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TiO₂ NANOCOMPOSITE PHOTOCATALYSTS FOR WATER DISINFECTION AND DECONTAMINATION UNDER SOLAR IRRADIATION

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SUMMARY

The ever increasing standards for providing clean water have put more stress on water disinfection and decontamination technologies. TiO₂-based photocatalytical treatment has become a promising water purification technology. Currently there are still problems for the existing TiO₂-based photocatalysts which limit its wide industrial applications for water treatment. This study is intended to develop a group of novel TiO₂ nanocomposite photocatalysts to solve the drawbacks of current TiO₂ photocatalysts. The photocatalysts synthesized in this study have superior features favorable for water purification: (1) high photocatalytic efficiency; (2) easy recovery from treated water; (3) sensitive to solar light; (4) long-term antibacterial activity even without light irradiation.

This study initiated from electrospinning of TiO₂ nanofibers. Ag nanoparticles were then introduced to the as-prepared TiO₂ nanofibers (band gap wavelength 380 nm) to form Ag/TiO₂ nanofiber composites (more than 400 nm) for the subsequent fabrication of Ag/TiO₂ nanofiber membrane, and characterized by SEM, XRD, EDS and UV-Vis analysis. Results confirmed that Ag nanoparticle deposition has enhanced the photocatalytic activity of TiO₂ nanofibers under solar irradiation, as well as provided intrinsic antibacterial capability. The Ag/TiO₂ nanofiber membrane/solar irradiation system achieved 3 log *E.coli* inactivation and 80 % dye (methylene blue (MB), 10 ppm) degradation within 30 min. This system has shown its advantages in cost effective water purification applications.

In order to further improve the photocatalytic efficiency of TiO₂, the small sized TiO₂ nanorods were introduced to incorporate with graphene oxide (GO) and Ag nanoparticles to form novel multifunctional nanocomposites (GO-TiO₂-Ag). At the first stage, binary GO-Ag nanocomposites were synthesized through a facile two-phase (toluene-water) method and confirmed by TEM, XRD, and XPS analysis. The GO-Ag nanocomposites showed an enhanced antibacterial activity compared with Ag nanoparticles, and photodegradation activity toward dye (acid orange (AO 7)) under

visible light irradiation. Based on this, ternary GO-TiO₂-Ag nanocomposites were synthesized via the same method. The GO-TiO₂-Ag nanocomposites demonstrated enhanced photocatalytic activities under solar irradiation compared with GO-TiO₂ and GO-Ag, with 100 % AO 7 and phenol removal (10 ppm) at 80 min and 4 h, respectively. The nanocomposites also exhibited superior intrinsic antibacterial activity toward *E.coli*, as well as enhanced photo-biocidal capability in a comparison to GO-TiO₂ and GO-Ag, with 3 log and 8.24 log *E.coli* removal at 30 min and 60 min, respectively. This high photocatalytic performance of GO-TiO₂-Ag nanocomposites makes them promising candidates in water purification applications.

To further enhance the solar utilization of the TiO₂ nanocomposite photocatalysts, a novel Ag₃PO₄ semiconductor was introduced to take over Ag nanoparticles to provide both visible light photocatalysts and antibacterial property. At present state, binary GO-Ag₃PO₄ nanocomposites as visible light photocatalysts have been fabricated through an ion-exchange method, and confirmed by SEM, EDS and XRD analysis. The GO-Ag₃PO₄ nanocomposites exhibited significantly higher photocatalytic activities under visible light irradiation compared with bare Ag₃PO₄, with 100 % AO 7 (50 ppm) and phenol (10 ppm) removal at only 10 min and 20 min, respectively. The GO-Ag₃PO₄ nanocomposite also showed both superior intrinsic antibacterial and visible light induced photocatalytic disinfection activities toward *E.coli*. Such binary GO-Ag₃PO₄ nanocomposites may find promising applications in water purification applications. This work proves the feasibility of synthesis and applications of ternary GO-TiO₂-Ag₃PO₄ nanocomposites in future.

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Journal

1. **Lei Liu**, Hongwei Bai, Jincheng Liu and Darren D. Sun. Multifunctional graphene oxide-TiO₂-Ag nanocomposites for high performance water disinfection and decontamination under solar irradiation. *Journal of Hazardous Materials*, 2013, 261, 214-223.
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5. Hongwei Bai*, **Lei Liu***, Zhaoyang Liu and Darren D. Sun. Hierarchical 3D dendritic TiO₂ nanospheres building with ultralong 1D nanoribbon/wires for high performance concurrent photocatalytic membrane water purification. *Water Research*, 2013, 47, 4126-4138. (* those authors contribute equally)
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7. Hongwei Bai, Zhaoyang Liu, **Lei Liu** and Darren D. Sun. Scale-up production of hierarchical TiO₂ nanorod spheres for photocatalytic eliminating contaminants and killing bacteria. *Chemistry-A European Journal*, 2013, 19, 3061-3070.

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Conference

1. **Lei Liu**, Hongwei Bai, Zhaoyang Liu and Darren D. Sun. Hierarchical 3D dendritic TiO_2 microspheres with nanoribbon/wires for concurrent photocatalytic water purification and membrane filtration. IWA Symposium on Environmental Nanotechnology, Nanjing, China, April 24-27, 2013.

2. **Lei Liu**, Jincheng Liu and Darren D. Sun. Disinfection and decontamination using novel Ag_3PO_4 -based photocatalyst under visible light irradiation. Water Convention, Singapore International Water Week (SIWW), Singapore, 1-4 July 2012.
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LIST OF ABBREVIATIONS AND SYMBOLS

0D: zero-dimensional

1D: one-dimensional

2D: two-dimensional

AgX (X= Br, Cl, I): silver halides

Ag₂O: silver oxide

Ag₂S: silver sulphide

Ag₃PO₄: silver orthophosphate

AO7: acid orange 7

AOPs: advanced oxidation processes

AFM: atomic force microscopy

cfu/mL: colony forming units per milliliter

CNTs: carbon nanotubes

CQDs: carbon quantum dots

DBPs: disinfection by-products

DMSO: dimethyl sulphoxide

DI: deionized

EG: ethylene glycol

EDS: energy dispersive detector

EPA: Environmental Protection Agency

FESEM: field emission scanning electron microscopy

GO: graphene oxide

HAP: hydroxyapatite

HRTEM: high-resolution transmission electron microscopy

H₂O₂: hydrogen peroxide

ICP: inductively coupled plasma

LB: Luria-Bertani nutrient

MB: methylene blue
MBR: membrane bioreactor
MF: microfiltration
NF: nanofiltration
nAg: silver nanoparticles
nC₆₀: fullerene nanoparticles
NOMs: natural organic matters
·O₂⁻: oxygen radicals
·OH: hydroxyl radicals
OLA: oleic acid
PBS: phosphate buffer
PCO: photocatalytic oxidation
PVP: polyvinylpyrrolidone
RGO: reduced graphene oxide
RO: reverse osmosis
ROs: reactive oxygen species
SEM: scanning electron microscopy
TEM: transmission electron microscopy
THF: tetrahydrofuran
THMs: trihalomethanes
TMP: trans-membrane pressure
TOC: total organic carbon
TTIP: titanium tetraisopropoxide
UF: ultrafiltration
UNICEF: United Nations International Children's Emergency Fund
USEPA: The United States Environmental Protection Agency
UV-Vis: ultraviolet-visible
WHO: World Health Organization
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction

CHAPTER 1: INTRODUCTION

1.1 Background

One of the most severe problems throughout the world is inadequate access to clean and safe water (Shannon, Bohn et al. 2008). It has been reported that lots of people suffered from the lack of clean water: 2.6 billion have little or no sanitation, 1.2 billion people lack access to safe drinking water, and millions of people die annually from diseases transmitted through unsafe water (Montgomery and Elimelech 2007). Even more are affected from diseases and contaminations. Diseases caused by waterborne bacteria and viruses have devastating effects on public health (Lima, Moore et al. 2000). Meanwhile, in both developing and developed nations, more and more new contaminants as emerging micropollutants are introduced into the water bodies (Wintgens, Salehi et al. 2008). These contaminants are known to be very harmful to humans and environment, which cause the public health and environmental concerns globally. Large amount of efforts have been devoted in searching for better technology for disinfection and decontamination of the polluted water bodies.

Conventional methods for water disinfection and decontamination can solve many of these problems. However, these treatment methods usually require large amount of energy, chemicals and land space. Thus it also involves considerable infusion of capital, engineering expertise and infrastructure, all of which precludes their wide use, especially in developing countries. Furthermore, intensive chemical treatments including the use of ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, alum and ferric salts, coagulation and filtration aids, anti-scalants, corrosion control chemicals, ion exchange resins and regenerants, and residuals resulting from treatments such as sludge, brines, toxic waste, can potentially cause problems to the environment (Shannon, Bohn et al. 2008). More effective, robust, low-cost methods to disinfect and decontaminate water from source to point-of-use are

urgently needed, without further stressing the environment or endangering human health by the treatment itself.

Advanced oxidation processes (AOPs) are considered as the most widely used water treatment technologies in the near future, as it can be used not only for decontamination of organic micropollutants in water but also for disinfection to remove pathogens (Gogate and Pandit 2004; Gogate and Pandit 2004; Blanco-Galvez, Fernandez-Ibanez et al. 2007). AOPs rely on the formation of highly reactive hydroxyl radicals ($\cdot\text{OH}$), which can - degrade many of the most recalcitrant molecules and microorganisms. On one hand, the radicals generated from AOPs are not-selective, which are useful for wastewater treatment and provide solutions for pollution problems (Comninellis, Kapalka et al. 2008). On the other hand, there are different $\cdot\text{OH}$ radical generation methods from AOPs, which can be adapted to specific treatment requirements. Many oxidation processes, such as TiO_2/UV , $\text{H}_2\text{O}_2/\text{UV}$, Photo-Fenton, and ozone (O_3 , O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$) are currently employed for decontamination and disinfection of polluted water (Malato, Fernandez-Ibanez et al. 2009). However, the high cost is the main disadvantage for AOPs applications due to the use of UV lamps or/and ozone production (Munoz, Rieradevall et al. 2005). Therefore, there is a need in searching for cost-effective AOP technologies particularly by using solar irradiation.

Semiconductor-mediated heterogeneous photocatalysis is one of the promising AOPs for water purification, as it can be potentially used under solar irradiation without generating harmful by-products (Mills, Davies et al. 1993; Hoffmann, Martin et al. 1995). Various semiconductor-based photocatalysts have been explored, including metal oxides and sulphides such as TiO_2 , ZnO , CdS , ZnS , CdS and their derivatives (Mills and LeHunte 1997). Among these semiconductors, TiO_2 is regarded as the most efficient and toxic-free environmental friendly photocatalyst due to its unique properties of chemical stability, biocompatibility, high photoactivity and readily availability (Linsebigler, Lu et al. 1995; Chen and Mao 2007). Although many papers have been reported on the applications of TiO_2 for environmental purification, till now

TiO₂ has not been widely applied in water industries due to its limitations (Malato, Fernandez-Ibanez et al. 2009).

Lower electron transfer rate to oxygen and higher electron-hole recombination rate are the major limitations which could result in the lower photooxidation rate of organic compounds on photocatalyst surface. Hence the efficiency of the photooxidation of TiO₂ photocatalyst is low (Herrmann 1999). In addition, the wide band gap (3.2 eV for anatase) of TiO₂ photocatalyst restricts the use of visible light. In order to improve the efficiency, some researches introduced the use of nanosized TiO₂ photocatalyst directly. However, the nanosized TiO₂ photocatalyst tend to aggregate in aqueous suspension, leading to a rapid loss in active sites and photocatalytic efficiency (Mills and LeHunte 1997). Furthermore, separation, recovery and reuse of nanosized TiO₂ particulates pose another key obstacle to practical applications.

Therefore, the exploration of high-performance TiO₂-based photocatalysts and reaction systems which can overcome the drawbacks of the existing nanosized TiO₂ particulates, as well as to extend use of visible light (~ 40 % of sunlight) is of significant importance and highly desired. The development of novel TiO₂ nanocomposites integrating TiO₂ nanostructures with different functional nanomaterials may provide good approaches to achieve the above mentioned goals.

1.2 Research questions, Objectives and Significance

The main question left in current research work on TiO₂-based nanocomposite photocatalysts for water purification is how to improve their efficiencies. In this study, the author is trying to answer the following research questions:

- (1) How to synthesize high-performance TiO₂-based nanocomposite photocatalysts?

- (2) What are the efficiencies of the synthesized photocatalysts for water disinfection and decontamination under solar irradiation?
- (3) How to recover and reuse the synthesized photocatalysts?

The overall objective of this study is to develop high-performance TiO₂ nanocomposite photocatalysts for water purification, especially for effective disinfection of waterborne pathogens and decontamination of organic pollutants. In general, the photocatalysts synthesized in this study should have important features: (1) high photocatalytic efficiency; (2) easy recovery from treated water; (3) sensitive to solar light; (4) long-term antibacterial activity even without light irradiation. Based on these features, a group of novel TiO₂-based nanocomposite photocatalysts by integrating TiO₂ nanostructures with silver (Ag)/silver-based nanoparticles or/and graphene oxide (GO) sheets were developed.

Firstly, TiO₂ nanofibers have been introduced with Ag nanoparticles to form Ag/TiO₂ nanofiber composites, for concurrent photocatalytic water purification and membrane filtration, so as to achieve enhanced photocatalytic efficiency, intrinsic antibacterial activity and easy recovery of the nanocomposites. Secondly, to further improve the photocatalytic efficiency of TiO₂, smaller-sized TiO₂ nanorods with higher specific surface area was introduced. Two-dimensional GO structure was introduced as a supporter for nanosized Ag nanoparticles and TiO₂ nanorods to form GO-Ag and GO-TiO₂-Ag nanocomposites, which have multifunction abilities and are able to be used under solar irradiation for decontamination and disinfection of water. Lastly, to further enhance the solar utilization (especially visible light), new visible light induced photocatalyst Ag₃PO₄ has been chosen to be combined with GO to form GO-Ag₃PO₄ nanocomposites for water disinfection and decontamination, and for future study of GO-TiO₂-Ag₃PO₄ nanocomposites purpose.

The detailed objectives of this project are:

- (1) To synthesize and characterize novel TiO₂ nanocomposite photocatalysts as Ag/TiO₂ nanofiber composites, ternary GO-TiO₂-Ag nanocomposites and GO-

TiO₂-Ag₃PO₄ nanocomposites (binary GO-Ag nanocomposites and GO-Ag₃PO₄ nanocomposites were synthesized and studied prior to the study of ternary nanocomposites).

- (2) To investigate the disinfection and decontamination activities of the synthesized nanocomposite photocatalysts under solar/visible light irradiation.
- (3) To study the mechanisms of the interaction between selected pathogens and pollutants and the photocatalysts, and to optimize the strategy of the treatment process.

Significance and benefits of this research are as follows:

The significance of this project is to effectively disinfect and decontaminate water with TiO₂-based solar photocatalysis. The effective solar photocatalysis technologies could provide opportunities to both developing and developed nations for sustainable environmental development particularly in providing high quality of drinking water.

In particular, the main innovations of this study include:

- (1) Fabrication of novel Ag/TiO₂ nanofiber composites for water disinfection and decontamination under solar irradiation and concurrent membrane filtration.
- (2) Synthesis of highly monodispersed Ag nanoparticles on GO sheets, which achieve enhanced water disinfection, and high-performance visible light degradation of dye pollutants.
- (3) Synthesis of multifunctional GO-TiO₂-Ag nanocomposites for highly effective disinfection and decontamination of water under solar irradiation.
- (4) Synthesis of novel GO-Ag₃PO₄ nanocomposites as a highly efficient and stable visible light induced photocatalyst for water purification.

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

1.3 Thesis overview

This thesis comprises of 8 chapters. **Chapter 1** is the introduction, which gives a brief introduction to the research background, objectives and significance of the works, and the organization of the report. **Chapter 2** covers the literature review about the development of disinfection and decontamination technologies, the TiO₂-based AOPs in water treatment applications, the limitations and the approaches for improvement of TiO₂ photocatalysts. Recent development of solar photocatalysis is also included. The development of graphene-based hybrid nanomaterials for water treatment is also included in this chapter.

Chapter 3 is the materials and methodology, which introduces the common chemicals and materials, detailed material synthesis and characterization techniques applied in this study. The detailed disinfection and decontamination evaluation experiments are also included in this chapter.

Chapter 4 reports the preparation and characterization of Ag/TiO₂ nanofiber composites, and its application for concurrent water photocatalytic disinfection/degradation under solar irradiation and membrane filtration.

Chapter 5 investigates the synthesis of GO-Ag nanocomposites by a facile two-phase method, and its application for bacterial inactivation. The dye degradation over the GO-Ag nanocomposites was also evaluated and discussed.

Based on the research of Chapter 5, **Chapter 6** further reports on the preparation and characterization of multidimensional GO-TiO₂-Ag nanocomposites via the same method used in Chapter 5. The disinfection of bacteria and decontamination of organic pollutants over the synthesized nanocomposites were evaluated and discussed.

Chapter 7 presents the synthesis of novel GO-Ag₃PO₄ nanocomposites as visible light induced photocatalysts, and their applications for water disinfection and decontamination.

Chapter 8 covers the conclusions and recommendations.

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

CHAPTER 2: LITERATURE REVIEW

2.1 Water disinfection technologies

To provide high quality drinking water through affordable and robust disinfection processes without any disinfection by-products are the serious challenges for today's water industry. Waterborne pathogens have a devastating effect on public health. According to the World Health Organization (WHO) and United Nations International Children's Emergency Fund (UNICEF), polluted drinking water and lack of sanitation are responsible for the death of approximately 4500-5000 children every day (WHO 2007). Waterborne infectious agents include a variety of protozoa, fungi, bacteria, helminthes, viruses (WHO 2003). While some infectious agents have been eradicated or diminished, new ones continue to emerge, hence disinfecting water has become more and more challenging.

The existing drinking water treatment processes such as coagulation, flocculation, and sedimentation can remove up to 90 % of bacteria, 70 % of viruses and 90 % of protozoa. Filtration processes (e.g. granular, slow sand, precoat and membrane filtration) with proper design and adequate operation, can act as a consistent and effective barrier for microbial pathogens removal, which are able to remove approximately 99 % of bacteria (Malato, Fernandez-Ibanez et al. 2009). However, depending on the water source, the remaining bacteria or viruses might still be able to cause diseases. Therefore, a completely safe drinking water disinfection technique is required.

Water disinfection is mainly achieved by destroying the microorganisms, and this mechanism involved is most commonly understood as the destroying of the organism protein structure and inhibition of the enzymatic activities (Lawrence and Block 1983). The commonly used drinking water disinfection techniques including chlorination (chlorine and its derivatives), ozonation and UV-C are safest against most of infectious

agents. However, there still exist some drawbacks of the traditional disinfection techniques, which calls out for new strategies of better disinfection technologies for high-quality water production.

2.1.1 Chlorination

Free chlorine is the main disinfectant widely used by the water industry because of its potency and low cost. It can effectively inactivate most of the bacteria and enteric viruses (WHO 2006). However, free chlorine is ineffective in controlling waterborne pathogens such as *C.parvum* and *Mycobacterium avium*, the latter of which is ubiquitous in biofilms within water distribution system (Shannon, Bohn et al. 2008). Another alarming disadvantage of free chlorine is the appearance of its disinfection by-products (DBPs), organohalides, especially trihalomethanes (THMs) in chlorinated drinking water. Organohalides were first found in the 1970s. Recently organohalides have also been found to be potentially mutagenic and carcinogenic to human health (Yang and Cheng 2007; Lu, Zhang et al. 2009). Till now, more than 600 DBPs have been reported in the literature (Krasner, Weinberg et al. 2006). Considering the mechanisms of DBPs formation, it has been predicted that DBPs will be formed once the chemical oxidants are used in water treatment. Recent US disinfection regulations require the control of *C. parvum* oocysts while minimizing the formation of certain DBPs, which might force some drinking water utilities to abandon free chlorine disinfection technique for the implementation of alternative technologies (United States Environmental Protection Agency. 40 CFR Parts 9 2006; United States Environmental Protection Agency. 40 CFR Parts 9 2006).

Chlorine dioxide is one of the alternative disinfection processes instead of free chlorine. The strong oxidation property of chlorine dioxide can be used for disinfection process to destroy most of the pathogens, and at the same time to provide a stable residual for secondary disinfection during water transfer. Importantly, chlorine dioxide does not react with natural organic matter to form THM. However, other DBPs as un-reacted

chlorite ions and chlorate ions may have possible adverse health effects (Aranda-Rodriguez, Koudjonou et al. 2008).

Chloramine is commonly used as a secondary disinfectant in municipal water distribution systems as an alternative to free chlorine. As a low-cost control option for the THM Rule (McGuire and Meadow 1988), chloramine has been increasingly used to control the formation of THMs. However, chloramine is a weak disinfectant against viruses and cysts. Besides, adding chloramines to the water may increase health risks to human (Miranda, Kim et al. 2007). Chloramination is associated with the formation of nitrosamines (commonly detected as N-nitrosodimethylamine (NDMA)), which are emerging by-products of health and regulatory concern (Mitch, Sharp et al. 2003). Although the N-nitrosamines are present at significantly lower concentrations (nanogram per litre) than the regulated drinking water DBPs, they are significantly more toxic than the regulated DBPs (Richardson, Plewa et al. 2007). Therefore, the formation of nitrosamines in drinking waters has become a significant concern and been well investigated (Krasner, Mitch et al. 2013; Kristiana, Tan et al. 2013; Doederer, Gernjak et al. 2014).

2.1.2 Ozonation

Ozonation is another alternative for disinfection and odour control in water supplies. Ozone is very effective in controlling *C. parvum* oocysts and viruses. However, ozone can form the DBP carcinogen in water containing bromide ions. The process combining ozone with chlorine can form other unregulated DBPs such as haloacetonitriles and iodoacetic acid, which may be more toxic and carcinogenic than those associated with free chlorine (Krasner, Weinberg et al. 2006; Muellner, Wagner et al. 2007). Besides, the ozonation process requires expensive equipment to generate the disinfectant onsite which is associated with increased costs and process complexity.

