO₂ membrane multifunctional membrane opens up a promising avenue for practical wastewater purification.

In the subsequent work, the as-fabricated GO-SO₃H/TiO₂ (SGO-TiO₂) membrane was further applied in oil-water separation field considering the increasingly oily wastewater from the industries and occasional marine oil spills. The SGO-TiO₂ membrane exhibited extremely high efficiency of separating various oil-water mixtures, including free oil-water mixtures and surfactant stabilized oil-in-water emulsions due to the superhydrophilic and underwater superoleophobic properties. In addition, this pressure-driven SGO-TiO₂ membrane greatly reduced the time of de-emulsification, compared with conventional gravity-driven membranes. Furthermore, the SGO-TiO₂ membrane showed outstanding anti-oil fouling and self-cleaning activities because of the strong photocatalytic ability under UV irradiation, which endowed the long term applicability of this membrane. Hence, this SGO-TiO₂ membrane is suitable for treating various oil-water mixtures, such as oily wastewater from petroleum industry, bilge water and oil spills.

In summary, four kinds of TiO_2 nanostructures were synthesized for photodegradation of organic pollutants. It was found that the photocatalytic activity of TiO_2 can be enhanced by controlling the morphology of TiO_2 and adding GO sheets. In addition, the GO- TiO_2 membrane was fabricated by using the as-synthesized GO- TiO_2 composites for wastewater purification. Furthermore, a novel SGO- TiO_2 membrane was fabricated by modification of GO sheets. The results demonstrated that this multifunctional SGO- TiO_2 membrane was suitable for numerous applications, such as treating NOMs and bacteria contained wastewater, and oily wastewater even under different pH conditions. This study can be a good reference for the future development of novel membranes for wastewater purification and oil-water separation.

8.2 Recommendations

In this work, a novel multifunctional membrane was fabricated for wastewater purification and oil-water separation. Some future works are needed to complement this study to expand this membrane to practical applications. The recommendations include the following aspects:

1. The anti-fouling properties of the membranes were only investigated using NOMs and oils as standard pollutants. Other fouling types could be studied in the future, including colloidal fouling, bio-fouling and etc.
2. The activities of the fabricated membranes were investigated under UV light irradiation, which was energy intensive. Considering the high cost of energy input, the future investigation of this membrane could be carried out under visible light.
3. The experiments of this work were performed in lab at “bench scale”. The future studies could be carried out at “pilot scale” to evaluate the performance in practical applications.

4. This novel membrane could be applied for other applications, such as photocatalytic hydrogen production and solar cells.

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