2.1.3 Ultraviolet light disinfection

Disinfection by UV is considered as a cost-effective and easily implementable system for drinking water disinfection. UV spectrum is divided into four regions: vacuum UV (100~200 nm), UV-C (200~280 nm), UV-B (280~315 nm), and UV-A (315~400 nm). UV disinfection primarily uses UV-B and UV-C to inactivate microorganisms. Although these UV systems can inactivate most of the bacteria and protozoa at reasonable intensity, it may not effectively inactivate some viruses. Moreover, UV disinfection could not guarantee biological safety of tap water because the effect of UV irradiation could not have the residual effects throughout distribution system (Choi and Choi 2010).

2.1.4 Nanomaterials and silver nanomaterials for disinfection

The rapid growth in nanotechnology has spurred significant interest in the environmental applications of nanomaterials. Nanomaterials are excellent adsorbents, catalysts, and sensors due to their large specific surface area and high reactivity. More recently, several natural and engineered nanomaterials have been shown to display strong antimicrobial properties, including chitosan (Qi, Xu et al. 2004), silver nanoparticles (nAg) (Morones, Elechiguerra et al. 2005), photocatalytic TiO₂ (Cho, Chung et al. 2005), fullerol (Badireddy, Hotze et al. 2007), fullerene nanoparticles (nC₆₀) (Lyon, Adams et al. 2006), and carbon nanotubes (CNT) (Kang, Pinault et al. 2007; Kang, Herzberg et al. 2008). Unlike conventional chemical disinfectants, these antimicrobial nanomaterials are not strong oxidants and are relatively inert in water. Therefore, they are not expected to produce harmful DBPs. If properly incorporated into treatment processes, they have the potential to enhance or replace conventional disinfection methods. The current and potential applications of antimicrobial nanomaterials are summarised in Table 2.1 (Li, Mahendra et al. 2008). Among these, TiO₂ is the most popular materials used for water treatment, because of its high

photocatalytic activity, high stability and low-cost. A detailed introduction of TiO₂-based AOPs will be discussed in chapter 2.3.

Nanomaterial	Antimicrobial mechanism	Current applications	Potential future applications
Chitosan	Membrane damage, Chelation of trace metals	Personal care products, microbicide in agriculture and biomedical products, food wraps, biomedical, flocculants in water and wastewater treatment	Immobilizer of bacteria, enzymes and other biological molecules, biosorbents
nAg	Release of Ag ⁺ ions, disruption of cell membrane and electron transport, DNA damage	Portable water filters, clothing, medical devices, coatings for washing machines, refrigerators, and food containers	Surface coatings, membranes
TiO ₂	Production of ROS, cell membrane and cell wall damage	Air purifiers, water treatment systems for organic contaminant degradation	Solar and UV disinfection of water and wastewater, reactive membranes, biofouling-resistant surfaces
CNT	Physically compromise cell envelop	None	Biofouling-resistant membranes, carbon hollow fibres, packed bed filters
ZnO	Intracellular accumulation of nanoparticles, cell membrane damage, H ₂ O ₂ production, release of Zn ²⁺ ions	Antibacterial creams, lotions and ointment, deodorant, self-cleaning glass and ceramics	Surface coating, mouthwash

Table 2.1 Current and potential applications of antimicrobial nanomaterials (Li and Mahendra et al. 2008).

Silver (Ag) nanoparticles are known to exhibit the highest bactericidal activity and biocompatibility amongst all the antibacterial nanomaterials (Kloepfer, Mielke et al. 2005; Gummy, Morais et al. 2006; Li, Mahendra et al. 2008). Different forms of silver nanomaterials have been developed including Ag nanoparticles (Arora, Jain et al. 2009),

silver chloride particles (Choi, Deng et al. 2008), silver-impregnated zeolite (Cowan, Abshire et al. 2003), silver modified carbon materials (Yoon, Byeon et al. 2008), dendrimer-silver complexes (Lesniak, Bielinska et al. 2005), polymer-silver nanoparticle composites (Damm and Munstedt 2008), silver-TiO₂ nanocomposites (Amin, Pazouki et al. 2009). Silver nanomaterials have been shown to be a broad-spectrum bactericide to bacteria, fungi and viruses (Marambio-Jones and Hoek 2010). Due to their promising antibacterial capability, Ag nanoparticles have attracted numerous studies on its application as an antiseptic, disinfectant and pharmaceutical agent (Kumar, Vemula et al. 2008; Oyanedel-Craver and Smith 2008; Pal, Yoon et al. 2009). To date, the mechanism of anti-bacterial activity of Ag nanoparticles remains debatable which includes: (i) the release of silver ions and the generation of Reactive Oxygen Species (ROSs), and the interaction with membrane proteins which affects the relative function; (ii) adhesion of nanoparticles to the surface leading to the membrane destruction; (iii) the penetration of Ag nanoparticles into bacterial cell, release silver ions and thus affect DNA, resulting in the damage of the cells (Sondi and Salopek-Sondi 2004; Morones, Elechiguerra et al. 2005). The various observed and hypothesized interactions between silver nanomaterials and microorganisms are summarized in Figure 2.1 (Marambio-Jones and Hoek 2010).

Studies have also shown that the toxicity of Ag nanoparticles is size dependent. The smaller sized ones show higher antibacterial activity (< 10 nm) (Morones, Elechiguerra et al. 2005). Since the antibacterial activity of Ag nanoparticles relies on the size of Ag nanoparticles and on the interaction between Ag nanoparticles and the bacteria, monodispersed Ag nanoparticles with uniform small size are desirable for the water disinfection process. Nevertheless, considering the cytotoxicity of the nanoparticle itself, the recovery of Ag nanoparticles without DBPs is of significant importance in water treatment process.

Figure 2.1 Diagram summarizing nano-scaled silver interaction with bacterial cells (Marambio-Jones and Hoek 2010).

2.1.5 Trends of disinfection technologies

The effective control of waterborne pathogens in drinking water calls for the development of new disinfection strategies, including multi-barrier approaches that provide reliable physicochemical removal processes such as coagulation, flocculation, sedimentation and membrane filtration, along with effective photon-based and/or chemical inactivation (Shannon, Bohn et al. 2008). A futuristic disinfection method involves the combined use of photons and engineered nanostructures. Although UV is effective for inactivating waterborne bacteria and protozoa cysts and oocysts, it is not very effective for viral pathogens. However, disinfection processes involving photocatalytic materials such as TiO_2 with UV light is capable of inactivating viruses. Moreover, new photocatalysts such as nitrogen-doped TiO_2 can be activated with visible light, which could potentially inactivate pathogens with much lower energy such as solar than UV (Kang, Zhang et al. 2008). Materials and systems that could

utilize the low-cost visible light and sunlight to achieve sufficiently high throughput disinfection activity are of particular interest.

2.2 Water decontamination technologies

With industrialization and population growth, environmental contamination is becoming an overwhelming problem all over the world. The goal for water decontamination is to remove any toxic substance from water or wastewater affordably and robustly. Depending on the origin of water or wastewater source, the contaminants vary widely, from heavy metals to natural and synthetic organics. This study will focus on the treatment technologies for water pollution caused by organic matter.

2.2.1 Drinking water decontamination technologies

Drinking water or portable water is water of sufficiently high quality that could be consumed directly by human. Besides the waterborne pathogens, natural organic matters (NOMs) are the major contaminants present in drinking water source including rivers, lakes, reservoirs etc (Zularisam, Ismail et al. 2006). NOMs may produce undesirable colour and tastes, form fouling problem during membrane filtration and react with disinfectants to generate carcinogenic DBPs (Wang, Liao et al. 2001; Palmer, Eggins et al. 2002; Zularisam, Ismail et al. 2007). Conventional decontamination methods of drinking water such as adsorption, coagulation and membrane filtration have all been applied for the removal of NOMs. However, these technologies were found to be non-ideal because of low removal rates, high operational cost and high chemical intensity. On the other hand, with industrialization and population growth, more and more contaminants such as emerging anthropogenic organic pollutants, particularly those with high toxicity but at very low concentration,

have put more stress on water treatment, and also driven the conventional technologies to near its limit (Wintgens, Salehi et al. 2008). Advanced oxidation processes (AOPs) may become alternative technologies for decontamination of drinking water, because they may achieve total degradation of organic pollutants without adding stress to the treated water (Lin and Wang 2011).

2.2.2 Wastewater decontamination technologies

Traditional municipal wastewater is treated by activated sludge systems which use suspended microbes to remove organics and nutrients, followed by large sedimentation tanks to separate the solid and liquid fractions. Thus the effluent could be suitable for discharge to surface waters or to some industries with low water quality requirement. Typically, the biological treatment needs large space and long residence times, while certain contaminants in treated water are not removed. With the development of membrane technology, the membrane bioreactor (MBR) is now actively being expanded (Daigger, Rittmann et al. 2005; Yang, Cicek et al. 2006). This technology combines the activated sludge process with microfiltration (MF) or ultrafiltration (UF) membranes, which can produce high-quality effluent that is suitable for unrestricted irrigation and other industrial applications.

Nowadays, as the scarcity of drinking water has become a worldwide problem, the reclamation and reuse of water calls for technology to capture clean water from municipal or industrial wastewaters at potable standards. Current wastewater reuse systems use a conventional activated sludge process, followed by a membrane pre-treatment of the secondary biologically treated effluent, and a subsequent reverse osmosis (RO) system as a final barrier to contaminants, when followed by UV disinfection, as shown in Figure 2.2 (Shannon, Bohn et al. 2008). The membrane fouling problems significantly reduce the lifespan of membranes and increase the cost of the whole process. Futuristic direct reuse systems envisioned involve only two steps: a single-stage of MBR (obviating the need for an RO stage), and a photocatalytic

reactor to provide an absolute barrier to pathogens and to destroy low molecular-weight organic contaminants that may pass through the nanofiltration (NF) barrier (Shannon, Bohn et al. 2008).

Figure 2.2 Membrane bioreactor treatment system for direct conversion to potable water (Shannon, Bohn et al. 2008).

Industrial wastewaters have various compositions depending on the type of industry and materials processed. Some of these wastewaters can be organically strong and easily biodegradable, thus the traditional biological treatment method for the decontamination of such industrial wastewater is used. Nevertheless, with rapid industrialization, many toxic or non-biodegradable organic compounds have been found in industrial wastewaters, which add difficulties to the traditional biological treatment. The decontamination of many emerging anthropogenic organic pollutants requires novel techniques to chemically transform them into non-hazardous compounds. Among these, chemical oxidation treatments, especially AOPs are well known for their capacity for oxidizing and mineralizing most of organic contaminants (Comninellis, Kapalka et al. 2008). Futuristic treatments may be an integration of AOPs as a pre-treatment to convert non-biodegradable to biodegradable organic contaminants prior to conventional biological treatment processes, thus the conventional biological treatment process may be improved.

2.3 TiO₂-based photocatalysis for water disinfection and decontamination

There is an increasing need for new and effective methods for disinfection of total waterborne pathogens, and the decontamination for the complete mineralization of a wide range of organic compounds in water treatment. In the near future, AOPs may become the most widely used water treatment technologies (Gogate and Pandit 2004; Gogate and Pandit 2004; Blanco-Galvez, Fernandez-Ibanez et al. 2007). The processes can be categorized into three types:

- (1) Photolysis.
- (2) Homogeneous photocatalysis.
- (3) Heterogeneous photocatalysis.

The photolysis methods are based on UV, H₂O₂/UV, O₃/UV and H₂O₂/O₃/UV combinations (Malato, Fernandez-Ibanez et al. 2009). In direct UV photolysis, the incident light is absorbed by the contaminants for the subsequent degradation in its photochemically excited state. This process depends strongly on the light absorptivity of the targeted contaminants. Since most of the contaminants are not highly photochemically active, this process is difficult to achieve under conventional conditions. For the H₂O₂/UV and O₃/UV processes, the oxidative degradation occurs through the chemical generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) which attack most organic compounds. The necessity of UV light limits the broad use of solar, resulting in the increased energy consumption and equipment requirements.

Homogeneous photocatalysis is based on photo-Fenton processes. Reactive hydroxyl radicals are produced in the presence of Fe²⁺/Fe³⁺/H₂O₂, and UV or visible light and may enhance the process (Zepp, Faust et al. 1992). Photo-Fenton processes are probably among the most applied AOPs for the treatment of industrial wastewater (Legrini, Oliveros et al. 1993). However, since the process is pH dependent, the need

for acidification is the major drawback which could increase the total treatment costs and limits its broad application.

The heterogeneous photocatalysis process involves solid materials, usually semiconductor catalysts which may absorb appropriate light and generate chemical oxidants such as hydroxyl radicals in situ from dissolved oxygen (Malato, Fernandez-Ibanez et al. 2009). Considering the strong oxidation-reduction power for environmental cleaning, possible utilization of solar light, and potential to be environmental friendly, heterogeneous photocatalysis is significant and promising in environmental applications. Therefore, this work is focused on the AOPs with heterogeneous photocatalysis. Various semiconductor-based photocatalysts have been explored, including TiO_2 , ZnO , WO_3 , SrTiO_3 , BiVO_4 , CdS , ZnS , CdSe and their derivatives (Mills and LeHunte 1997). Among these, TiO_2 is regarded as the most efficient and environmental friendly photocatalyst due to its unique properties of chemical stability, biocompatibility and high photoactivity with relatively low cost (Linsebigler, Lu et al. 1995; Chen and Mao 2007).

2.3.1 Introduction of TiO_2 photocatalysis

TiO_2 is n-type semiconductor. Since its commercial production in the early twentieth century, TiO_2 has been widely used as pigment product (Pfaff and Reynders 1999), paints (Braun, Baidins et al. 1992), cosmetics as sunscreens (Salvador, Pascual-Marti et al. 2000), toothpaste (Pacheco, Prairie et al. 1993), etc. In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode using ultraviolet (UV) light (Fujishima and Honda 1972). Since then, numerous efforts have been devoted to the research of TiO_2 materials, which has led to many promising applications in field of photocatalysis, photovoltaics, photo-electrochromics and sensors (Hagfeldt and Gratzel 1995; Linsebigler, Lu et al. 1995; Mills and LeHunte 1997; Gratzel 2001). These applications involve energy and environmental issues. The

effective application depends not only on the properties of TiO_2 itself and TiO_2 -based materials, but also the interactions of TiO_2 materials with the environment.

As the most promising photocatalyst, TiO_2 materials are expected to play an important role in providing solutions to many serious environmental pollution problems (Mills and LeHunte 1997; Chen and Mao 2007). TiO_2 -based photocatalytic oxidation (PCO) has been applied to solve various environmental problems including water and air purification. The mineralization of several classes of compounds including chlorinated aromatics, surfactants, pesticides and herbicides has been reported (Chen and Ray 1998; Chen and Ray 1999; Chen, Ollis et al. 1999; Topalov, Molnar-Gabor et al. 2000; Lewandowski and Ollis 2003). The destruction of microorganisms such as bacteria and viruses (Lee, Nishida et al. 1997; Kuhn, Chaberny et al. 2003) has also been reported. Moreover, TiO_2 is inexpensive, commercially available, non-toxic, non-polluting, and stable under illumination, resistant to strong acid or base and display high catalysis activity. Hence research interests on TiO_2 photocatalysis have increased significantly.

2.3.2 Mechanism of TiO_2 photocatalysis

TiO_2 crystals are in three major different structures: rutile, anatase and brookite. However, only rutile and anatase play the role in the photocatalytic application. The two crystal structures differ in the distortion of each octahedron by the assembly pattern of the octahedral chains, as shown in Figure 2.3. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 . Anatase phase, the stable phase of TiO_2 at low temperature, has gained applications for photodecomposition and solar energy conversion because of its high photoactivities, while rutile is a stable phase of TiO_2 at high temperature by contrary. And anatase has been found more photo-activity than rutile in most of the cases (Tsai and Cheng 1997; Ding, Lu et al. 2000). The lower photocatalytic activity of rutile was due to its low band-gaps leading to a higher electron-hole recombination rate (Tsai and Cheng 1997).

Figure 2.3 Lattice structure of rutile and anatase TiO_2 (Linsebigler, Lu et al. 1995).

A semiconductor is commonly characterized by the energy gap between the electronically populated valence and largely vacant conduction band. Irradiation of semiconductor particles with light energy equal to or greater than the band gap of the semiconductor will promote an electron from the valence band to the conduction band. The bandgap of TiO_2 is approximately 3.2 eV (Linsebigler, Lu et al. 1995). The band-edge position of TiO_2 is also important in photocatalysis. The ability of a semiconductor to behave as a photocatalyst for a redox reaction is governed by the position of its conduction and band-edge positions. TiO_2 has a valence band potential of +3.1 eV and a conduction band potential of -0.1 eV, relative to a normal hydrogen electrode. Many organic compounds have a potential above that of the TiO_2 valence band and therefore can be oxidized.

The mechanism of TiO_2 photocatalysis has been illustrated by Hoffmann in 1995, as shown in Figure 2.4 (Hoffmann, Martin et al. 1995). The following seven steps simply summarized the mechanism of the heterogeneous photocatalysis.

- (1) Formation of charge carriers by a photon;
- (2) Charge carrier recombination to liberate heat;

- (3) Initiation of an oxidative pathway by a valence-band hole;
- (4) Initiation of a reductive pathway by a conduction-band electron;
- (5) Further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products;
- (6) Trapping of a conduction-band electron in a dangling surficial bond to yield Ti(III);
- (7) Trapping of a valence-band hole at a surficial titanol group.

Figure 2.4 Primary steps in the photo-electrochemical mechanism (Hoffmann, Martin et al. 1995).

In most conditions with semiconductor photocatalysts, oxygen (O_2) is present to act as the primary electron acceptor. And consequently hydrogen peroxide (H_2O_2) is formed via the above mechanism. Meanwhile, hydroxyl radicals are formed on the surface of TiO_2 by the reaction of holes (h_{vb}^+), with adsorbed H_2O , hydroxide, or surface titanol groups ($>TiOH$). These processes are summarized and illustrated in Figure 2.5. Nevertheless, this process is a complicated surface reaction affected by many factors. More detailed mechanism about the surface reactions occurred on TiO_2 can be found in many excellent reviews (Hoffmann, Martin et al. 1995; Linsebigler, Lu et al. 1995; Chen and Mao 2007).

real water industries due to some limitations. Firstly, nanosized TiO_2 photocatalyst tend to aggregate in suspension, leading to a rapid loss in active sites and photocatalytic efficiency. The most commonly used commercial TiO_2 photocatalyst is Degussa P25, which is composed of anatase and rutile TiO_2 with an average size of around 25 nm. However, these P25 particles usually are not present individually in aqueous systems, but rather as physically unstable complexes, primary aggregates to 0.1 μm , which reduces the surface area dramatically (Mills and LeHunte 1997). Secondly, Low electron transfer rate to oxygen and high electron-hole recombination rate significantly limit the rate of TiO_2 photooxidation of organic compounds on the catalyst surface (Linsebigler, Lu et al. 1995; Herrmann 1999). The low photocatalytic degradation rate of pollutants increases the reaction time, and reduces the removal efficiency, which both pose difficulties in the application of TiO_2 for an actual water treatment plant. Thirdly, the wide bandgap (3.2 eV for anatase) of TiO_2 photocatalyst requires UV light, which results in the technology to be energy-intensive. This restricts its broad applications worldwide, especially in developing countries. Fourthly, the activity of TiO_2 is strongly dependent on its size, morphology and crystallographical properties (Yu, Yu et al. 2002). Lastly, separation, recovery and reuse of the nanosized TiO_2 particulates pose a key obstacle to practical applications.

2.3.4 Approaches to improve TiO_2 photocatalytic efficiency

In general, these limitations of TiO_2 nanomaterials mentioned above could be concluded into three aspects: 1) nanosized TiO_2 leads to loss of specific surface area because of easy aggregation, and difficulties in recovery; 2) its broad band gap (3.0 eV for the rutile phase and 3.2 eV for the anatase phase) restricts its utilisation of solar energy; and 3), the fast electron-hole recombination decreases its photocatalytic efficiency. Hence, certain technical approaches should be applied to improve the photocatalytic efficiency of TiO_2 correspondingly to each of the above-mentioned problems.

- (1) Maximization of the specific surface area of TiO₂ nanomaterials. The specific surface area is strongly dependent on the morphology, size, structure and the dispersibility of the material. The technical issue may be addressed by either creating porous photocatalyst structures or dispersing the nanosized photocatalyst on a highly porous support solid surface. Recently various morphologies of one-dimensional (1D) nanostructured TiO₂, including nanowires, nanofibers, nanorods and nanotubes have been synthesized (Kasuga, Hiramatsu et al. 1998; Li and Xia 2003; Yuan and Su 2004). These materials have higher specific surface area than commercial P25 and may easily be recovered from treated water due to their special morphology. These structures could also be assembled into a hierarchical porous structures to further increase the specific surface area and allow for light harvesting, which is well reviewed (Pan, Dou et al. 2010).
- (2) Another approach to improve the performance of TiO₂ nanomaterials is to increase their optical activity by shifting the onset of the response from the UV to the visible regions (Burda, Lou et al. 2003; Chen, Lou et al. 2005). There are several ways to achieve this approach. Firstly, doping other elements onto TiO₂ nanomaterials, to narrow the bandgap, thus altering the optical properties of the TiO₂ nanomaterials. These include metal-doping using La, W, V, Ce, Zr, Fe and Cu, and nonmetal-doping using B, C, N, F, S, Cl, and Br (Hattori, Yamamoto et al. 1998; Burda, Lou et al. 2003; Choi, Umebayashi et al. 2004; Luo, Takata et al. 2004; Nagaveni, Hegde et al. 2004; Ohno, Akiyoshi et al. 2004). Secondly, sensitizing TiO₂ with other organic compounds such as dyes can improve its optical activity in the visible light region (Adachi, Murata et al. 2004). Thirdly, coupling collective oscillations of the electrons in the conduction band of metal nanoparticle surfaces to those in the conduction band of TiO₂ nanomaterials in metal-TiO₂ nanocomposites can improve its performance, such as Ag and Au nanoparticles (Kawahara, Suzuki et al. 2005; Tian and Tatsuma 2005). Lastly, modification of the TiO₂ nanomaterial surface with other semiconductors can alter the charge-transfer properties between TiO₂ and the surrounding

environment, thus improving its performance. These semiconductors include PbS, AgI, CdS, CdSe, InP and so on (Vogel, Hoyer et al. 1994; Fitzmaurice, Frei et al. 1995; Hoyer and Konenkamp 1995; Zaban, Micic et al. 1998; Shen, Arae et al. 2004).

- (3) Anti-recombination of generated electrons and holes is a key way to improve the performance of TiO₂ nanomaterials. The effective way to achieve this is to transfer the generated electrons from a high energy position to a low energy position (Pan, Zhang et al. 2008). Coupling metal nanoparticles such as Ag, Au, and other semiconductors could effectively restrict the electron-hole recombination (Wang, Zhao et al. 2008; Song, Wang et al. 2011; Wang, Su et al. 2011). The Fermi levels of these noble metals are lower than that of TiO₂. Therefore, the photo-excited electrons can be transferred from conduction band to metal particles deposited on the surface of TiO₂. These metals reduce the possibility of electron-hole recombination, causing efficient charge separation and higher photocatalytic reaction rates. Therefore, noble metals with these properties can help electron transfer, leading to higher photocatalytic activity (Ni, Leung et al. 2007). Recently, coupling TiO₂ with two-dimensional (2D) carbon material graphene is a new approach to prevent the charge recombination of TiO₂ (Liu, Bai et al. 2010; Zhang, Lv et al. 2010; Liu, Liu et al. 2011).

Since the approaches mentioned above are all essential for improving the photocatalytic activity of TiO₂-based materials, an ideal approach is to consider all of these aspects to optimize the materials synthesized in order to achieve high-performance nanocomposite photocatalysts for water disinfection and decontamination.

2.3.5 Solar photocatalysis

Recently, increasing attentions have been focused on photocatalytic processes using solar irradiation, because solar is more cost effective than UV irradiation. The solar

photocatalysis consists of those which could make use of the near-ultraviolet band and visible light spectrum to photo-excite the catalysis. Since UV is only a small fraction of the sun's energy ($\sim 4\%$), as shown in Figure 2.6, shifting the onset of the response of the photocatalysis from the UV to the visible regions is of significant importance. Some common semiconductor photocatalysts have been summarized as shown in Table 2.2. Among these, some have the band gap belonging to the region of UV spectrum (< 400 nm), such as TiO_2 , SnO_2 , ZnS . As for these catalysts, proper modification or improvement is needed to enlarge their light absorption in the visible regions. Some semiconductors, however, have the band gap in the visible-light region, such as ZnO , WO_3 , CdS , which can absorb a larger fraction of the solar spectrum.

Silver-based compounds have been recognized as one of the most promising alternatives to the visible-light photocatalysts due to their excellent visible light response, including silver halides (AgX , $\text{X} = \text{Br}, \text{Cl}, \text{I}$), silver oxide (Ag_2O) and silver sulphide (Ag_2S) (Wang, Li et al. 2011; Zhu, Chen et al. 2011; Yang, Zhang et al. 2012). Recently, a breakthrough was made by Ye et al., who reported the use of silver orthophosphate (Ag_3PO_4) as a new visible light photocatalyst for the oxidation of water and photodecomposition of organic compounds (Yi, Ye et al. 2010; Bi, Ouyang et al. 2011). Their results show that Ag_3PO_4 semiconductors have extremely high photooxidation capability for O_2 evolution from water, as well as high efficient organic dye degradation activity under visible light, significantly higher than that of commercial $\text{TiO}_{2-x}\text{N}_x$ (nitrogen doped titanium dioxide, $0 < x < 2$). However, these visible light photocatalysts may be unstable during the repetitive catalytic cycles. Therefore, it is highly desirable to develop effective strategies for improving the stability of these visible light photocatalysts and maintain or enhance their activities.

In general, the most important features of the solar photocatalysis for water treatment can be summarized as follows (Malato, Fernandez-Ibanez et al. 2009):

- (1) The process takes place at ambient temperature and without external pressure.

- (2) Complete oxidation of the organic, biological and some inorganic species into CO₂ can be occurred.
- (3) The oxygen necessary for the reaction can be directly obtained from air.
- (4) The photocatalyst is inexpensive, innocuous and can be reused.
- (5) The photocatalyst can be incorporated with different types of inert matrices.
- (6) The energy for photo-exciting can be obtained from the sun.

Figure 2.6 Solar spectrum at sea level with the sun at its zenith (Linsebigler, Lu et al. 1995; Malato).

Semiconductor	VB (V vs. NHE ± 0.1 V)	CB (V vs. NHE ± 0.1 V)	E _g (eV)	Band gap wavelength(nm)
TiO ₂	+3.1	-0.1	3.0	380
SnO ₂	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	2.8	440
ZnS	+1.4	-2.3	3.7	336
WO ₃	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887
GaP	+2.2	-0.1	2.3	540

Table 2.2 Band position (water at pH 1) for some common semiconductor photocatalysts (Malato, Fernandez-Ibanez et al. 2009).

2.3.6 Coupling TiO₂ photocatalysis with membrane technology for water purification

Membrane technology has been well developed and widely applied in advanced water treatment applications, as mentioned in Section 2.2 (Jacangelo, Trussell et al. 1997; Shannon, Bohn et al. 2008; Yamamura, Hashino et al. 2011). It includes the low pressure-driven membrane as MF/UF, and high pressure-driven membrane NF/RO. Compared with conventional water treatment technologies, membrane technology process could offer high quality drinking water with a small footprint. However, the inevitable membrane fouling issue is one of the major problems in using membrane filtration technology (Yuan and Zydney 1999).

As mentioned in Section 2.3.4, to overcome the drawbacks of separation and reuse of nanosized TiO₂ photocatalysts, membrane filtration has been applied (Sopajaree, Qasim et al. 1999). Hybrid photocatalysis-membrane processes are conducted in installations usually called “photocatalytic membrane reactor” (Damodar, You et al. 2010; Mozia 2010). This hybrid process can be divided into two main groups: catalysts in suspension and catalysts in/on membrane. In the case of the processes with nanosized TiO₂ in suspension, although it was approved that nanosized TiO₂ could be completely separated by MF or UF membrane, serious membrane fouling usually occurs by these nanomaterials due to the formation of dense cake layer on membrane surface and membrane pore blocking efficiency (Lee, Choo et al. 2001). Another attempt is to use nanosized TiO₂ to form unique multifunctional membranes which can provide concurrent separation and photocatalytic degradation of pollutants. Many research studies have been carried out to fabricate TiO₂ membranes by coating/immobilizing TiO₂ on various supports (Meulenberg, Mertens et al. 2006; Triani, Evans et al. 2006; Choi, Stathatos et al. 2007). Some work has reported about the TiO₂-based membrane such as Ag-TiO₂/hydroxyapatite (HAP)/Al₂O₃ composite membrane. It showed efficient removal of pathogen and humic acid and effective anti-fouling properties under UV irradiation (Ma, Fan et al. 2009). However, the photocatalytic efficiency of these coated TiO₂ membranes may be lower than that of

original nanosized TiO₂ photocatalyst. Since there is a direct correlation between the photocatalytic performance and the nanostructure of a semiconductor photocatalyst, searching for new heterogeneous photocatalysts with an appropriate crystal structure, high specific surface area and easy separation and reuse has been an intensively pursued topic (Pan, Dou et al. 2010). Recently various morphologies of one-dimensional (1D) nanostructured TiO₂, including nanowires, nanofibers, nanorods and nanotubes have been synthesized (Kasuga, Hiramatsu et al. 1998; Li and Xia 2003; Yuan and Su 2004). Zhang, et al. has successfully fabricated a high-performance multifunctional membrane made up of pure TiO₂ nanowires through hydrothermal process, which showed the ability of concurrent separation and photocatalytic degradation for water purification (Zhang, Du et al. 2008; Zhang, Zhang et al. 2009).

2.4 Graphene-based hybrid nanocomposites for water purification

As mentioned in Section 2.3.4, coupling TiO₂ with 2D carbon material graphene is a new approach to improve the photocatalytical efficiency of TiO₂ and to facilitate its recovery. Graphene development has attracted much attention by various researchers. The major focus of recent research development is to exploit a sp²-hybrid carbon network (Geim 2009). In particular, graphene is considered as an ideal two-dimensional reinforcing component for composite materials possessing superior carrier transport properties, high mechanical strength, extremely large surface area and fine thermal/chemical stability (Dikin, Stankovich et al. 2007; Lee, Wei et al. 2008; Geim 2009). Graphene oxide (GO) is a chemically modified graphene with hydroxyl and carboxyl groups, as shown in Figure 2.7, which favours its solubility in solvents and provide fertile opportunities for the construction of GO-based hybrid nanocomposites (Dikin, Stankovich et al. 2007; Dreyer, Park et al. 2010). The new GO-based hybrids with metal and metal oxide nanoparticles such as Pt, Au, Ag, TiO₂, ZnO, Fe₃O₄ have shown great potential applications in the area of optics, electronics, photocatalysts and sensors (Muszynski, Seger et al. 2008; Pasricha, Gupta et al. 2009; Zhou, Huang et al.

2009; Lightcap, Kosel et al. 2010; Liu, Bai et al. 2010; Xu, Zhang et al. 2011; Zhou, Zhu et al. 2011).

Figure 2.7 Structure of graphene oxide (Dreyer, Park et al. 2010).

Among various applications, the fabrication of GO-based hybrid photocatalysts, especially those for the photodegradation of pollutants, is currently an important research topic which has attracted large attention globally (Chen, Cai et al. 2010; Liu, Bai et al. 2010; Zhang, Lv et al. 2010). The excellent transparency, extremely high specific surface area, locally conjugated aromatic system, and unique electronic properties of GO, making it an ideal candidate as a photocatalyst carrier or promoter. In this regard, several well-defined hybridized composites in terms of GO and conventional semiconductors, such as GO-ZnO and GO-TiO₂ have been reported. The GO-TiO₂ and GO-ZnO hybrid composites have shown significant enhanced photocatalytic performance in degradation of pollutants (Liu, Bai et al. 2010; Du, Lai et al. 2011). The GO effectively reduced the electron-hole recombination by transferring the excited electrons from catalyst surface onto GO sheets and shifted the response region of TiO₂ to visible light (Yoo, Tran et al. 2011).

Besides these, the hybrids in terms of GO and novel metal nanoparticles may also provide new opportunities for water disinfection and degradation of pollutants. The graphene-Au nanocomposites exhibits a high photocatalytic decontamination

performance over dyes under visible light irradiation (Xiong, Zhang et al. 2010). Comparing to TiO₂, the GO-Au photocatalyst has four important features:

- (1) high adsorption ability toward organic dyes,
- (2) strong π - π interaction with dye chromophores,
- (3) efficient photosensitized electron injection and
- (4) slow electron recombination.

All of these features make the GO-Au composites good candidates for photocatalysis of decontamination.

Besides GO-Au, GO-Ag composites have been reported to show an high effective disinfection property, above that of the antibacterial activity of Ag nanoparticles (Shen, Shi et al. 2010). Das et al. (2011) reported that the antibacterial activity of Ag nanoparticles on GO is size and shape dependent, and Ma et al. (2011) also reported a synergistic effect of GO and Ag nanoparticles (Das, Sarma et al. 2011; Ma, Zhang et al. 2011).

Nevertheless, more development of desirable new methods for the synthesis of high-quality GO-based hybrid photocatalysts which can utilise the sunlight and also easy for recycle and reuse is needed. This technology would offer more attractive opportunities for pollutants elimination and bacteria disinfection for cost-effective water treatment and water quality improvement.

2.5 Summary

In summary, the literature review revealed that many research efforts have been drawn to improve the photocatalytic performance of TiO₂-based photocatalysis, and shift its bandgap response from UV to the visible light regions. However, some problems of the existing TiO₂-based photocatalysis limits its wide use in actual water treatment applications. These include: (1) the aggregation of TiO₂ particles leads to the rapid loss

of specific surface area; (2) the difficulty in the recovery of nanosized photocatalysis; (3) the rapid electron-hole recombination of TiO_2 leads to the loss of photocatalytic efficiency; and (4), the limitations in utilization of solar energy because of its large bandgap of TiO_2 . Therefore, the aim of this study is to solve the drawbacks mentioned above and to synthesize high-performance TiO_2 -based nanocomposite photocatalysts, especially for water disinfection of pathogens and decontamination of organic pollutants. In general, the synthesized nanocomposite photocatalysts should have the following important features:

- (1) be easily recovered from the treated water;
- (2) be conducted/enhanced under solar light or visible light;
- (3) achieve long-term antibacterial activity even without solar irradiation.

Improvements can be made based on approaches mentioned in section 2.3.4.

For the first feature, two approaches may be taken to achieve this:

- (1) the photocatalyst may be synthesized with large size, such as nanowires or nanofibers (length $> 1 \mu\text{m}$), which could be easily recovered by filtration, or be applied for photocatalytic disinfection/degradation and concurrent membrane filtration;
- (2) the photocatalyst could be synthesized with nano size, attaching on a large supporter, such as large GO sheet. Thus the large GO sheets could facilitate the recovery of the entire photocatalysts.

For the second feature, maximizing the specific surface area, minimizing the recombination of electron-holes and extending the utilization of solar spectrum are the three approaches to improve the photocatalytic efficiency of photocatalyst. The specific surface area of the photocatalyst is dependent on its morphology. For instance, mesoporous TiO_2 nanofibers and small monodispersed TiO_2 nanoparticles/nanorods may have large specific surface area. The modification of TiO_2 with proper materials may effectively extending the utilization of the solar spectrum, while minimizing the

recombination of electron-hole, such as combining metal nanoparticles or graphene with TiO₂ photocatalysts.

For the third feature, combining photocatalysts with antibacterial materials is an effective way to achieve long-term antibacterial activity. Since Ag nanoparticles or silver-based nanomaterials are one of the highest antibacterial materials among the nanomaterials, synthesis of silver-based photocatalysts could achieve a high-performance disinfection property and long-term antibacterial capability.

Therefore, considering the above mentioned factors, in this work, a group of novel TiO₂-based nanocomposite photocatalysts were developed by introducing silver (Ag) or/and graphene oxide (GO) sheets, silver-based nanomaterials, to solve the above mentioned drawbacks of TiO₂ and to achieve those important features for broad applications in the water purification field.

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Materials

Analytical grade tetra-n-butyl titanate (>98 %), titanium tetra-isopropoxide (TTIP, 98 %), acetic acid, silver nitrate (AgNO_3 , 99 %), silver acetate (CH_3COOAg , 99 %), ethylene glycol (EG, anhydrous, 99.8 %), polyvinylpyrrolidone (PVP, M_w 55,000), F-127, sodium nitrate (NaNO_3 , 99 %), potassium permanganate (KMnO_4 , 99 %), hydrogen peroxide (H_2O_2 , 35 %), concentrated sulfuric acid (HCl , 36.5 %), oleic acid (OLA, 99 %), tert-butylamine, acid orange (AO 7, 99 %), and phenol (99 %), sodium hydrogen phosphate (Na_2HPO_4 , 99 %), and sodium hydrate (NaOH , 99 %) were obtained from Sigma-Aldrich. Natural graphite (SP1) was purchased from Bay Carbon Company (USA). Toluene, acetone, ethanol (absolute), and tetrahydrofuran (THF), dimethyl sulphoxide (DMSO) were purchased from Merk Ltd (Singapore). All reagents were used without further purification. The deionized (DI) water was produced from Millipore Milli-Q water purification system.

3.2 Material synthesis

3.2.1 Synthesis of TiO_2 nanofibers by Electrospinning

TiO_2 nanofibers were fabricated using electrospinning technique (Formo, Lee et al. 2008). Briefly, a solution containing 2.3 mL Tetra-n-butyl titanate, 2 mL acetic acid, 0.68 g PVP, and 8 mL ethanol was well mixed before use. The solution was passed through a syringe with a needle at the tip. The needle was electrified using 16 kV DC through a high-voltage DC supply (Dongwen High Voltage Power Supply, China). The setup of the electrospinning is shown in Figure 3.1. The solution was ejected continuously using a syringe pump (NE-1000, USA) at a rate of 1.2 mL/h. The fibers

were collected on an aluminum foil collector and left overnight in air for complete hydrolysis. The TiO₂ nanofibers were then calcinated in air at 550 °C for 1 h.

Figure 3.1 Schematic diagram of electrospinning setup for fabrication of TiO₂ nanofibers.

3.2.2 Synthesis of Ag/TiO₂ nanofiber composites

To incorporate the TiO₂ nanofibers with Ag nanoparticles, 100 mg TiO₂ and 20 mL EG were initially added into a 3-neck flask (fitted with a reflux condenser and a Teflon-coated stir bar) and heated at 160 °C. After 30 min, 5 mL of AgNO₃ solution (10 mg in EG) and 5 mL of PVP solution (100 mg in EG) were dripped (simultaneously) to the flask over a period of 10 min. The mixture was further heated to 160 °C for about 20 min. The final product was washed thoroughly with ethanol and distilled water to remove EG and excess PVP before further use.

3.2.3 Fabrication of Ag/TiO₂ nanofiber membrane

100 mg successfully synthesized Ag/TiO₂ nanofiber composites were dispersed in a surfactant (0.05 wt % F-127) solution and sonicated for 30 min to achieve a homogeneous suspension. The suspension was then filtered by a vacuum-filtration setup with a glass filter (ADVAVTEC, GC-50, 0.45 μ m). Residual surfactant left in the membrane was subsequently washed away using distilled water. After drying at 105 °C, the membrane was pressurized under 5 bar at 120 °C on a hot press to achieve compaction. Then, the membrane consists of a support layer of glass filter and a functional layer of Ag/TiO₂ nanofiber composites was formed. As a comparison, 100 mg commercial P25 and 100 mg pure TiO₂ nanofibers were also used to form membranes with the same method mentioned. (The term “Ag/TiO₂ nanofiber membrane” here and in Chapter 4 represents the membrane composed of Ag/TiO₂ nanofiber composites as function layer and commercial glass filter as support layer.)

3.2.4 Synthesis of GO

GO was synthesized according to the modification of Hummers’ method from natural graphite, and the process was described earlier (Hummers and Offeman 1958; Liu, Jeong et al. 2010). Briefly, graphite (0.5 g) and NaNO₃ (2 g) were mixed with 12 mL of H₂SO₄ (98 %) in a 500 mL flask. The mixture was stirred for 30 min within an ice bath to maintain the temperature below 5 °C. Under vigorous stirring, potassium permanganate (3 g) was added to the suspension. The rate of addition was carefully controlled to keep the reaction temperature below 5 °C for about 2 h. Then, the reaction temperature was increased to 35°C for 30 min, until the mixture gradually thickened as the reaction progressed. 40 mL DI water was added, and the reaction temperature was increased to 100 °C for 15 min. Then, 70 mL water and 10 ml H₂O₂ (30 %) were added separately into the mixture. For purification, the mixture was washed by rinsing and centrifugation with 5 % HCl and DI water for several times. After filtration and drying under vacuum, solid GO was obtained.

3.2.5 Synthesis of highly monodispersed Ag nanoparticles

Oleylamine-capped Ag nanoparticles were synthesized by reducing AgNO_3 in toluene, which was described previously (Shen, Hui et al. 2008). Briefly, a total of 0.5 mmol of AgNO_3 and 2 mL of oleylamine were dissolved in 50 mL of toluene in a 100 mL flask. The mixture was heated to 110 °C under nitrogen flow and this temperature was kept for 6 h before it was cooled down to room temperature. A total of 50 mL of ethanol was added into the solution, and the suspension was centrifuged at 6000 rpm for 3 min. The supernatant was discarded while the precipitate was redissolved in toluene to form a brownish-yellow solution.

3.2.6 Synthesis of GO-Ag nanocomposites by two-phase method

GO (15 mg) and DI water (100 mL) were added into a bottle (250 mL) and sonicated for 1 h before use. Ag nanoparticles (45 mg) dispersed in toluene (50 mL) were added into the GO water solution. The mixture was stirred for 12 h at room temperature to ensure Ag nanoparticles coordinated with GO sheets at the water/toluene interface. The GO-Ag nanocomposites were purified with acetone and centrifuged at 10 000rpm for 10 min. The obtained GO-Ag nanocomposites were then washed by THF to get rid of residual oleylamine on the Ag nanoparticles. The entire process is illustrated as shown in Figure 3.2. The final GO-Ag nanocomposites were freeze-dried at -50°C for 24 h.

3.2.7 Synthesis of TiO_2 nanorods

Oleic acid capped anatase TiO_2 nanorods were synthesized by the hydrothermal method (Liu, Bai et al. 2010; Liu, Liu et al. 2011). Briefly, 0.9 mL of tert-butylamine was added into 10 mL of DI water, while 0.9 mL of TTIP was added into 18 mL of oleic acid. The above two solutions were mixed and transferred to a Teflon-lined autoclave, and maintained at 180 °C for 6 h in oven. After the reaction, the mixture was precipitated with ethanol and washed with ethanol twice.

Figure 3.2 Steps for the synthesis of the GO-Ag nanocomposites: (a) Schematic presentation of the two-phase synthesis of GO-Ag nanocomposites; (b) Photographs of the two-phase synthesis of GO-Ag nanocomposites.

3.2.8 Synthesis of GO-TiO₂-Ag nanocomposites by two-phase method

GO-TiO₂-Ag nanocomposites were synthesized by a two-phase method, which was the same as that for the synthesis of GO-Ag nanocomposites mentioned in section 3.2.6. Briefly, GO (50 mg) and DI water (100 mL) were added into a bottle (250 mL) and sonicated for 1 h before use. TiO₂ nanorods (50 mg) and Ag nanoparticles (5, 10, 15 mg) dispersed in toluene (50 mL) were added into the GO water solution, named as GO-TiO₂-Ag-1, GO-TiO₂-Ag-2, and GO-TiO₂-Ag-3, respectively. The mixtures were stirred for 12 h at room temperature to ensure TiO₂ nanorods and Ag nanoparticles coordinated with GO sheets at the water/toluene interface. The GO-TiO₂-Ag nanocomposites were purified with acetone and centrifuged at 10 000 rpm for 10 min. The obtained GO-TiO₂-Ag nanocomposites were then washed by THF to get rid of residual surfactants. The final GO-TiO₂-Ag nanocomposites were freeze-dried at -50 °C for 24 h.

3.2.9 Synthesis of Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites

Bare Ag_3PO_4 samples were prepared by the ion-exchange method reported before (Bi, Ouyang et al. 2011). Briefly, 0.2 g CH_3COOAg was dissolved in 200 mL DI water. Na_2HPO_4 aqueous solution (0.015 M) was added drop by drop to the solution with magnetic stirring, until the initial white colour changed to yellow. The mixture was then washed with water to dissolve any unreacted raw material, and dried under atmospheric conditions. For the synthesis of $\text{GO-Ag}_3\text{PO}_4$ hybrid nanocomposites, 15 mg GO was first added to 200 mL DI water and sonicated for 2 h to get a well dispersed GO solution. Then 0.1 g CH_3COOAg was added to the GO solution whilst magnetically stirring for 1 h. Subsequently, Na_2HPO_4 aqueous solution (0.015 M) was added drop by drop to the solution, until the total mixture colour changed to olive green. The mixture was then washed with water to dissolve any unreacted raw material, and dried under atmospheric conditions.

3.3 Characterization methods

3.3.1 FESEM and EDS

Two types of field electron scanning microscopy (FESEM, Jeol JSM-6340F and JSM-7600F) were used to observe the morphologies of synthesized photocatalysts. The element composition of the samples was measured by an energy dispersive detector (EDS) (Oxford, 80 mm²) attached to the FESEM (Jeol JSM-7600F). Carbon tape and gold/platinum sputtering were used for the sample preparations.

3.3.2 TEM

The morphologies of synthesized photocatalysts were observed by transmission electron microscopy (TEM) (Jeol JEM-2010), working at an accelerated voltage of 200 kV. For the measurement of TEM, the samples were firstly dispersed in absolute

ethanol solution under ultrasonication, and then dipped in Cu grid ready for the TEM observation.

3.3.3 AFM

Atomic force microscopy (AFM) was carried out using a non-contact mode on a PSIA XE-150 scanning probe microscope (Park SE-100). The AFM sample was prepared by spin coating the dispersion water solution of samples onto Si substrate covered with 300 nm thick SiO₂.

3.3.4 XRD

X-ray powder diffraction (XRD) patterns were measured using Shimadzu XRD-6000 X-ray diffractometer with monochromated high-intensity Cu K α irradiation ($\lambda=1.5418\text{\AA}$) operated at 40 kV and 30 mA. The scanning rate was 2 °/min.

3.3.5 BET

BET surface area of synthesized photocatalysts were determined at liquid nitrogen temperature (77 K) using a micromeritics ASAP 2040 system. Before measurement, 0.1 g of sample was degassed under vacuum for 10 h at 250 °C.

3.3.6 UV-visble observation

The UV-Vis absorption spectra were recorded by using a Thermo Scientific Evolution 300 UV-vis spectrometer (Thermo Scientific, Massachusetts, USA).

3.3.7 XPS

X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a

Kratos Axis Ultra Spectrometer with a monochromic Al Ka source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. The carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (eV).

3.3.8 ICP

Silver ion was detected by Inductively Coupled Plasma (ICP, Perkin Elmer, optima 2000 DV).

3.4 Disinfection evaluation experiments

3.4.1 Materials

Escherichia coli (*E.coli*) was widely used for antibacterial or disinfection evaluation in environmental engineering, since its presence in environmental samples indicated the presence of fecal matter and the potential presence of pathogens. The *E.coli* encompasses an enormous population of bacteria that exhibit a high degree of genetic and phenotypic diversity. Most *E.coli* strains are harmless and part of the normal flora of the gut, while some serotypes can cause serious food poisoning in humans such as 0104:H4. In this work, *E.coli* K12, which are well-adapted to the laboratory environment, was chosen as the model pathogen for antibacterial activity tests. *E.coli* (K12 ER2925) was purchased from New England Biolab. *E.coli* was cultivated in Luria-Bertani nutrient solution at 37 °C for 18 h to obtain the exponential growth phase. The cells were harvested by centrifugation and washed with saline solution (0.9 % NaCl) to remove residual macromolecules. All glass apparatuses and solutions used in the experiments were autoclaved at 121 °C for 20 min to ensure sterility.

3.4.2 Evaluation of antibacterial activity of Ag/TiO₂ nanofiber membrane

The disinfection property of the Ag/TiO₂ nanofiber membrane was evaluated by assessing the inactivation of *E.coli* under solar irradiation. A solar simulator (Xenon arc lamp, Newport Oriel, 100 mW/cm²) was used as the light source, as shown in Figure 3.3. All the tests were conducted under the same height of the solar simulator to keep the light intensity constant. 5 mL water containing *E.coli* (10⁷ colony forming units per milliliter, cfu/mL) was filtered by the Ag/TiO₂ nanofiber membrane. A total of five Ag/TiO₂ nanofiber membranes were employed, and they were concurrently irradiated by the solar irradiation. At irradiation time of 5, 10, 15, 20, 30 min, one membrane was drawn to transfer the live bacteria onto an agar plate by washing out with phosphate buffer solution (PBS, pH 7.2). An aliquot of the solution was immediately diluted with PBS, and an appropriate dilution of the sample was spread on nutrient agar and incubated at 37°C for 24 h. The number of colonies formed was counted to determine the number of viable cells. All the above experiments were conducted in triplicates. Control experiments without P25 deposited membrane and with TiO₂ nanofiber membrane were also done at the same time. And to investigate the effect of solar irradiation, a control experiment without solar irradiation at the same condition was tested. To investigate the complete bacteria inactivation, the same experiments were carried out with extended irradiation time.

Figure 3.3 Image of solar simulator (Xenon arc lamp, Newport Oriel, 100 mW/cm²).

To investigate the role of reactive oxygen species (ROSs) in photocatalytic disinfection, especially the role of $\cdot\text{OH}$, disinfection reactions on the Ag/TiO₂ nanofiber membrane were carried out in the presence of DMSO at different concentrations. A control experiment of DMSO without membrane was carried out at the same time.

To investigate the ability of bacteria to undergo repair after photocatalytic disinfection, once photocatalytic disinfection treatment was completely performed, the bacteria residuals were washed off by saline solution from the membrane and kept in dark with aluminium foil cover at 37 °C to allow bacterial repair. At every 12 h dark incubation till 48 h, 0.1 mL aliquot samples were collected and directly plated onto LB plates and incubated at 37 °C for 24 h. Control experiment of sterilized DI water was also tested under the same condition.

The antibacterial activity of the Ag/TiO₂ nanofiber membrane was determined by incubating the membrane with *E.coli* cells on LB-agar media plate. The diluted *E.coli* cells were uniformly applied on LB culture medium plates and cultivated at 37°C for 2h. Then, the Ag/TiO₂ nanofiber membrane was added onto the LB plates for cultivation at 37°C for 24h. Control experiments of P25 deposited membrane and TiO₂ nanofiber membrane were also carried out at the same time.

3.4.3 Evaluation of the antibacterial activity of GO-Ag nanocomposites

E.coli cells were inoculated in saline solution containing 0, 20, 50, 80, 100 µg/mL of GO, Ag nanoparticles and GO-Ag nanocomposites, respectively, with a final cell concentration 10⁷-10⁸ cfu/mL. The mixture was incubated with gentle shaking for 2 h at 37 °C. The mixture was diluted with a gradient method and then applied uniformly on three LB culture medium plates per gradient solution. These plates were incubated at 37 °C for 24 h. The colony forming units were counted and compared with control plates to calculate the percentage of cell viability (C/C_0). At the concentration of 100 µg/mL of GO, Ag nanoparticles and GO-Ag nanocomposites, the mixture was taken

out at reaction time 0, 30, 60, 90 and 120 min to measure the time course of the antibacterial activity of samples.

The antibacterial activity of GO-Ag nanocomposites was further verified by LIVE/DEAD BacLight bacterial viability assay (Invitrogen, USA). SYTO 9 and propidium iodide (PI) stock solutions from the assay kit were mixed with an equal volume and added to the *E.coli* solution after 2 h incubation with 100 µg/mL of GO, Ag nanoparticles and GO-Ag nanocomposites, respectively. The mixtures were incubated at room temperature in the dark for 15 min and then observed by Leica TCS SP5 laser scanning confocal microscope (Leica Microsystems, Germany).

The morphological changes of *E.coli* were investigated by scanning electron microscopy (SEM, JEOL, 6340). After filtering the *E.coli* mixture with glass filter, the cells on the filter were quickly fixed with 2 % glutaraldehyde and 1 % osmium tetroxide. Then the cells on the filter were dehydrated with sequential treatment with 50, 70, 85, 90 and 100 % ethanol for 10 min. The filter was freeze dried at -50 °C before testing.

3.4.4 Evaluation of the antibacterial activity of GO-TiO₂-Ag nanocomposites

The photocatalytic disinfection was carried out under irradiation of the solar simulator. The nanocomposite concentration in the reaction solution was 100 µg/mL, and the bacterial cell concentration was about $\sim 10^8$ cfu/mL. The reaction volume was 30 mL. The reaction mixture was magnetically stirred throughout the experiment. During the photocatalytic disinfection treatment, an aliquot of the solution was immediately diluted with PBS, and an appropriate dilution of the sample was spread on nutrient agar and incubated at 37 °C for 24 h. The number of colonies formed was counted to determine the number of viable cells. All the above experiments were conducted in triplicates.

3.4.5 Evaluation of the antibacterial activity of GO-Ag₃PO₄ nanocomposites

To investigate the intrinsic antibacterial activity of the samples, *E.coli* cells were inoculated in PBS solution containing 20 mg/L Ag₃PO₄, GO-Ag₃PO₄ nanocomposites, respectively, with a final cell concentration 10⁷-10⁸ cfu/mL. The mixture was incubated with gentle shaking for 2 h at 37 °C. The mixture was diluted with a gradient method and then applied uniformly on three LB culture medium plates per gradient solution. These plates were incubated at 37 °C for 24 h. The colony forming units were counted and compared with control plates to calculate percentage of cell viability (C/C₀). Control experiments without materials were also carried out at the same time.

To investigate the photocatalytic degradation activity of GO-Ag₃PO₄ nanocomposites toward bacterial cells, the morphological changes of *E.coli* cells were monitored by scanning electron microscopy. The bacterial cells were inoculated in PBS solution containing 20 mg/L of Ag₃PO₄, GO-Ag₃PO₄ nanocomposites, respectively, with a final cell concentration ~10⁷ cfu/mL. The mixture solutions were kept under visible-light irradiation for 2 h. The light source used was 300 W Xe arc lamp equipped with a cold mirror to provide visible light (420 nm ≤ λ ≤ 630 nm, 80 mW/cm²) (Oriol, 300W model). After filtering the *E.coli* mixture solution, the cells on the filter were quickly fixed with 2 % glutaraldehyde and 1 % osmium tetroxide. Then the cells on the filter were dehydrated with sequential treatment of 50, 70, 85, 90 and 100 % ethanol for 10 min. The filter was freeze dried at -50 °C before test.

3.5 Decontamination evaluation experiments

3.5.1 Flux performance investigation of Ag/TiO₂ nanofiber membrane

The flux performances of Ag/TiO₂ nanofiber membrane, pure TiO₂ nanofiber membrane and P25 deposited membrane were investigated in a dead-end membrane system setup, which has been reported by Bai, et al., as shown in Figure 3.4 (Bai, Liu et

al. 2010). This bench-scale system was comprised of a membrane cell with a filtration cup volume of 60 mL. The effective membrane area was 13.4 cm^2 . Pressure was provided by a compressed N_2 gas cylinder, which was collected to the filtration cup. The trans-membrane pressure (TMP) used in experiments was 0.05 MPa. Permeate was collected and its mass was measured continuously over time using a weighing balance connected to a data logger. Data was collected every second and then averaged per minute. Permeate flux was calculated on the basis of permeate mass divided by effective surface area and filtration time, unit is $\text{L}/(\text{m}^2 \cdot \text{min})$.

Figure 3.4 Scheme of the bench scale system used for flux performance, concurrent filtration and solar photocatalytic disinfection/degradation tests.

3.5.2 Decontamination evaluation of Ag/TiO₂ nanofiber membrane under solar irradiation

The photodegradation capability of the Ag/TiO₂ nanofiber membrane to the organic pollutant was evaluated using a model pollutant Methylene Blue (MB). The same dead-end membrane filtration system setup was used as shown in Figure 3.4. For the

photodegradation of MB, 50 mL MB solution with an initial concentration of 10 mg/L (10 ppm) was filled into the filtration cup. The MB solution in the filtration cup was kept in dark for 1 h to reach the adsorption equilibrium, and then kept under solar simulator. The TMP was maintained around 0.05 MPa during the whole processes. 3 mL permeates were collected to measure the UV-adsorption value at 605 nm at an interval of 3 min for 30 min, as the major adsorption peak of MB used was around 605 nm (Mills, Sheik et al. 2009). As a contrast, the photodegradation of MB by P25 deposited membrane and TiO₂ nanofiber membrane was also conducted simultaneously. And the photodegradation of MB under solar irradiation without membrane was also tested at the same conditions. To investigate the complete mineralization of MB, the total organic carbon (TOC) of permeates was measured by a TOC analyzer (Tekmar Dohrmann Apollo 9000) at different reaction times.

3.5.3 Decontamination evaluation of GO-Ag nanocomposites under visible light irradiation

The photocatalytic decontamination capability of GO-Ag nanocomposites was evaluated using AO 7 under visible light irradiation (wavelength > 420 nm). The photocatalytic measurements were carried out in an open photoreactor. Before irradiation, a suspension containing 50 mL of 10 ppm AO 7 solution and 20 mg catalysts was sonicated for 5 min, and stirred for 30 min in the dark to allow sorption to reach equilibrium. Then, the mixture was irradiated with a solar simulator shown in Figure 3.3 (without the UV light). At a given time interval of irradiation, 1 mL aliquots were withdrawn. The residual concentration of AO 7 in the aliquots was analyzed using a UV-visible spectrophotometer.

3.5.4 Decontamination evaluation of GO-TiO₂-Ag nanocomposites under solar irradiation

The photocatalytic performance of the nanocomposites was evaluated by degrading pollutant dye AO 7 and phenol. For dye degradation, the catalysts (20 mg) were well dispersed into AO 7 dye solution (10 ppm, 50 mL). For the phenol degradation, the catalysts (50 mg) were well dispersed into phenol aqueous solution (10 ppm, 50 mL). The mixtures were kept stirring in dark for 30 min to reach the adsorption equilibrium. The solar simulator was used as the light source. At certain time intervals, a given amount of reaction solution was collected and centrifuged to remove photocatalysts for analysis. As for the stability tests, the photocatalysts were collected by centrifugation for repeated experiments. The concentrations of AO 7 and phenol were monitored by UV-Vis spectrophotometer, and were determined by their characteristic absorption wavelength at 485 nm, 270 nm, respectively.

3.5.5 Decontamination evaluation of GO-Ag₃PO₄ nanocomposites under visible light irradiation

The photocatalytic performance of the photocatalysts was evaluated by degradation of pollutant dye AO7 and phenol. For the dye degradation, the catalysts (20 mg) were put into AO7 dye solution (50 ppm, 50 mL). For the phenol degradation, the catalysts (50 mg) were put into phenol aqueous solution (10 ppm, 50 mL). The mixtures were stirred in dark for 30 min to reach the adsorption equilibrium. The light source used was a 300 W Xe arc lamp equipped with a cold mirror to provide visible light ($420\text{ nm} \leq \lambda \leq 630\text{ nm}$, 80 mW/cm^2) (Oriel, 300W model). At certain time intervals of visible-light irradiation, reaction solution was collected and centrifuged to remove photocatalysts for analysis. The concentrations of AO7 and phenol were monitored by UV-Vis spectroscopy, and were determined by its maximum absorption wavelength at 485 nm and 270 nm, respectively.

CHAPTER 4: AG/TIO₂ NANOFIBER COMPOSITES FOR WATER DISINFECTION/DECONTAMINATION UNDER SOLAR IRRADIATION AND CONCURRENT MEMBRANE FILTRATION

4.1 Introduction

The use of noble metal/TiO₂ nanocomposites is an effective way to enhance the photocatalytic activity of TiO₂ owing to the efficient electron-hole separation by noble metals, as mentioned in Section 2.3.4 (Tian and Tatsuma 2004; Tian and Tatsuma 2005; Kubacka, Ferrer et al. 2008). Among the metallic species such as Ag, Au, Pt, which can be incorporated onto TiO₂ surface, silver has shown an enhanced electron-hole separation and interfacial charge transfer ability, as well as the increase of the visible light excitation of TiO₂ (Yu, Xiong et al. 2005; Seery, George et al. 2007; Kubacka, Ferrer et al. 2008). Meanwhile, Ag nanoparticles are known to exhibit the highest bactericidal activity and biocompatibility amongst all the antibacterial nanomaterials (Kloepfer, Mielke et al. 2005; Gummy, Morais et al. 2006; Li, Mahendra et al. 2008).

To achieve the separation and reuse of nanosized TiO₂ photocatalysts, usually post-treatment using membrane filtration or immobilizing TiO₂ on various supports have been applied, as mentioned in Section 2.3.6 (Meulenberg, Mertens et al. 2006; Triani, Evans et al. 2006; Choi, Stathatos et al. 2007). Zhang, et al. has successfully fabricated the high-performance TiO₂ nanowire membrane, which showed the ability of concurrent separation and photocatalytic degradation for water purification (Zhang, Du et al. 2008; Zhang, Zhang et al. 2009). The use of electrospinning technique to fabricate TiO₂ nanofibers is another simple and versatile method (Li and Xia 2003; Formo, Lee et al. 2008). Comparing to hydrothermally prepared TiO₂ nanowires, the electrospun TiO₂ nanofibers are able to provide even higher photocatalytic efficiency as a result of

highly crystallized TiO₂ and higher specific surface area due to their mesoporous structure (Zhang, Xu et al. 2009).

Taking the advantages of Ag nanoparticles, electrospun TiO₂ nanofibers and membrane filtration into account, Ag/TiO₂ nanofiber composites were synthesized and used for photocatalytic disinfection/degradation and concurrent membrane filtration. The solar simulator was used herein to initiate the photocatalytic reactions instead of UV irradiation. This Ag/TiO₂ nanofiber membrane/solar irradiation system has several important features:

- (1) The one-dimensional mesoporous TiO₂ nanofibers and the nano-structured Ag create multi-channelled reaction spaces convenient for mass transfer. This remarkably increases the accessible surface areas for photodegradation of contaminants;
- (2) Ag nanoparticles modified TiO₂ may significantly strengthen the photocatalytic efficiency of TiO₂ by retarding the recombination of electron-holes and increasing the utilization of solar light;
- (3) The uniformly loaded Ag nanoparticles on Ag/TiO₂ nanofiber membranes possess high antibacterial activity, which can offer opportunities for both disinfection and membrane fouling mitigation;
- (4) Concurrent photocatalytic degradation of contaminants and membrane filtration may be achieved without post-treatment for material recovery.

4.2 Results and discussion

4.2.1 Characterization of Ag/TiO₂ nanofiber composites

Electrospinning offers a simple and versatile solution to the large-scale production of nanofibers with various materials, especially for TiO₂ nanofibers (Li and Xia 2003). The morphology of the TiO₂ nanofibers can be well-controlled by critically adjusting

the solution viscosity and applied electric field intensity. Figure 4.1a shows the SEM image of the TiO₂ nanofibers after calcinations. The diameter of the fibers ranged from 150-200 nm, while the length of the fibers was longer than 10 μ m. Previous work applied co-electrospinning for the deposition of Ag nanoparticles on TiO₂ nanofibers (Jin, Zhang et al. 2007). However, Ag ion is easily oxidized to Ag₂O rather than the desired Ag nanoparticles during calcinations at high temperature. The polyol synthesis is a soft and environmental friendly fabrication of Ag nanostructures with controlled shapes and properties (Wiley, Sun et al. 2007). For this study, in-situ polyol synthesis was used for the deposition of Ag nanoparticles on TiO₂ nanofibers. Figure 4.1b shows the SEM image of Ag/TiO₂ nanofiber composites, illustrating that Ag nanoparticles were uniformly deposited on TiO₂ nanofibers. Both high magnification SEM image and TEM image of Ag/TiO₂ nanofiber composites (Figures 4.1c and 4.1d) clearly show that the Ag nanoparticles with size round 50 nm have been successfully deposited on the surface of TiO₂ nanofibers. The Ag deposition was further verified by EDS analysis, and the loading amount was estimated to be 4.65 wt. %, as shown in Figure 4.2. To the best of the author's knowledge, this is the first time polyol synthesis has been used for the deposition of Ag nanoparticles on TiO₂ nanofibers. Compared to the traditional chemical reduction and photo-deposition of Ag nanoparticles on TiO₂ nanomaterials, this method does not involve any toxic chemical or UV light, while could precisely control the growth of Ag nanoparticles on TiO₂ nanofibers.

To further establish the chemical properties of the Ag/TiO₂ nanofiber composites, XRD and UV-Vis spectra were employed. Figure 4.3 shows that both XRD patterns of pure TiO₂ nanofibers and Ag/TiO₂ nanofiber composites have diffraction peaks relating to (101), (004), (200), (105), (211), and (204) planes of anatase phase of TiO₂, which was favored for better photocatalytic oxidation reaction than rutile phase. In the curve of Ag/TiO₂ nanofiber composites, clear peaks of Ag (111), (200), (220), and (311) further confirmed that the Ag nanoparticles had been successfully deposited on TiO₂ nanofibers. The absorption spectra of the TiO₂ nanofibers and Ag/TiO₂ nanofiber composites are presented in Figure 4.4. The band edge of pure TiO₂ nanofibers was

near 380 nm, while after deposition with Ag nanoparticles, the band edge of Ag/TiO₂ nanofibers increased to more than 400 nm. This implies that the Ag/TiO₂ nanofiber composites could absorb light in near UV and visible region.

Figure 4.1 Characterization of Ag/TiO₂ nanofiber composites: (a) SEM image of pure TiO₂ nanofibers after calcinations, (b)-(c) SEM images of Ag/TiO₂ nanofiber composites at different magnifications, (d) TEM image of Ag/TiO₂ nanofiber composites.

Figure 4.2 EDS spectra and element contents of Ag/TiO₂ nanofiber composites. The other peaks on the spectra were Au because of Au coating before test.

Figure 4.3 XRD patterns of pure TiO₂ nanofibers and Ag/TiO₂ nanofiber composites.

Figure 4.4 UV-Vis spectra of pure TiO_2 nanofibers and Ag/TiO_2 nanofiber composites.

4.2.2 Characterization of Ag/TiO_2 nanofiber membrane

The hypothesis of this experiment is illustrated in Figure 4.5a. Traditional membrane filtration can only remove pathogens or pollutants from water, rather than inactivating or degrading them. As a result, the pathogenic bacteria, viruses and toxic pollutants still pose risks to the environment and these pollutants also cause membrane fouling problems. A new type of membrane which could simultaneously block and degrade pathogens and organic pollutants from water has significant importance in membrane application. So this work is attempting to combine photocatalysis process with membrane filtration, to achieve filtration, disinfection and degradation concurrently, without further post-treatment of material recovery. The Ag/TiO_2 nanofiber membrane was prepared with a two-step process: vacuum filtration of the Ag/TiO_2 nanofiber composite suspension on the glass filter, and a hot press process to compress the membrane formed on a glass filter. The thickness of the Ag/TiO_2 nanofiber composite functional layer (membrane) was easily controlled by adjusting suspension volumes of Ag/TiO_2 nanofiber composites. Figure 4.5b shows a digital image of the as-prepared

Ag/TiO₂ nanofiber membrane, which consists of a support layer of commercial glass filter and a functional layer of Ag/TiO₂ nanofiber composites, and the as-prepared membrane which was flexible and could be formed in desired shape.

Figure 4.5 (a) Schematic program of the hypothesis of Ag/TiO₂ nanofiber membrane; (b) Photograph of Ag/TiO₂ nanofiber membrane.

The flux performance of the Ag/TiO₂ nanofiber membrane was determined using a lab-scale dead-end apparatus, as illustrated in Figure 3.4. Pure TiO₂ nanofiber membrane and P25 deposited membrane were also tested for comparison. Figure 4.6 displays the relationships between permeate flux and TMP. Clearly, the permeate flux of the pure TiO₂ nanofiber membrane and Ag/TiO₂ nanofiber membrane are proportional to TMP with a well-fitted regression line ($R^2 > 0.99$), which implies that both TiO₂ nanofiber and Ag/TiO₂ nanofiber membrane had good permeate flux performance. However, the permeate flux of the commercial P25 deposited on glass filter (membrane) was not well proportional to TMP ($R^2 = 0.77$). At the same TMP, the P25 deposited membrane showed significant decrease in flux compared to TiO₂ nanofiber membrane and Ag/TiO₂ nanofiber membrane. These results illustrated that one-dimensional TiO₂

nanostructures were favourable to maintain membrane flux compared to commercial P25, as the P25 particles caused the great membrane flux reduction. This was due to the rapid deposition of P25 particles onto the membrane surface to form a fouling layer instead of the formation of a multifunctional layer. Moreover, the results show slightly decrease of flux of Ag/TiO₂ nanofiber membrane compared with pure TiO₂ nanofiber membrane, which may be due to the Ag deposition.

Figure 4.6 Change in permeate flux of P25 deposited membrane, pure TiO₂ nanofiber membrane and Ag/TiO₂ nanofiber membrane under different TMP.

4.2.3 Photocatalytic disinfection evaluation of Ag/TiO₂ nanofiber membrane under solar irradiation

E.coli was chosen as a representative waterborne pathogen, and a solar simulator (100 mW/cm²) was used as the source of solar irradiation. The photocatalytic inactivation of *E.coli* using different membranes under different conditions is presented in Figure 4.7. A solar control was carried out in the absence of membrane under solar simulator

irradiation. Figure 4.7 clearly indicated that 99.0 % of the bacteria survived after 30 min solar irradiation. These results revealed that the solar irradiation intensity had no obvious antibacterial effect on *E.coli* within 30 min.

The antibacterial activities of the membranes without solar irradiation were also investigated as a comparison. Both of the P25 deposited membrane and TiO₂ nanofiber membrane showed no antibacterial capability in the absence of solar irradiation, implying that TiO₂ itself is not toxic to the bacteria (Figure 4.7). However, the bacterial survival fraction on Ag/TiO₂ nanofiber membrane decreased dramatically to 50 % after 30 min in the absence of solar irradiation (Figure 4.7). These results revealed that the Ag nanoparticles on the Ag/TiO₂ nanofiber membrane had excellent antibacterial capability. In the presence of solar irradiation, both of the P25 deposited membrane and TiO₂ nanofiber membrane exhibited antibacterial capability on *E.coli*, as shown in Figure 4.7. The TiO₂ nanofiber membrane showed higher photocatalytic disinfection capability than P25 deposited membrane. Possible reason for this phenomenon could be that the specific surface area of TiO₂ nanofibers were much higher (BET specific surface area 85.6 m²/g) than P25 powder (34.3 m²/g), which played a key role in photocatalytic activity. Concurrently, one-dimensional nanofibers could retain more effective surface area than nanoparticles when a membrane was formed, which was in agreement with the results of the previous study (Zhang, Xu et al. 2009). Surprisingly, when employing Ag/TiO₂ nanofiber membrane under solar irradiation, 99.9 % of *E.coli* was inactivated within 30 min, as shown in Figure 4.7.

In order to compare the effects under various conditions, the results were evaluated by inactivation rate constant κ using first-order kinetics (Chen, Yang et al. 2009). The rate constant increased in the order of the following sequence: Solar ($(1.10 \pm 0.06) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.91$) < A ($(1.40 \pm 0.09) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.79$) < B ($(2.10 \pm 0.16) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.78$) < B with solar ($(7.80 \pm 0.25) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.90$) < A with solar ($(1.00 \pm 0.05) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.98$) < C ($(1.71 \pm 0.13) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.91$) < C with solar ($(3.42 \pm 0.11) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.97$) (A=TiO₂ nanofiber membrane, B=P25 deposited membrane, C=Ag/TiO₂ nanofiber membrane). The inactivation contributed

by the Ag nanoparticle fraction of Ag/TiO₂ nanofiber membrane was estimated to be about 0.016 min⁻¹, while the photocatalytic disinfection effect of Ag/TiO₂ nanofiber membrane was estimated to be about 0.018 min⁻¹, which was higher than the photocatalytic disinfection effect comparing to the pure TiO₂ nanofiber membrane at 0.01 min⁻¹. These results confirmed that the Ag deposition could enhance the photocatalytic antibacterial capability of TiO₂ nanofiber under solar irradiation.

Figure 4.7 Photocatalytic disinfection of *E. coli* on different membranes under various conditions (initial bacteria concentration: 10⁷ cfu/mL, solar intensity: 100 mW/cm²). Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

As discussed above, besides silver nanoparticles, the photocatalytic disinfection also contributes to the bacteria inactivation in this Ag/TiO₂ nanofiber membrane/solar system. To further confirm this, a ·OH scavenger test was employed. Dimethyl sulphoxide (DMSO) was reported to scavenge ·OH in TiO₂ photocatalysis system

(Salih 2002). Experiments were performed using Ag/TiO₂ nanofiber membrane at different DMSO concentrations. Figure 4.8 shows that parallel to the increment of DMSO concentration, an obvious increase in bacteria survival was observed. When 40 mM DMSO was added into the system, the bacteria survival rate increased back to that of Ag/TiO₂ nanofiber membrane without solar irradiation (Figures 4.7 and 4.8). Control experiment using DMSO (40 mM) in the absence of Ag/TiO₂ nanofiber membrane did not show obvious antibacterial ability. This is a clear indication that a high yield of ·OH was generated in this Ag/TiO₂ nanofiber membrane/solar irradiation system. Moreover, the ·OH is primarily responsible for the photocatalytic disinfection in Ag/TiO₂ nanofiber membrane/solar irradiation system.

Figure 4.8 Photocatalytic disinfection of *E.coli* in Ag/TiO₂ nanofiber membrane/solar irradiation system in the presence of ·OH scavenger DMSO at different concentrations (Control experiment was carried out at 40 mM DMSO without membrane, and initial bacteria concentration: 10⁷ cfu/mL, solar intensity: 100 mW/cm²). Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

Before bacterial regrowth test, a complete disinfection over Ag/TiO₂ nanofiber membrane was investigated. Figure 4.9 shows that a complete bacteria inactivation with initial concentration of 10⁷ cfu/mL was achieved within 70 min in this Ag/TiO₂ nanofiber membrane/solar irradiation system. To investigate the ability of bacteria to undergo repair after photocatalytic disinfection, once the photocatalytic disinfection treatment was completely performed, the bacteria was washed off from the membrane and kept in dark at 37 °C to allow bacterial repair. Following a 48 h recovery period, no bacterial count could be detected. This revealed that the photocatalytic disinfection of Ag/TiO₂ nanofiber membrane/solar irradiation system had led to irreversible damage to the bacterial cells or brought the bacteria to a “not-culturable” state, indicating bacteria were unable to recover unless favourable conditions were provided (Dunlop, Byrne et al. 2002; Leung, Chan et al. 2008).

Figure 4.9 Complete *E. coli* inactivation in Ag/TiO₂ nanofiber membrane/solar irradiation system. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

4.2.4 The antibacterial activity of Ag/TiO₂ nanofiber membrane

In order to investigate the intrinsic chemical antibacterial strength of the Ag nanoparticles and to test the anti-biofouling property of Ag/TiO₂ nanofiber membrane, a standard Kirby-Bauer approach was applied. *E.coli* was inoculated with Ag/TiO₂ nanofiber membrane on agar plates for 24 h. P25 deposited membrane and TiO₂ nanofiber membrane were also investigated at the same time as a comparison. The results are shown in Figure 4.10. Clearly, there was no bacteria growth around the Ag/TiO₂ nanofiber membrane, indicating that some amount of Ag ions released from the membrane restrained the bacteria growth. However, there was no inhibition zone around P25 deposited membrane and TiO₂ nanofiber membrane. These results indicated that the Ag ions could play important role in disinfection property of Ag/TiO₂ nanofiber membrane, which was in good agreement with similar published work of Ag decorated ceramic composite (Lv, Liu et al. 2009). Thus these results also implied the excellent anti-biofouling property of Ag/TiO₂ nanofiber membrane.

Figure 4.10 Photographs of zone of inhibition test results. Comparison of the P25 deposited membrane, pure TiO₂ nanofiber membrane and Ag/TiO₂ nanofiber membrane with incubating with *E.coli* for 24 h.

4.2.5 Decontamination evaluation of Ag/TiO₂ nanofiber membrane under solar irradiation

Figure 4.11 Photocatalytic degradation of MB with different membranes. The initial concentration of MB was 10 ppm. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The photocatalytic decontamination property of Ag/TiO₂ nanofiber membrane was investigated by examination of organic pollutant MB under solar irradiation. As shown in Figure 4.11, insignificant removal of MB occurred without membrane in the presence of 30 min solar irradiation, which was due to the photolysis of MB. The data could also be satisfactorily analyzed by first-order kinetic equation to obtain the rate constant. In the presence of P25 deposited membrane under solar irradiation, a slow degradation (rate constant, $(7.60 \pm 0.32) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.98$) was observed, while in the presence of TiO₂ nanofiber membrane, a relatively fast degradation (rate constant, $(1.37 \pm 0.09) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.80$) was achieved. When applying the Ag/TiO₂ nanofiber membrane, the MB degradation rate could be significantly improved as shown in Figure 11 (rate constant, $(2.11 \pm 0.11) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.90$). The 30 min

solar irradiation could remove nearly 80 % of MB. The results of photocatalytic detoxification were in good agreement with the results of photocatalytic disinfection. It further confirmed that TiO₂ nanofiber membrane had higher photocatalytic efficiency than P25 deposited membrane. Moreover, Ag/TiO₂ nanofiber membrane had significantly enhanced photocatalytic activity compared to pure TiO₂ nanofiber membrane.

Figure 4.12 TOC of permeates during photocatalytic degradation of MB in Ag/TiO₂ nanofiber membrane/solar irradiation system. The initial concentration of MB was 10 ppm. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

To investigate the complete mineralization of dye in Ag/TiO₂ nanofiber membrane/solar irradiation system, the total organic carbon (TOC) of MB was analyzed (Figure 4.12). The result shows that the complete mineralization of MB in Ag/TiO₂ nanofiber membrane/solar irradiation system was achieved after 80 min solar irradiation. This result implies that the Ag/TiO₂ nanofiber membrane had performed self-cleaning under solar irradiation when it was trapped with organic dye.

4.2.6 Reusability test

Figure 4.13 Reusability experiments for (a) photocatalytic disinfection, (b) degradation of MB in Ag/TiO₂ nanofiber membrane/solar irradiation system. Membrane wash by DI water was carried out before each recycle. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The reusability test of Ag/TiO₂ nanofiber membrane/solar irradiation system for disinfection and MB degradation were evaluated separately. As initially reported by Jacoby et al. (1998), complete oxidation of bacterial cells into carbon dioxide by photocatalysis was confirmed with 75 h UV irradiation in the presence of *E. coli* and TiO₂ (Jacoby, Maness et al. 1998). It has been further confirmed by different research groups with different photocatalytic disinfection systems (Sun, Tay et al. 2003; Leung, Chan et al. 2008; Cheng, Chan et al. 2010). According to these reported works, it may take a long reaction time to achieve the complete mineralization of bacterial cells in photocatalytic disinfection system. As a result, the Ag/TiO₂ nanofiber membrane was washed by DI water to remove bacteria residuals before reuse. Experiment results show that the photocatalytic disinfection activity of Ag/TiO₂ nanofiber membrane/solar irradiation system has no obvious decrease after continuous five times' recycle (Figure 4.13a). Meanwhile, since the complete mineralization of MB was achieved after 70 min solar irradiation, the reusability test of MB degradation of Ag/TiO₂ nanofiber

membrane/solar irradiation system was evaluated without washing. Figure 4.13b shows that there was no obvious photocatalytic degradation activity decreases after continuous five times' recycle. These results indicate the good stability and reusability of our Ag/TiO₂ nanofiber membrane/solar irradiation system for photocatalytic disinfection and dye degradation.

4.2.7 Mechanism on high-performance photocatalytic disinfection and dye degradation of Ag/TiO₂ nanofiber membrane under solar irradiation

The photocatalytic activities of Ag/TiO₂ nanocomposites from different works are difficult to be compared, as many factors such as structure morphology, silver loading amount and the system used may all affect their photocatalytic activities (Sung-Suh, Choi et al. 2004; Xin, Jing et al. 2005; Malato, Fernandez-Ibanez et al. 2009; van Grieken, Marugán et al. 2009; Ma, Xiong et al. 2011; Xiong, Ma et al. 2011). The exact mechanism of the role of silver loading has been widely investigated. Some researchers reported that increasing amount of silver could increase the rate of degradation of dye (Seery, George et al. 2007). Others concluded that the optimal Ag loading of Ag/TiO₂ nanofiber composites is relatively small, and the optimal amount is different for photocatalytic detoxification and disinfection (Ma, Xiong et al. 2011; Xiong, Ma et al. 2011). In this work, the Ag loading (4.65 wt %) of Ag/TiO₂ nanofiber membrane was relatively high, however, its disinfection and detoxification properties under solar irradiation is relatively high. Several reasons could support these findings. Firstly, the Ag loading amount and the TiO₂ active sites are the two essential parts for the photocatalytic activity of Ag/TiO₂. The higher electron-hole recombination inhibition is achieved at higher Ag loading rate according to Schottky barrier formation (Xin, Jing et al. 2005). And the increasing of Ag loading will increase the O₂ adsorption to produce more reactive oxygen species (ROSs) for photooxidation (Xiong, Ma et al. 2011). However, to the contrary, the excess Ag loading on TiO₂ surface could reduce the active sites, which could reduce the photocatalytic activity of Ag/TiO₂ (Xin, Jing et al. 2005). Therefore, it is important to load Ag on TiO₂ surface while maintain sufficient

active sites. The Ag nanoparticles of this work were homogeneously dispersed on TiO₂ nanofibers, while maintaining sufficient active sites on TiO₂ nanofiber surface, as shown in Figure 4.1b-1d. And the BET specific surface area of Ag/TiO₂ nanofiber composites had increased from 85.6 m²/g (pure TiO₂ nanofibers) to 102.3 m²/g. All these were contributed to the enhanced electron-hole recombination inhibition, increased O₂ adsorption and increased active sites, all leading to the higher photocatalytic disinfection and detoxification. Secondly, the disinfection tests indicated that the intrinsic antibacterial activity of Ag nanoparticles played a key role in Ag/TiO₂ disinfection, and higher Ag loading could lead to the higher antibacterial activity (Morones, Elechiguerra et al. 2005). Therefore, the high Ag loading amount of Ag/TiO₂ nanofiber membrane was beneficial for the water purification in this particular system.

4.2.8 Discussion on practical water disinfection and decontamination applicability of Ag/TiO₂ nanofiber membrane under solar irradiation

The United States Environmental Protection Agency (EPA) surface water treatment rule requires 99.9 % (3 log) removal/inactivation of bacteria and 99.99 % (4 log) removal/inactivation of viruses (USEPA 2009). In this work, 99.9 % *E.coli* removal was achieved within 30 min. This indicates that the system is feasible for surface water treatment. However, if this system is used for the treatment of highly polluted water, contact time extension is needed to achieve complete disinfection. The experiment results show that a 7 log *E.coli* inactivation was achieved within 70 min reaction time under this test system. The result proved that, enough contact time could ensure the complete bacteria disinfection under this system. Moreover, the final silver ion concentration after the treatment is measured to be less than 0.1 ppm, which is under the silver ion limits of EPA requirement for drinking water treatment (USEPA 2009).

The commonly used drinking water disinfection techniques include physical removal of microorganisms (coagulation, sedimentation and filtration) and chemical inactivation

(chlorine, chloramines, ozone and UV light). Although disinfection methods currently can effectively control microbial pathogens, there still exist some limitations for providing high-quality drinking water. The physical method could not destroy pathogens, which may still possess risks to the environment. Chemical disinfectants commonly used by the water industry such as free chlorine, chloramines and ozone can react with constituents in natural water to form harmful DBPs (Krasner, Weinberg et al. 2006). As an alternative, UV disinfection is more environmental friendly. However, it may not effectively inactivate some viruses (Choi and Choi 2010). Moreover, both ozonation and UV disinfection have non-residual effects. In this work, we are trying to combine photocatalytic disinfection with physical membrane filtration, which could take advantages of both two methods. Moreover, the Ag nanoparticles could provide the antibacterial activity of the catalysts even under dark condition. Compared with traditional disinfection methods, our membrane/solar irradiation system have several advantages: (1) cost-effective disinfection in the use of solar irradiation; (2) acceptable disinfection efficiency; (3) irreversible pathogen inactivation; (4) no obvious DBPs in treated water.

The long disinfection contact time of the Ag/TiO₂ nanofiber membrane/solar irradiation system may be a challenge in practical membrane application. However, this system combines membrane filtration with photocatalytic disinfection process, which allows the bacteria to be filtered on the membrane surface to get efficient disinfection contact time. Nevertheless, the bacteria residues remain on membrane surface after treatment, as the complete mineralization of bacterial cells may take a long time. This may add risk to membrane fouling problem. Moreover, before practical application of this system, the disinfection evaluation of other microbial pathogens and viruses should be investigated in the near future.

As for water decontamination of this system, the author used MB dye as an example. The experimental results show that total TOC removal of 10 ppm MB needs 80 min solar irradiation. This result proved that enough contact time could ensure the complete dye degradation under this system. The author also tested other organic pollutants

including AO 7 dye and phenol, even longer contact time were required for their complete removal. This long decontamination contact time also may be a challenge in practical membrane applications.

4.3 Conclusion

In summary, Ag/TiO₂ nanofiber composites were fabricated via electrospinning followed by a polyol synthesis method. A novel Ag/TiO₂ nanofiber membrane was fabricated using the as-prepared Ag/TiO₂ nanofiber composites by filtration method. This novel membrane was able to maintain good permeate flux at low TMP. The Ag/TiO₂ nanofiber membrane showed significantly enhanced disinfection capability towards *E.coli* and photocatalytic degradation activity of the organic pollutants studied under solar irradiation compared with pure TiO₂ nanofiber membrane and commercial P25 deposited membrane. The excellent intrinsic antibacterial capability of Ag/TiO₂ nanofiber membrane was also able to significantly inhibit bacterial growth, which will be beneficial for membrane biofouling control. As demonstrated in this portion of the study, this high-performance Ag/TiO₂ nanofiber membrane is able to perform photocatalytic disinfection/degradation under solar irradiation and concurrent membrane filtration. Such excellent performances will lead to extensive cost effective water purification applications in the near future.

Nevertheless, there is still room for improvements to further enhance the photocatalytic efficiency of TiO₂-based photocatalysts and thus shorten required contact times for water disinfection and decontamination.

CHAPTER 5: GO-AG NANOCOMPOSITES FOR WATER DISINFECTION AND PHOTOCATALYTIC DECONTAMINATION UNDER VISIBLE LIGHT IRRADIATION

5.1 Introduction

Chapter 4 confirmed that the combination of Ag nanoparticles and TiO₂ nanofibers exhibit enhanced photocatalytic activity of TiO₂ as well as high antibacterial activity due to both Ag nanoparticles and photocatalytic activity of the Ag/TiO₂ nanofiber composites. However, it is also concluded that improvements to further enhance the photocatalytic efficiency of TiO₂-based photocatalysts to ensure shorter contact times for water disinfection and decontamination is highly desired.

As mentioned in Section 2.3.4, improvement of TiO₂ photocatalytic efficiency may be achieved by maximizing the specific surface area of TiO₂ nanomaterials. Since the specific surface area is strongly dependent on the morphology, size, structure and the dispensability of the material, smaller sized TiO₂ nanoparticles/rods in a well-dispersed form may exhibit higher photocatalytic activity. However, the particle aggregation and nanomaterial recovery are two large challenges in using small nanomaterials for industrial applications. Also as mentioned in Section 2.3.4, coupling TiO₂ with 2D carbon material graphene is a new approach to improve the efficiency of TiO₂ and to facilitate its recovery. As a result, the work reported in Chapters 5 and 6 will discuss the possibilities of synthesis of novel ternary GO-TiO₂-Ag nanocomposites for water disinfection and decontamination under solar irradiation. To simplify this study, binary GO-Ag nanocomposites will be firstly investigated in Chapter 5.

Ag nanoparticles are known to exhibit the highest bactericidal activity and biocompatibility amongst all the antibacterial nanomaterials (Morones, Elechiguerra et

al. 2005; Marambio-Jones and Hoek 2010; Knetsch and Koole 2011). Monodispersed Ag nanoparticles of small size are desirable for antibacterial control systems. However, the particle aggregation problem and nanomaterial recovery are also two significant challenges in using Ag nanoparticles. Graphene, however, is considered as an ideal 2D reinforcing component for composite materials. GO-Ag nanocomposites are considered effective antibacterial materials. Moreover, considering the effective photocatalytic degradation of dyes over GO-Au nanocomposites under visible light, GO-Ag nanocomposites may pose the same photocatalytic activity towards dyes (Xiong, Zhang et al. 2010).

The synthesis of GO-Ag nanocomposites has been reported by several researchers, mostly using a solution-based single-step method to reduce Ag^+ ions on GO sheets (Xu and Wang 2009; Zhou, Huang et al. 2009; Shen, Shi et al. 2010; Tang, Shen et al. 2010; Das, Sarma et al. 2011; Ma, Zhang et al. 2011; Tien, Huang et al. 2011). However, this single-step approach has difficulty in controlling the morphology and size of Ag nanoparticles on GO sheets, because Ag nanoparticles are formed onto GO sheets directly during Ag^+ reduction. Since the antibacterial activity of Ag nanoparticles relies heavily on its size, precise size control of the Ag nanoparticles anchored on GO sheets is essential. One recent work reported a dry decoration of GO with Ag nanocrystals from an arc plasma source using electrostatic force (Lu, Mao et al. 2009). However, the use of an extra electric field limits its broad application in reality.

Hence, this portion of the study aims to develop a facile two-phase method that embeds Ag nanoparticles onto GO sheets. It is worth highlighting that this method can be used for the successful anchorage of highly monodispersed Ag nanoparticles on GO sheets at the water/toluene interface. It is a remarkable advancement over existing methods of synthesis of GO-Ag nanocomposites and may provide a universal approach for the synthesis of high quality GO-metal/metal oxide composites. Moreover, assembling the Ag nanoparticles on large GO sheets can remarkably enhance antibacterial activity and photocatalytic degradation of dyes under visible light irradiation. Large GO sheets also

facilitate the recovery of GO-Ag nanocomposites by simple filtration, which is beneficial for the applications in environmental engineering and other fields.

5.2 Results and discussion

5.2.1 Preparation and characterization of GO-Ag nanocomposites

The morphology and size of the oleylamine-capped Ag nanoparticles may be well-controlled via the organic phase synthesis (Chen, Feng et al. 2007; Shen, Hui et al. 2008). Oleylamine-capped Ag nanoparticles were well dispersed in toluene, while hydrophilic GO sheets were well dispersed in deionized (DI) water, as shown in photographs of Figure 3.2 in Chapter 3. The aqueous solution of GO and the toluene solution of Ag nanoparticles were mixed and stirred for 12 h to ensure the self-assembly of Ag nanoparticles onto the GO sheets in the water/toluene interface. It has been reported that metal nanoparticles can interact with the GO sheets through electrostatic binding, physisorption and charge-transfer interactions (Muszynski, Seger et al. 2008). Meanwhile, the large GO sheets act as excellent support and stabilizer for the Ag nanoparticles, avoiding nanoparticle aggregation. After centrifugation of the mixture and washing off extra oleylamine, the pure GO-Ag nanocomposites are formed and well dispersed in water as shown in Figure 3.2 of Chapter 3. The hydrophilic property to the GO-Ag nanocomposites is ascribed to the carboxyl and hydroxyl groups of the GO sheets. This two-phase method is facile and reproducible and can be widely used for the synthesis of other GO-metal nanocomposites.

Figure 5.1 AFM image of single-sheet graphene oxide.

AFM was used to verify the numbers of GO layer synthesized. An AFM image of GO sheets is shown in Figure 5.1. From the two line scans, the thickness of GO sheets is measured around 1.1 nm, which is slightly larger than reported apparent thickness of single-sheet graphene due to the oxygen groups (Novoselov, Geim et al. 2004). The measured thickness of GO assures that the GO synthesized is exfoliated into single sheets in water. The typical size of GO sheets is more than 2 μm. The TEM was used to analyze the morphology of GO-Ag nanocomposites. Figure 5.2a illustrates that oleylamine-capped Ag nanoparticles synthesized in toluene are highly monodispersed with a uniform size of 6 nm, which are able to provide superior antibacterial capability. Figure 5.2b illustrates that the size of the GO sheets synthesized is larger than 2 μm. Since the potential cytotoxicity of engineered nanomaterials is of significant consideration when exposed to the environment (Auffan, Rose et al. 2009; Thubagere and Reinhard 2010), the GO sheets with a large size may benefit the recovery of GO-Ag nanocomposite materials after disinfection by simple filtration. The GO sheets are

uniformly covered by Ag nanoparticles as is shown in Figures 5.2c and 5.2d. The image in Figure 5.2d reveals a single GO-Ag nanocomposite sheet. It can be observed clearly that Ag nanoparticles are well monodispersed on GO sheet without any aggregation. Both the edge of GO sheet and the nanostructure of the Ag nanoparticles are clearly observable in the higher magnification of Figure 5.2e, while there are no Ag nanoparticles outside the GO sheets. Figure 5.2f shows the high-resolution TEM images of GO-Ag nanocomposites from Figure 5.2e. The measured lattice-fringe spacing of the nanoparticles is 0.236 nm, which corresponds to the (111) crystal plane of Ag nanoparticles. These images of TEM confirm that the highly monodispersed Ag nanoparticles with uniform size around 6 nm are successfully synthesized and well located on GO sheets by the two-phase approach. Compared with the reported works, our Ag nanoparticles on GO sheets appear to be highly monodispersed with smaller uniform size (Shen, Shi et al. 2010; Das, Sarma et al. 2011; Liu, Liu et al. 2011).

Figure 5.2 TEM images of Ag nanoparticles (a), GO sheets (b), GO-Ag nanocomposites ((c), (d), (e) and (f)). Inset of (d) is the size distribution of Ag nanoparticles on GO sheets.

Figure 5.3 (a) XRD patterns of GO sheets, oleylamine-capped Ag nanoparticles and GO-Ag nanocomposites. (b) XPS spectra of GO-Ag nanocomposites (Inset table is the element weight percentage).

To further validate the GO-Ag nanocomposites as well as to value the mass ratio of Ag/GO, XRD and XPS were applied to measurements. Figure 5.3a shows the XRD patterns of GO sheets, oleylamine-capped Ag nanoparticles and GO-Ag nanocomposites. The curve of GO sheets shows a diffraction peak at 2θ value around 11.9° , which may be due to interlamellar water trapped between hydrophilic graphene oxide sheets (Park, An et al. 2009). In the curve of oleylamine-capped Ag nanoparticles, the clear peaks at 2θ values of about 38.1° , 44.3° , 64.5° and 77.5° are assigned to the (111), (200), (220), and (311) crystallographic planes of face-centered cubic (fcc) Ag nanoparticles, respectively (JCPDS No. 07-0783). The average particle size of the Ag nanoparticles was calculated to be 6.6 nm from Ag (111) peak based on Scherrer's equation. The curve of GO-Ag nanocomposites is without change in comparison with Ag nanoparticles. No obvious diffraction peaks of GO were observed in the GO-Ag nanocomposites, because the regular stack of GO was destroyed by the intercalation of Ag nanoparticles, which is consistent with other reported works about GO-metal nanocomposites (Novoselov, Geim et al. 2004; Shen, Shi et al. 2010; Das, Sarma et al. 2011). The crystallite size of Ag nanoparticles on GO sheets was

calculated to be 7.2 nm, which is in good agreement with the result of TEM. The XRD results confirm the Ag nanoparticles have successfully located onto the GO sheets. The XPS spectrum of GO-Ag nanocomposites in Figure 5.3b shows the major element peaks belong to C 1s, O 1s and Ag 3d, respectively. The weight percentage of each element analyzed by CasaXPS software according to the peaks, as shown in the inset of Figure 5.3b. The weight percentage of Ag nanoparticles in GO-Ag nanocomposites is 66.27 %, illustrating the mass ratio of Ag/GO is about 2/1.

5.2.2 Antibacterial activity of GO-Ag nanocomposites

The antibacterial activity of GO-Ag nanocomposites was evaluated by a colony forming count method. *E.coli* was chosen as the model waterborne pathogen in this experiment. Figure 5.4a shows that with the increase of the concentration of GO-Ag nanocomposites, the number of bacteria decrease dramatically; 99 % of *E.coli* cells have been killed at a concentration of 80 $\mu\text{g/mL}$. Results demonstrate that the GO-Ag nanocomposites have high-performance antibacterial capability at relatively low concentration. In control experiments, the antibacterial activity of pure GO sheets and pure Ag nanoparticles were also tested. The pure GO sheets show low antibacterial activity to *E.coli* cells; 10 % of *E.coli* cells were inactivated at a concentration of 80 $\mu\text{g/mL}$, and 17 % at a concentration of 100 $\mu\text{g/mL}$ (Figure 5.4a). This result differs from the recent published report which concludes that GO has high antibacterial activity for *E.coli* (Hu, Peng et al. 2010). Possible reason for this phenomenon is that GO sheets used in this study have different oxygen-containing group content compared with those used by some other investigators. This may affect the interaction between GO and bacteria cells. Figure 5.4a shows that pure Ag nanoparticles have good antibacterial activity; 86 % of *E.coli* cells were killed at a concentration of 80 $\mu\text{g/mL}$, and 96 % at a concentration of 100 $\mu\text{g/mL}$. These results indicate that the pure Ag nanoparticles synthesized here have effective antibacterial activity and contribute the major part to the antibacterial capability of GO-Ag nanocomposites. To clearly find out

the difference of antibacterial efficiency between the pure Ag nanoparticles and GO-Ag composites, the actual number of *E.coli* (initial concentration of 3×10^7 cfu/mL) to be inactivated was counted according to the concentration of samples and shown in Figure 5.4b. GO sheets themselves show nearly no log decrease of *E.coli* cells at the concentration of 100 $\mu\text{g/mL}$, and Ag nanoparticles indicate a 1.5 log decrease in *E.coli* cells at the same concentration. However, the GO-Ag nanocomposites show a 4 log decrease of *E.coli* cells at the concentration of 100 $\mu\text{g/mL}$. These results clearly illustrate that at the same concentration, pure GO sheets shows little antibacterial activity, while GO-Ag nanocomposites have much higher antibacterial activity than pure Ag nanoparticles. Considering that the actual percentage of Ag nanoparticles of GO-Ag nanocomposites is about 66 %, which means that 100 $\mu\text{g/mL}$ of GO-Ag nanocomposites equal to 66 $\mu\text{g/mL}$ of Ag nanoparticles, one can conclude that GO-Ag nanocomposites display remarkable enhanced antibacterial activity compared to pure Ag nanoparticles.

Figure 5.4 Antibacterial activity of GO sheets, Ag nanoparticles and GO-Ag nanocomposites at different concentration with the initial *E.coli* concentration of 3×10^7 cfu/mL: (a) *E.coli* viability percentage; (b) Log_{10} *E.coli* viability. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The time course for the *E.coli* inactivation was investigated to determine the disinfection rate of GO-Ag nanocomposites. As illustrated in Figure 5.5 at the same concentration, GO-Ag nanocomposites demonstrate the highest disinfection rate (rate constant, $(1.25 \pm 0.04) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.96$) compared to pure GO (rate constant, $(1.50 \pm 0.07) \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.93$) and pure Ag nanoparticles (rate constant, $(1.03 \pm 0.03) \times 10^{-2} \text{ min}^{-1}$, $R^2 = 0.99$). This result agrees with the results obtained above to further confirm that GO-Ag nanocomposites have enhanced antibacterial activity compared to pure GO and pure Ag nanoparticles.

Figure 5.5 Time course for antibacterial activity of 100 µg/mL of GO sheets, Ag nanoparticles and GO-Ag nanocomposites, with an initial *E.coli* concentration of 3×10^7 cfu/mL. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

To verify the reliability of the colony forming count method in this particular study, the antibacterial activity of GO-Ag nanocomposites by a LIVE/DEAD BacLight bacterial viability kit was examined further. With an appropriate mixture of the SYTO 9 and propidium iodide (PI), bacteria with intact cell membranes stain fluorescent green;

whereas, bacteria with damaged membranes stain fluorescent red. Actual images of bacteria were recorded as well by microscope at the same time. Figure 5.6a shows that *E.coli* in the control experiment dispersed well in saline solution, and most of the *E.coli* survived as indicated by the green color. After incubation with GO, *E.coli* cells aggregated together on the GO sheets as shown in the image detected by Figure 5.6b. However, most of the *E.coli* cells were still alive exhibiting green color. This confirms that GO sheets have low toxicity to *E.coli*. Figure 5.6c provides the images of *E.coli* in the presence of 100 $\mu\text{g/mL}$ Ag nanoparticles and shows that most of the *E.coli* cells were dead as indicated by the red color. Figure 5.6d shows that nearly all the *E.coli* cells were inactivated exhibiting a red color at a concentration of 100 $\mu\text{g/mL}$ GO-Ag nanocomposites. Results of this fluorescence-based assay is in good agreement with the results obtained by the colony forming count method. Therefore, it can be concluded that GO itself has lower antibacterial activity, and pure Ag nanoparticles have higher antibacterial activity towards *E.coli* at the size of 6 nm. The GO sheets and Ag nanoparticles exhibit a synergetic effect on antibacterial activity when combined into GO-Ag nanocomposites.

5.2.3 Recovery and Mechanism of the antibacterial activity of GO-Ag nanocomposites

Recovery of the nanomaterials is essential to avoid nano-toxicity to the ecosystem. A glass filter with pore size of 0.45 μm was used as a membrane filter for the recovery of the nanomaterials from the disinfected water. SEM was used to investigate the morphology of *E.coli* cells after disinfection and membrane filtration process. Without GO-Ag nanocomposites, *E.coli* cells remained in good state as shown in Figure 5.7a. However, with an increasing dosage of GO-Ag nanocomposites, the damage to *E.coli* cells increased. This is illustrated in Figures 4.7b,c and d. Figure 5.7b reveals that GO sheets can adsorb *E.coli* cells. In the presence of 20 $\mu\text{g/mL}$ GO-Ag nanocomposites, most of the *E.coli* cells gathered on the GO sheets and remained in good state. In the presence of 50 $\mu\text{g/mL}$ of GO-Ag nanocomposite, the image of the *E.coli* cells on the

Figure 5.6 Actual microscopic images and fluorescence microscopic images of bacteria after incubation with different samples in saline solution for 2 h: (a) *E.coli* without samples; (b) *E.coli* with 100 $\mu\text{g/mL}$ of GO sheets; (c) *E.coli* with 100 $\mu\text{g/mL}$ of Ag nanoparticle; (d) *E.coli* with 100 $\mu\text{g/mL}$ of GO-Ag nanocomposites.

GO-Ag nanocomposites reveals that the cell walls of the bacteria have been damaged significantly as shown in Figure 5.7c. With a concentration of 100 $\mu\text{g/mL}$ GO-Ag nanocomposites most of the bacteria in solution were destroyed as shown in Figure 5.7d.

Figure 5.7 SEM images of *E.coli* after membrane filtration with different concentration of GO-Ag nanocomposites: (a) 0 $\mu\text{g/mL}$, (b) 20 $\mu\text{g/mL}$, (c) 50 $\mu\text{g/mL}$, (d) 100 $\mu\text{g/mL}$.

The SEM results shown in Figure 5.7 imply a possible mechanisms of antibacterial activity of GO-Ag nanocomposites: Firstly, the bacteria were adsorbed and gathered onto the surface of the water solubel GO sheets, which may enhance the interaction between bacteria and Ag nanoparticles on the GO sheets. Some researchers have

reported that GO sheets show high non-specific binding capability to microbes (Park, Mohanty et al. 2010). Secondly, the bacterial cell walls were damaged by Ag nanoparticles when the nanoparticles were in contact with the bacteria. Eventually the bacteria are then destroyed. Obviously, Ag nanoparticles play a key role in the antibacterial process. However, pure Ag nanoparticles showed much lower antibacterial activity than GO-Ag nanocomposites. This may be due to the aggregation of pure Ag nanoparticles during the antibacterial process, leading to the reduction of active specific surface area of Ag nanoparticles. Moreover, pure Ag nanoparticles modified with surfactant may prevent the release of silver ion, and further hinder the adhesion of Ag nanoparticles to the bacterial cell surface (Marambio-Jones and Hoek 2010). However, GO sheets play a positive role in the adhesion of bacterial to the surface of the GO-Ag nanocomposites, which may remarkably increase the interaction between the Ag nanoparticles and the bacterial surface. Since the GO-Ag nanocomposites showed effective antibacterial activity to the bacteria, it may also be applied to act as anti-biofouling agents, as the formation of biofilm is one of the major problems in membrane filtration process in water treatment industry (Ye, Majumdar et al. 2010). The images of SEM reveal that GO-Ag nanocomposites can be easily recovered from treated water by filtration without a residual of disinfection material pollutant remaining.

5.2.4 Photocatalytic degradation of dyes over GO-Ag nanocomposites under visible light irradiation

The photocatalytic activity of GO-Ag nanocomposites was evaluated using AO 7 under visible light irradiation. Results are shown in Figure 5.8. It is observed that the concentration of AO 7 is poorly reduced under visible light irradiation in the absence of the photocatalyst. When GO or GO-Ag nanocomposites are introduced into the system, it is noted that ~ 7 % of AO 7 molecules are adsorbed by the composites when reaching the equilibrium adsorption state in the dark. This may be attributed to the hybridization of GO sheets, which have been proven to facilitate the adsorption of pollutant

molecules owing to non-covalent intermolecular forces (Liu, Bai et al. 2010; Xiong, Zhang et al. 2010; Liu, Liu et al. 2011). However, it had nearly no degradation of AO 7 in the presence of GO sheets under visible light, indicating that pure GO has no photocatalytic activity towards dye. In the presence of GO-Ag nanocomposites, ~ 40 % of AO 7 could be degraded within 120 min.

Figure 5.8 Degradation of AO 7 under visible light (catalyst: 20 mg, initial AO 7: 10 ppm, reaction volume: 50 mL).

5.2.5 Mechanism of photocatalytic degradation of dyes over GO-Ag nanocomposites under visible light irradiation

The mechanism of this process can be illustrated as shown in Figure 5.9. The electron exited from dye may be effectively transferred to Ag nanoparticles via GO sheets, which react with absorbed oxygen on Ag nanoparticles to produce ROSs, leading to the AO 7 degradation. Compared to TiO_2 , this type of GO-Ag nanocomposite photocatalyst possess several important features: (1) adsorption ability towards organic dyes due to the interaction of π -conjugated and ion-dipole interactions between dyes

and GO sheets; (2) efficient photosensitized electron injection; and (3), Reduced electron recombination tendency. The details of this mechanism will be further illustrated in Chapter 6. Therefore, it is highly desirable to develop new methods for the synthesis of high-quality GO-based hybrids, such as GO-TiO₂-Ag nanocomposites, which are solar powered and recyclable, so as to provide more cost effective solutions for pollutant elimination and bacteria disinfection in environmental applications.

Figure 5.9 Mechanism of the photocatalytic degradation of dye.

5.3 Conclusion

In summary, monodispersed Ag nanoparticles were anchored successfully on large GO sheets by a facile two-phase assembling method. The GO-Ag nanocomposites show remarkably enhanced antibacterial activity towards *E.coli* compared to the original Ag nanoparticles. The high-performance disinfection property of GO-Ag nanocomposites may be due to the adsorption of the bacteria by GO sheets through non-specific binding. The GO sheets can effectively stabilize Ag nanoparticles to prevent their aggregation. The recovery of GO-Ag nanocomposites can be implemented by a simple filtration due to the large GO sheets. Moreover, the GO-Ag nanocomposites show good photocatalytic degradation ability for dye degradation under visible light irradiation. Given the superior antibacterial activity, the good photocatalytic dye

degradation ability of GO-Ag nanocomposites and the fact that GO-Ag nanocomposites can be easily recovered, this author expects this new nanocomposite to offer promising opportunities in the applications of environment engineering and other fields. The successful synthesis as well as the good disinfection and decontamination properties of this binary GO-Ag nanocomposites also provide feasibility of synthesis and applications of the ternary GO-TiO₂-Ag nanocomposites.

CHAPTER 6: GO-TiO₂-Ag NANOCOMPOSITES FOR WATER DISINFECTION AND DECONTAMINATION UNDER SOLAR IRRADIATION

6.1 Introduction

Results presented in Chapter 5 have demonstrated successful synthesizing of the binary GO-Ag nanocomposites, as well as their excellent antibacterial activity toward pathogen *E.coli* and photocatalytic decontamination ability toward dyes. Based on these results, this chapter will further develop the novel multifunctional ternary GO-TiO₂-Ag nanocomposites.

As mentioned in Section 2.4, GO-based hybrid photocatalysts are currently popular research topics globally (Chen, Cai et al. 2010; Liu, Bai et al. 2010; Zhang, Lv et al. 2010). GO-TiO₂ hybrid composites have shown significant enhanced photocatalytic performance for the degradation of pollutants (Liu, Bai et al. 2010; Du, Lai et al. 2011). The GO may effectively retard the electron-hole recombination and shift the response region of TiO₂ to the visible light spectrum (Yoo, Tran et al. 2011). Liu, et al. also revealed that the GO-TiO₂ nanorod composites have higher photocatalytic activity than GO-TiO₂ nanoparticle composites (with the same diameter) due to more active (101) facets of 1-dimensional TiO₂ nanorods (Liu, Liu et al. 2011). The hybrids in terms of GO and novel metal nanoparticles may also provide new opportunities for water disinfection and degradation of pollutants. The work presented in Chapter 5 reveals that GO-Ag nanocomposites show excellent antibacterial activity as well as good photocatalytic dye degradation capability under visible light irradiation.

Considering the individual effects of 2D GO sheets, 1D TiO₂ nanorods and 0D Ag nanoparticles on the enhancement of photocatalytic activity and antibacterial capability, it is of great interest to combine these different dimensional materials together as a hybrid structure, to determine if additive enhancement of semiconductor photocatalytic

activity may be realized. Based on the synthesis of high-quality GO-Ag nanocomposites, in this work, for the first time, this author constructed novel nanocomposites composed of GO sheets, TiO₂ nanorods and Ag nanoparticles via a two-phase method.

The photocatalytic activities of the nanocomposites were evaluated by degrading organic dye (AO 7), phenol and bacteria (*E.coli*) under solar irradiation conditions. In addition, the influence of Ag nanoparticles content and the hypothetical mechanism of the photocatalysis process are presented. This nanocomposite overcomes the traditional drawbacks of TiO₂ and integrates the advantages of each respective component, possessing more superior merits over previous TiO₂-based photocatalysts, including: (1) suppressing recombination of photogenerated electron-hole pairs through an effective charge transfer route from TiO₂ to GO to Ag, in favour of effective photocatalytic activity under solar irradiation; (2) providing additional photocatalytic active sites for dye degradation in terms of GO-Ag composite; (3) providing additional antibacterial property due to the Ag nanoparticles; and (4), easy recovery from aqueous solution through simple filtration owing to the large GO sheets.

6.2 Results and discussion

6.2.1 Characterization of GO-TiO₂-Ag nanocomposites

TEM was used for nanocomposite morphology observation. The typical size of GO sheets is more than 2 μm , which was confirmed by TEM image as shown in Figure 6.1a. The large GO sheets will assist in the easy recovery of the nanocomposites with a simple filtration process. Figure 6.1b shows that oleylamine-capped Ag nanoparticles synthesized in toluene are highly monodispersed with uniform size of 4-6 nm. These Ag nanoparticles are able to provide superior antibacterial capability. Previous studies have shown that the toxicity of Ag nanoparticles is size dependent with the smaller sized ones (< 10 nm) exhibiting higher antibacterial activity because of the larger

specific surface area and easier cell penetration (Morones, Elechiguerra et al. 2005; Marambio-Jones and Hoek 2010). Figure 6.1c reveals that Ag nanoparticles are well anchored on GO sheet, while no Ag nanoparticles are found outside the GO sheets. This further indicates that the GO-Ag nanocomposites could be synthesized by our developed two-phase method (Liu, Liu et al. 2011). The morphologies of TiO₂ nanorods and GO-TiO₂ nanorod composites are shown in Figure 6.1d and 6.1e, respectively. It can be seen from Figure 6.1d that the as-prepared TiO₂ nanorods are of 3-5 nm in diameter and 20-50 nm in length. Figure 6.1e illustrates that the TiO₂ nanorods are distributed homogeneously on GO sheet without aggregation, which is in good agreement with reported works (Liu, Bai et al. 2010; Liu, Liu et al. 2011). Figures 6.1f-1h show the morphologies of the GO-TiO₂-Ag nanocomposites. As shown in Figures 6.1f and 6.1g, TiO₂ nanorods and Ag nanoparticles are uniformly anchored throughout the GO sheet, and the size of this GO sheet is also larger than 2 μm . Thus the GO sheets synthesized in our experiments typically have a large size. Figure 6.1h clearly exhibits the morphologies of Ag nanoparticles and TiO₂ nanorods anchored on the GO sheet, and the lattice spacing of 0.24 nm and 0.35 nm corresponds to the (111) and (101) crystal planes of Ag and TiO₂, respectively (Liu, Bai et al. 2010). The sizes of these nanostructures are similar to those in samples of GO-Ag and GO-TiO₂. These TEM images provide strong evidence that GO-Ag, GO-TiO₂ and GO-TiO₂-Ag based on large GO sheets have been successfully synthesized via the two-phase method.

It should be noted that the ratio of TiO₂ and GO has no evident effect on the photocatalytic activity of GO-TiO₂ nanorod composites (Liu, Liu et al. 2011). However, the influence of the Ag nanoparticle content in GO-TiO₂-Ag nanocomposites for their photocatalytic activities is still unclear. Here, the effect of Ag nanoparticles on the photocatalytic activity of the GO-TiO₂-Ag nanocomposites was investigated by synthesizing different GO-TiO₂-Ag nanocomposites (GO-TiO₂-Ag-1, GO-TiO₂-Ag-2, GO-TiO₂-Ag-3). EDS was used to determine the quantity of elements in the GO-TiO₂-Ag nanocomposites including C, O, Ti and Ag individually. Figures 6.2a-2c include the EDS spectra and element contents of GO-TiO₂-Ag-1, GO-TiO₂-Ag-2, GO-TiO₂-Ag-3,

respectively. And the Ag (wt %) of GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 were calculated to be 1.9 %, 4.68 % and 9.72 %, respectively, while the TiO₂ (wt %) of corresponding nanocomposites are 50.37 %, 49.41 %, 49.94 %, respectively, as shown in Table 6.1. These results imply that the amount of TiO₂ nanorods in GO-TiO₂-Ag-1, GO-TiO₂-Ag-2, and GO-TiO₂-Ag-3 are nearly the same, while the amount of Ag nanoparticles varies.

Figure 6.1 TEM images of (a) GO sheet, (b) Ag nanoparticles, (c) GO-Ag nanocomposites, (d) TiO₂ nanorods, (e) GO-TiO₂ nanorod composites, (f) (g) and (h) GO-TiO₂-Ag nanocomposites.

Figure 6.2 EDS spectra and element contents of GO-TiO₂-Ag nanocomposites with different Ag amount: GO-TiO₂-Ag-1 (a), GO-TiO₂-Ag-2 (b) and GO-TiO₂-Ag-3 (c).

Table 6.1 Elemental compositions of GO-TiO₂-Ag calculated from EDS spectra

Element	GO-TiO ₂ -Ag-1 (wt %)	GO-TiO ₂ -Ag-2 (wt %)	GO-TiO ₂ -Ag-3 (wt %)
C	21.42	21.8	14.74
O	46.45	43.88	45.58
Ti	30.23	29.64	29.96
Ag	1.9	4.68	9.72
Total	100	100	100
TiO₂	50.37	49.41	49.94

Table 6.1 Elemental compositions of GO-TiO₂-Ag calculated from EDS spectra.

To further validate the TiO₂ nanorods and Ag nanoparticles anchored onto the GO sheets, XRD was applied. Figure 6.3a shows the XRD patterns of GO sheets, GO-Ag nanocomposites, GO-TiO₂ nanorod composites and GO-TiO₂-Ag-3. The curve of GO sheets shows a diffraction peak at 2θ value around 11.9° , indicating the possibility of interlamellar water trapped between hydrophilic graphene oxide sheets (Park, An et al. 2009). The diffraction peaks at 2θ value of 38.1° , 44.3° , 64.5° and 77.5° are assigned to the (111), (200), (220), and (311) crystallographic planes of face-centered cubic Ag nanoparticles, respectively (JCPDS No. 07-0783). In addition, the diffraction peaks at

25.2°, 37.8°, 47.9°, 54°, and 62.6° are assigned to the (101), (004), (200), (105) and (204) reflections of anatase TiO₂, respectively (JCPDS No. 21-1272). No diffraction peaks of GO are observed in GO-Ag, GO-TiO₂ and GO-TiO₂-Ag nanocomposites because the regular stack of GO was destroyed by the intercalation of Ag or/and TiO₂, which is consistent with other reported studies concerning GO-based composites (Shen, Shi et al. 2010). The XRD results further confirm that the Ag nanoparticles and TiO₂ nanorods are successfully anchored on GO sheets.

Figure 6.3b exhibits UV-vis absorption spectra of TiO₂ nanorods, GO-TiO₂, GO-Ag and GO-TiO₂-Ag-3 nanocomposites. The TiO₂ nanorods curve shows the absorption edge at around 330 nm, which indicates a strong quantum size effect in TiO₂ nanorods with small diameter (Liu, Bai et al. 2010). The enhanced absorption of GO-TiO₂ in the whole visible region can be attributed to the presence of GO, which has also been observed in the curves of GO-Ag and GO-TiO₂-Ag nanocomposites. Also after combined with GO sheets, the absorption edge of GO-TiO₂ was found to have a significant red shift to 400 nm which is caused by the bonding effect between GO and TiO₂. Therefore, the introduction of GO into the matrix of GO-TiO₂ effectively promotes the visible light response of the nanocomposites which can be attributed to electronic interactions between GO and TiO₂ (Zhang, Lv et al. 2010; Zhang, Tang et al. 2010; Zhang, Tang et al. 2011). Such an extended optical absorption has also been observed in previous reports regarding GO-semiconductor photocatalysts for degradation of organic pollutants (Liu, Bai et al. 2010; Zhang, Lv et al. 2010; Zhang, Tang et al. 2010; Liu, Liu et al. 2011; Zhang, Tang et al. 2011). There are obvious absorption peaks of Ag nanoparticles both in GO-Ag and GO-TiO₂-Ag nanocomposites around 450 nm, which have a red shift compared with that of typical small Ag nanoparticles (around 400 nm) due to their binding with GO sheets (Evanoff Jr and Chumanov 2005; Choi, Deng et al. 2008). Moreover, the absorption edge of GO-TiO₂-Ag nanocomposites has further red shifted compared with GO-TiO₂ due to the Ag nanoparticles. This variation of the absorption property of GO-TiO₂-Ag

nanocomposites is expected to enhance the utilizing efficiency of solar energy for photocatalysis.

Figure 6.3 (a) XRD patterns of GO sheets, GO-Ag, GO-TiO₂ and GO-TiO₂-Ag nanocomposites, (b) UV-vis absorbance spectra of TiO₂ nanorods, GO-TiO₂, GO-Ag and GO-TiO₂-Ag nanocomposites.

6.2.2 Decontamination evaluation of GO-TiO₂-Ag nanocomposites under solar irradiation

The photocatalytic degradation of AO 7 under solar irradiation was conducted to evaluate the photocatalytic performance of GO-Ag, GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3. Results are shown in Figure 6.4a. It is observed that the concentration of AO 7 is only slightly reduced under solar irradiation in the absence of the photocatalyst. When GO-based composites are introduced into the system, it is noted that 5-7 % of AO 7 molecules are adsorbed by the composites when reaching the adsorption equilibrium state in the dark. This may be attributed to the hybridization of GO sheets which have been proven to facilitate the adsorption of pollutant molecules owing to the non-covalent intermolecular forces (Liu, Bai et al. 2010; Xiong, Zhang et al. 2010; Liu, Liu et al. 2012). In the presence of GO-Ag nanocomposites, 38 % of AO 7 was degraded within 120 min. This may be due to the electrons generated by the

excited dye (dye^{*}) under visible light, which has been observed in other GO-metal composites/dye systems such as RGO-Au and RGO-Cu (Xiong, Zhang et al. 2010; Xiong, Zhang et al. 2011). The GO-TiO₂ nanorod composites exhibit excellent photocatalytic degradation efficiency: 80 % of AO 7 was degraded within 120 min. However, in the presence of GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3, the AO 7 removal efficiency achieved 99.3 % (120 min), 100 % (120 min) and 100 % (80 min), respectively. In order to distinguish the effects of different materials, the kinetic degradation curves were simulated by first-order degradation equation to obtain the rate constants. The rate constants of GO-Ag, GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 are $(2.60 \pm 0.10) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.96$), $(6.00 \pm 0.24) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$), $(7.30 \pm 0.29) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.97$), $(1.33 \pm 0.05) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.99$) and $(1.58 \pm 0.06) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.97$), respectively. The amount of TiO₂ nanorods in GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 are nearly the same (~50 %), and the total amount of Ag nanoparticles in GO-Ag nanocomposites are the same as that of GO-TiO₂-Ag-3. It is obvious that GO-TiO₂-Ag nanocomposites have significantly enhanced photocatalytic activity toward AO 7 degradation under solar irradiation than GO-Ag or GO-TiO₂. Considering the actual amount of TiO₂ and Ag nanomaterials in the system, GO-TiO₂-Ag-3 exhibited a synergistic effect of photocatalytic degradation of AO 7 rather than physically adding the activities of GO-Ag and GO-TiO₂ together. These results indicate that the integration of Ag nanoparticles, TiO₂ nanorods with GO sheets together could significantly enhance the photocatalytic activity of the nanocomposites. Moreover, the enhancement of photocatalytic dye degradation over this novel nanocomposite could be increased by increasing the Ag amount.

The stability investigation of GO-TiO₂-Ag nanocomposites was evaluated by repeating the photodegradation of AO 7 dye with GO-TiO₂-Ag-3 for five repetitions. As shown in Figure 6.4b, there is no obvious decrease of photocatalytic degradation activity of the GO-TiO₂-Ag nanocomposites toward AO 7 over each repeated cycle. This result

indicates good stability of the novel GO-TiO₂-Ag nanocomposites for dye degradation process.

Figure 6.4 (a) Photocatalytic activities of the control, GO-Ag, GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 nanocomposites for photodegradation of AO 7 under solar irradiation (20 mg of photocatalysts, initial concentration of AO 7 10 ppm, reaction volume 50 mL). (b) Five consecutive cycling photodegradation curves of the AO 7 dye over GO-TiO₂-Ag-3 nanocomposites under solar irradiation. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The photocatalytic performance of the GO-TiO₂-Ag nanocomposites was further evaluated by the photodegradation of phenol aqueous solution under solar irradiation, as shown in Figure 6.5a. Prior to irradiation, only 4 % phenol was adsorption by all GO-based nanocomposites. There was no phenol removal observed under solar irradiation without the photocatalysts, implying that the phenol has no photolysis. In the presence of GO-Ag, there is also no phenol removal under solar irradiation, which differs from that of the AO 7 degradation process. This is because phenol itself can not absorb solar light to generate electrons like AO 7. In the presence of GO-TiO₂ nanorod

composites, 55 % of phenol is reduced within 4 h solar irradiation, with a degradation rate constant of $(2.10 \pm 0.06) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$). However, in the presence of GO-TiO₂-Ag nanocomposites, there is significant improvement of phenol removal under the same condition. The removal efficiency of phenol over GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 is 99.3 % (4 h), 100 % (4 h) and 99.5 % (4 h), with degradation rate constants of $(3.70 \pm 0.12) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$), $(3.80 \pm 0.16) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$) and $(3.70 \pm 0.25) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$), respectively. The GO-TiO₂-Ag-2 shows slightly higher photocatalytic degradation efficiency. However, further increasing the amount of Ag nanoparticles does not increase the photocatalytic activity of the nanocomposites.

Figure 6.5 (a) Photocatalytic activities of the control, GO-Ag, GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 nanocomposites for photodegradation of phenol under solar irradiation (50 mg of photocatalysts, initial concentration of phenol 10 ppm, reaction volume 50 mL). (b) Five consecutive cycling photodegradation curves of phenol over GO-TiO₂-Ag-2 nanocomposites under solar irradiation. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The author also tested the stability of GO-TiO₂-Ag nanocomposites by repeating the photodegradation of phenol with GO-TiO₂-Ag-2 over five repetitions. As shown in Figure 6.5b, there is no obvious decrease of photocatalytic degradation activity of the GO-TiO₂-Ag nanocomposites toward phenol for each repeated cycle. This result further confirms the superior stability of the novel GO-TiO₂-Ag nanocomposites for organic pollutant degradation processes.

6.2.3 Disinfection evaluation of GO-TiO₂-Ag nanocomposites under solar irradiation

Figure 6.6 (a) Bacterial viability in the presence of the control, GO-TiO₂, GO-Ag, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 with and without solar irradiation; (b) magnification of the lines with block diagram of (a). (Dosage of photocatalysts: 100 µg/mL, initial *E. coli* concentration: 1.75×10^8 cfu/mL) Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

E. coli was chosen as a representative waterborne pathogen in this experiment. Figure 6.6 summarized the results of antibacterial capabilities of GO-Ag, GO-TiO₂, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 (initial concentration of bacteria 1.75×10^8 cfu/mL) with and without solar irradiation. It can be seen from Figures 6.6a-6b that

Figure 6.7 The survival ration of *E.coli* cells vs. time in the presence of the control, GO-TiO₂, GO-Ag, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 with and without solar irradiation (dosage of photocatalysts: 100 µg/mL, initial *E.coli* concentration: 1.75×10^8 cfu/mL) Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

both solar irradiation without photocatalysts and GO-TiO₂ without solar irradiation exhibit relatively poor inactivation of *E.coli*. These results confirm that solar light, GO and TiO₂ used here exhibit no significant antibacterial activities toward *E.coli*. In comparison, the GO-Ag and GO-TiO₂-Ag nanocomposites exhibit antibacterial activities in the absence of solar irradiation. There are 0.4, 0.11, 0.17, 0.48 log decreases of bacterial cells in the presence of GO-Ag, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3, respectively. These data may also be evaluated by plotting the bacterial survival rate (C/C_0) over time, as shown in Figure 6.7. The bacterial inactivation efficiency of GO-Ag, GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 is 60 %, 23 %, 32 % and 67 % with 120 min, respectively. The actual Ag

concentrations in GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3 solutions are 1.9, 4.68, and 9.72 µg/mL, respectively, while the total amount of Ag nanoparticles in GO-Ag is the same as that of GO-TiO₂-Ag-3. Thus, these results illustrate that involving Ag nanoparticles into the nanocomposites achieve excellent antibacterial activities even without solar irradiation, which will benefit their disinfection applications. Moreover, results show that the antibacterial activities of nanocomposites which are related to Ag nanoparticles is dose-dependent with the bacterial inactivation rate increasing by increasing Ag amount in the nanocomposites. This is in good agreement with the findings of reported work (Liu, Liu et al. 2011).

Figure 6.8 Five consecutive cycling photocatalytic disinfection of *E.coli* over GO-TiO₂-Ag-2 nanocomposites under solar irradiation (dosage of photocatalysts: 100 µg/mL, initial *E.coli* concentration: 1.75×10^8 cfu/mL). Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

Figure 6.6a illustrates that in the presence of GO-TiO₂ and GO-TiO₂-Ag nanocomposites under solar irradiation, the bacterial inactivation efficiency significantly increased. In the presence of GO-TiO₂ nanorod composites, a 5.1 log decrease of bacterial cells (120 min) was observed with a bacterial inactivation rate constant of $(4.11 \pm 0.16) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.98$). However, in the presence of GO-TiO₂-Ag-1, GO-TiO₂-Ag-2 and GO-TiO₂-Ag-3, there are 7.15 log (120 min), 8.24 log (complete inactivation, 90 min) and 8.24 log (complete inactivation, 120 min) decreases of bacterial cells with rate constants of $(5.96 \pm 0.20) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.99$), $(9.85 \pm 0.26) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.97$) and $(7.16 \pm 0.16) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.96$), respectively. Nevertheless, there are no obvious differences of bacterial inactivation between GO-Ag with and without solar irradiation. This is because under these conditions the GO-Ag nanocomposites could not act as photocatalysts, which is the same as the situation for phenol degradation. Results clearly show that the integration of Ag nanoparticles, TiO₂ nanorods with GO sheets together significantly enhance the photocatalytic disinfection efficiency of the nanocomposites. Taking the individual bacterial inactivation activities of GO-TiO₂ and GO-Ag into considerations, the GO-TiO₂-Ag nanocomposites exhibit a synergistic effect of photocatalytic disinfection toward *E.coli*. GO-TiO₂-Ag-2 shows the highest photocatalytic antibacterial activity. A further increase in the amount of Ag nanoparticles did not increase the photocatalytic activity of the nanocomposites correspondingly. However, it could increase the intrinsic antibacterial activity of the nanocomposites. The photocatalytic disinfection results under solar irradiation conditions agree well with the photodegradation of phenol. Results of repeated disinfection experiments with GO-TiO₂-Ag-2 further validate the good stability of the nanocomposites (Figure 6.8).

6.2.4 Mechanism of photocatalytic decontamination/disinfection activities of GO-TiO₂-Ag nanocomposites under solar irradiation

The proceeding results of photocatalytic degradation of AO 7, phenol and *E.coli* confirmed that the novel GO-TiO₂-Ag nanocomposites have significantly enhanced

photocatalytic activity than GO-TiO₂ under solar irradiation. However, the optimal amount of Ag nanoparticles of GO-TiO₂-Ag nanocomposites is different between AO 7 and phenol/bacteria degradation. The mechanisms responsible for each will be discussed here.

An efficient charge separation/transfer is crucial for the enhancement of photocatalytic activities of catalysts, as it can retard the recombination of electron-hole pairs (Hoffmann, Martin et al. 1995; Chen, Ma et al. 2010). In the case of AO 7 degradation, the stepwise structure of energy levels is shown in Figure 6.9. The solar irradiation consists of UV (4 %) and visible light spectrum (~40 %) to photo-excite the photocatalysts. As a result, there are two photocatalytic routes for AO 7 degradation. On the one hand, the UV and near UV light from solar may excite TiO₂ to generate electrons and holes. Considering the potential of the conduction band of TiO₂ (-4.2 eV) vs. vacuum and the work function of GO (-4.42 eV), photoinduced electrons may easily be transferred from TiO₂ to GO sheets (Yang, Zhai et al. 2010; Lv, Pan et al. 2012). The work function of the mainly located surface (111) of Ag nanoparticles is -4.74 eV, which is lower than that of GO (Yoo, Cuong et al. 2012). Hence, the photoinduced electrons may further be transferred from GO to the Ag nanoparticle surface, as shown in Figure 6.9. This transfer mechanism is expected to significantly suppress the recombination of photoinduced electrons and holes, which enhances the photocatalytic performance of GO-TiO₂-Ag nanocomposites. Hence, these electrons can react with adsorbed oxidants (usually O₂) to produce reactive oxygen radicals ($\cdot\text{O}_2^-$), while the holes may react with H₂O/OH⁻ to generate hydroxyl radicals ($\cdot\text{OH}$). These active radicals can eventually participate in dye degradation. On the other hand, the AO 7 (dye) rather than TiO₂ is excited by visible light which generates electrons from the excited dye (dye^{*}). These dye-sensitized electrons may be transferred from dye^{*} to TiO₂, then to GO, and finally to the Ag nanoparticle surface. However, if the dye molecules are attached to the GO sheets, these dye-sensitized electrons may directly transfer from dye^{*} to GO, and then to the surface of the Ag nanoparticles. These electron transfers may significantly suppress the recombination of electrons and dye^{*},

thus enhance the self-degradation and photocatalytic degradation of dye. The same mechanism has been well illustrated in other GO-metal nanocomposite/visible-light systems for dye degradation including RGO-Au and RGO-Cu (Xiong, Zhang et al. 2010; Xiong, Zhang et al. 2011). The Ag nanoparticles are important in this system, as both the photoinduced electrons and dye-sensitized electrons would transfer to the Ag nanoparticle surface to react with O_2 . More Ag nanoparticles supply more reactive sites for electron transfer to retard electron-hole (TiO_2) and electron-dye* recombination, as well as for electron/ O_2 reaction to produce more reactive radicals. Therefore, the increase in the amount of Ag nanoparticle can result in an increased dye degradation rate by both photodegradation and self-degradation processes. As a result, the GO- TiO_2 -Ag-3 with the highest Ag nanoparticles content exhibits the highest photocatalytic dye degradation among the three nanocomposites.

Figure 6.9 Schematic diagram of energy levels of GO- TiO_2 -Ag nanocomposites.

In the case of phenol and bacterial degradation with GO-TiO₂-Ag under solar irradiation, only one electron transfer route exists, from the excited TiO₂ to GO to the surface of Ag nanoparticles. The photoinduced electrons and holes may generate reactive radicals for phenol degradation and bacterial inactivation. This process has been well illustrated (Maness, Smolinski et al. 1999; Liu, Liu et al. 2011; Liu, Liu et al. 2012; Liu, Liu et al. 2012). This transfer mechanism could remarkably suppress the recombination of photoinduced electrons and holes of TiO₂, and thus enhance the photocatalytic performance of GO-TiO₂-Ag nanocomposites. The amount of Ag nanoparticle and the TiO₂ active sites are two essential parts for the photocatalysis. The amount of photoinduced electrons is dependent on the amount of TiO₂ on GO sheets, while the proper amount of Ag nanoparticles on GO may effectively retard the recombination of electron-holes. However, the excess of Ag nanoparticles may be useless for anti-recombination of electron-holes because the total amount of photoinduced electrons from TiO₂ is limited. However, excess Ag nanoparticles on GO sheets could increase the electron-hole recombination by increasing the contact sites of electrons from Ag surface back to TiO₂ nanorods. As a result, there is an optimal ratio of TiO₂ nanorods and Ag nanoparticles in the GO-TiO₂-Ag nanocomposites for phenol/bacterial degradation. Results of this work show that GO-TiO₂-Ag-2 exhibited the highest photocatalytic degradation activities for phenol and *E.coli*. The GO-TiO₂-Ag-3 shows slightly decreased photocatalytic activities compared with GO-TiO₂-Ag-2. Although this mechanism also exists in the case of dye degradation, the excess Ag nanoparticles may facilitate the anti-recombination of self-sensitized electron-holes of dye to enhance the self-degradation of dye. This results in an increase in photocatalytic activities of the nanocomposites rather than decrease in their activities.

6.2.5 Discussion on practical water disinfection and decontamination applicability of GO-TiO₂-Ag nanocomposites

As mentioned in Section 4.2.8, the EPA surface water treatment rule requires 99.9 % (3 log) removal/inactivation of bacteria and 99.99 % (4 log) removal/inactivation of viruses (USEPA 2009). In this work, at the GO-TiO₂-Ag-2 concentration of 100 µg/mL, 3 log *E.coli* removal was achieved within 30 min, while 8.24 log *E.coli* removal was achieved within 60 min. This indicates that the system appears feasible for surface water treatment and that sufficient contact time could ensure complete bacteria disinfection under this system. Moreover, the final silver ion concentration after the treatment is measured to be less than 0.05 ppm, which is under the silver ion limits of EPA for drinking water treatment (USEPA 2009). Compared with the disinfection results of Ag/TiO₂ nanofiber membrane/solar irradiation system (7 log removal with 70 min), this GO-TiO₂-Ag-2/solar irradiation system may achieve higher bacterial removal even at a higher initial bacterial concentration. This result confirms that this system has a higher antibacterial activity than the Ag/TiO₂ nanofiber membrane/solar irradiation system. Nevertheless, before practical application of this system, the disinfection evaluation of other microbial pathogens and viruses should be investigated in the near future.

As for water decontamination applications of this system, the author used relatively resistant organic AO 7 dye and phenol (instead of MB dye in chapter 4) as model pollutants. Experimental results demonstrate that total AO 7 and phenol removal with an initial concentration of 10 ppm requires 80 min and 4 h in the presence of GO-TiO₂-Ag-3, GO-TiO₂-Ag-2 under solar irradiation, respectively. These results indicate that with sufficient contact time complete dye and phenol degradation can be achieved using this system. These results also imply that this system has higher photocatalytic degradation activities toward organic pollutants than Ag/TiO₂ nanofiber membrane/solar irradiation systems.

6.3 Conclusion

In summary, multifunctional nanocomposites consisting of GO sheets, TiO₂ nanorods and Ag nanoparticles (GO-TiO₂-Ag) have been successfully synthesized via a two-phase method. GO-TiO₂-Ag nanocomposites show remarkably enhanced photocatalytic degradation activities toward AO 7 and phenol under solar irradiation compared with GO-TiO₂ and GO-Ag. The novel nanocomposites also exhibit excellent intrinsic antibacterial activity toward *E.coli* due to the Ag nanoparticles. Furthermore, the GO-TiO₂-Ag nanocomposites/solar irradiation system illustrates a significantly enhanced photocatalytic bacterial inactivation compared with GO-TiO₂ and GO-Ag. The mechanism of action implies that Ag nanoparticles are expected to significantly suppress recombination of photoinduced electrons and holes, thus enhance the photocatalytic performance of GO-TiO₂-Ag nanocomposites. The influence of Ag nanoparticles in the nanocomposites for their photocatalytic activities was investigated. Results indicate that the optimal Ag loading for dye degradation is different from that of phenol/bacterial degradation under solar irradiation. Given the superior photocatalytic activities of GO-TiO₂-Ag nanoparticles toward organic pollutants and waterborne pathogen under solar irradiation, and the fact that they could be easily recovered relying on the large GO sheets, it is believable that the new GO-TiO₂-Ag nanocomposites offer promising opportunities in the applications of water purification and other fields. Moreover, this work demonstrates a novel strategy of careful design of multidimensional photocatalysts by coupling GO with other nanostructures for development of next-generation photocatalysts.

Although the photocatalytic efficiency and disinfection capability of GO-TiO₂-Ag nanocomposites have been improved compared with Ag/TiO₂ nanofiber composites, there is still room for improvement in the photocatalytic efficiency of TiO₂-based photocatalysts to allow for the shorter contact times for water disinfection and decontamination by enhancing the visible light absorption of solar light.

CHAPTER 7: GO- Ag_3PO_4 NANOCOMPOSITE PHOTOCATALYSTS FOR WATER DISINFECTION AND DECONTAMINATION UNDER VISIBLE LIGHT IRRADIATION

7.1 Introduction

Chapters 5 and 6 confirmed the feasibility of fabrication of multifunctional ternary GO- TiO_2 -Ag nanocomposites composed with 0D Ag nanoparticles, 1D TiO_2 nanorods and 2D GO sheets. Based on the results of chapters 4-6, it is now known that by introducing small TiO_2 nanorods and Ag nanoparticles together with large GO sheets, the photocatalytic degradation efficiency of nanocomposites toward dye pollutants under solar irradiation has been improved compared with that of Ag/ TiO_2 nanofiber composites. The GO- TiO_2 -Ag nanocomposites also exhibited excellent intrinsic antibacterial property and high-performance photocatalytic disinfection activity under solar irradiation. However, for the degradation toward relatively resistant organic pollutants like phenol, long reaction times are still needed for the GO- TiO_2 -Ag nanocomposites under solar irradiation. As a result, there is a need to further enhance the photocatalytic efficiency of TiO_2 -based photocatalysts to ensure shorter contact times for water disinfection and decontamination, by further enhancing the solar utilization, especially in the visible light region.

One effective way to enhance the visible light absorption of TiO_2 -based photocatalysts is the coupling of TiO_2 with other visible light semiconductors, as mentioned in Section 2.3.4. Very recently, silver orthophosphate (Ag_3PO_4) was found as a new visible light photocatalyst for the oxidation of water and photodecomposition of organic compounds (Yi, Ye et al. 2010; Bi, Ouyang et al. 2011). They indicate that the Ag_3PO_4 semiconductor has an extremely high efficient organic dye degradation activity under visible light, significantly higher than that of commercial $\text{TiO}_{2-x}\text{N}_x$. However, there

exists one major limitation of this novel photocatalyst which may prevent its wide use in environmental and energy fields. Ag_3PO_4 photocatalyst is unstable upon photo-illumination and it is easily corroded by the photogenerated electrons ($4\text{Ag}_3\text{PO}_4 + 6\text{H}_2\text{O} + 12\text{h}^+ + 12\text{e}^- \rightarrow 12\text{Ag} + 4\text{H}_3\text{PO}_4 + 3\text{O}_2$) (Yi, Ye et al. 2010). If no electron acceptor such as AgNO_3 is involved in the system, the total Ag_3PO_4 photocatalyst may decompose during the photocatalysis process. Therefore, it is highly desirable to develop effective strategies to improve the stability of the Ag_3PO_4 photocatalyst. Recently, AgX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), Ag nanoparticles and carbon quantum dots (CQDs) were introduced for the modification of Ag_3PO_4 (Bi, Ouyang et al. 2011; Cao, Luo et al. 2012; Liu, Fang et al. 2012; Zhang, Huang et al. 2012). The AgX , Ag nanoparticles and CQDs can promote the transfer and separation of photogenerated electron-hole pairs on Ag_3PO_4 particles and thus improve its stability by decreasing its photocorrosion. Nevertheless, a new, simple method which could improve the photocatalytic stability of Ag_3PO_4 while facilitating its recovery is still required for environmental applications.

As mentioned in Section 2.4, graphene/graphene oxide (GO) is considered as an ideal 2D reinforcing component for composite materials due to its specific properties. Besides GO/ZnO , GO/TiO_2 , the GO sheets have also been introduced to improve the photocatalytic activity of silver halides such as $\text{GO}/\text{Ag}/\text{AgX}$ (Zhu, Chen et al. 2011). The GO-based nanocrystalline composites show significantly enhanced photocatalytic performance for the degradation of pollutants. This is because GO sheets can facilitate the charge transfer and suppress the recombination of electron-hole pairs of photocatalysts in these systems. The foregoing illustrate the unique properties of GO making it an ideal supporter and host for enhancing the photocatalytic properties of Ag_3PO_4 .

Silver-based nanomaterials have been shown to be a broad-spectrum bactericide to bacteria, fungi and viruses (Marambio-Jones and Hoek 2010). Although little is known about the antibacterial activity of this new Ag_3PO_4 semiconductor, it is thought to have a certain intrinsic antibacterial activity due to its Ag^+ release.

Based on the results presented in Chapter 6 and the abovementioned facts of the new visible light induced Ag_3PO_4 photocatalyst, it is of great interest to develop novel multifunctional ternary $\text{GO-TiO}_2\text{-Ag}_3\text{PO}_4$ nanocomposites, which are composed of Ag_3PO_4 nanoparticles and TiO_2 nanorods together with large GO sheets. The Ag_3PO_4 semiconductor may then takes over the Ag nanoparticles to provide both visible light induced photocatalyst and antibacterial agents. To simplify this study, binary $\text{GO-Ag}_3\text{PO}_4$ nanocomposites will be firstly investigated this Chapter.

In this work, for the first time, a novel GO enwrapped Ag_3PO_4 ($\text{GO-Ag}_3\text{PO}_4$) nanocomposite is designed as a highly efficient visible light induced photocatalyst. A facile ion-exchange method for growing Ag_3PO_4 crystals on GO sheets is developed. The obtained $\text{GO-Ag}_3\text{PO}_4$ nanocomposites exhibit enhanced photocatalytic activities and stability toward organic pollutant degradation under visible light irradiation. Moreover, the novel $\text{GO-Ag}_3\text{PO}_4$ nanocomposites display excellent intrinsic antibacterial and enhanced photocatalytic disinfection capability of bacterial cells under visible light irradiation, due to the synergistic effects of GO sheets and Ag_3PO_4 photocatalyst. As far as this author is aware, this is the first report concerning the photocatalytic antibacterial activity of Ag_3PO_4 crystals and Ag_3PO_4 -based composites. The advantages of involving large GO sheets into the system are: 1) GO can work as a support and electron acceptor to suppress the charge recombination of Ag_3PO_4 and enhance the photocatalytic activity and stability of Ag_3PO_4 ; and 2), the large size of GO sheets can facilitate the recovery of the composite by simple filtration. All these features make the $\text{GO-Ag}_3\text{PO}_4$ nanocomposites a promising candidate for water purification under visible light irradiation.

7.2 Results and discussion

7.2.1 Characterization of GO-Ag₃PO₄ nanocomposites

The strategy for the fabrication of GO-Ag₃PO₄ nanocomposite is shown in Figure 7.1. The functional groups such as hydroxyl, carbonyl of GO stabilize silver ions, and the Ag₃PO₄ particles form on GO sheets when eventually adding HPO₄²⁻ into solution.

Figure 7.1 Schematic representation for the synthesis of GO enwrapped Ag₃PO₄ nanocomposites.

Figures 7.2a-2b show typical SEM images of bare Ag₃PO₄ particles synthesized by reacting silver acetate with Na₂HPO₄ in aqueous solutions at different magnifications. It can be clearly seen that the Ag₃PO₄ particles possess regular rhombic dodecahedral morphology with an average diameter of 500 nm, which is in agreement with the results reported by Bi, et al (Bi, Ouyang et al. 2011). When involving GO sheets into the system, well-defined Ag₃PO₄ crystals, whose surface is distinctly enwrapped with gauze-like GO sheets are obtained, as shown in Figures 7.2c-2d. The morphology and size of the Ag₃PO₄ in the GO-Ag₃PO₄ system remain the same as that of bare Ag₃PO₄. The color of the sample solution is changed from yellow of bare Ag₃PO₄ to olive green of GO-Ag₃PO₄, due to the existence of GO sheets, as shown in the insets of Figures 7.2a and 2c. These SEM images confirm that GO sheets can serve as a supporter and surfactant to enwrap Ag₃PO₄ particles in this particular system. This is in good agreement with reports that GO has been demonstrated to act as a surfactant in GO-based hybrid system and also can effectively retard particle aggregations (Pasricha, Gupta et al. 2009; Zhu, Chen et al. 2011). The Ag₃PO₄ nanoparticles enwrapped by GO

sheets are further verified by EDS analysis, and the Ag_3PO_4 content of $\text{GO-Ag}_3\text{PO}_4$ nanocomposites calculated to be around 83 % according to EDS analysis (Figure 7.3).

Figure 7.2 Typical SEM images of synthesized Ag_3PO_4 particles (a) (b), and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites (c) (d). Insets of (a) and (c) are photographs of Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposite solution, respectively.

To further validate that Ag_3PO_4 is anchored onto the GO sheets, XRD was applied to the measurements. Figure 7.4a shows the XRD patterns of GO sheets, bare Ag_3PO_4 particles and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites. The GO sheets curve illustrates a diffraction peak at 2θ value around 11.9° , which may be due to interlamellar water trapped between hydrophilic graphene oxide sheets (Park, An et al. 2009). The XRD patterns also clearly show that all of the diffraction peaks of bare Ag_3PO_4 can be indexed to the body-centered cubic structure of Ag_3PO_4 (JCPDS no.06-0505), which is in good agreement with previous reported work (Bi, Ouyang et al. 2011). The GO-

Ag_3PO_4 nanocomposites curve is without change in comparison with bare Ag_3PO_4 particles. No obvious diffraction peaks of GO are observed in the GO- Ag_3PO_4 nanocomposites, because the regular stack of GO is destroyed by the intercalation of Ag_3PO_4 particles. This is consistent with other reported works about GO-based composites (Liu, Bai et al. 2010; Shen, Shi et al. 2010; Das, Sarma et al. 2011). The XRD results confirm that the Ag_3PO_4 crystals have successfully located onto the GO sheets.

Figure 7.3 EDS spectra and element contents of GO- Ag_3PO_4 nanocomposites. The Au peaks in the spectra are because of Au coating for sample preparation.

The UV-Vis spectral measurement was employed to monitor the changes in the absorption of the samples, as shown in Figure 7.4b. As indicated bare Ag_3PO_4 can absorb solar energy at a wavelength shorter than 530 nm. While the typical UV-Vis spectrum of GO exhibits two characteristic peaks, a maximum at 230 nm, which corresponds to $\pi-\pi^*$ transitions of aromatic C-C bonds, and a shoulder at 303 nm, which is attributed to $n-\pi^*$ transitions of C=O bonds (Figure 7.4b) (Paredes, Villar-Rodil et al. 2008). In the GO- Ag_3PO_4 composite sample, absorption toward the visible light region is remarkably enhanced compared to bare Ag_3PO_4 particles. This suggests that Ag_3PO_4 particles are enwrapped by GO sheets. This result also implies that the GO- Ag_3PO_4 nanocomposites are suitable to be used as visible-light-induced photocatalysts.

Figure 7.4 (a) XRD patterns of GO sheets, Ag_3PO_4 particles and GO- Ag_3PO_4 nanocomposites, (b) UV-Vis absorbance spectra of GO sheets, Ag_3PO_4 particles and GO- Ag_3PO_4 nanocomposites.

7.2.2 Decontamination evaluation of GO- Ag_3PO_4 nanocomposites under visible light irradiation

The photocatalytic performance of bare Ag_3PO_4 and GO- Ag_3PO_4 nanocomposites was investigated in terms of photodegradation of organic dye AO7 under visible-light

irradiation. The normalized temporal concentration changes of AO7 during the photodegradation process are shown in Figure 7.6, which are based on the real-time UV-Vis absorption spectra of dye continuously with increasing irradiation time (Figure 7.5). Before monitoring the photocatalytic activity of photocatalysts, a simple adsorption of AO7 by GO sheets was investigated. It is noted that around 6 % of AO7 molecules are adsorbed by GO- Ag_3PO_4 nanocomposites when reaching the equilibrium adsorption state under the dark reaction, while less than 2 % are adsorbed on bare Ag_3PO_4 particles. The high adsorption capability of composite material to dye may be attributed to the hybridization of GO sheets, which have been proved to facilitate the adsorption of pollutant molecules, owing to the non-covalent intermolecular forces (Xiong, Zhang et al. 2010; Zhang, Lv et al. 2010). The adsorption abilities of GO to different kinds of dye molecules are quite different depending on the properties of organic dyes. For example, it shows relatively low adsorption ability to acid orange (Xiong, Zhang et al. 2010).

Figure 7.5 Typical real-time absorption spectra of AO7 dye during the photodegradation process over bare Ag_3PO_4 (a), GO- Ag_3PO_4 nanocomposites (b) under visible light irradiation. The black curves marked as -30 min is the absorption spectra detected from the original AO7 solution before the dark adsorption experiment.

Figure 7.6 Photocatalytic activities of control, Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites for photodegradation of AO7 under visible light irradiation. (20 mg of sample, initial concentration of AO7 50 ppm) Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The photocatalytic degradation of AO7 was carried out under visible light irradiation ($420 \text{ nm} \leq \lambda \leq 630 \text{ nm}$, 80 mW/cm^2). As shown in Figure 7.6, insignificant removal of AO7 occurred in the presence of 40 min visible-light irradiation, which was due to the weak photolysis of AO7. In the presence of bare Ag_3PO_4 particles, an approximate 100 % degradation of AO7 is achieved within 20 min. This illustrates that bare Ag_3PO_4 particles exhibit excellent photocatalytic activities for the degradation of AO7 under visible light irradiation. However, in the presence of the $\text{GO-Ag}_3\text{PO}_4$ nanocomposites, a sudden drop of the dye concentration occurs, and an approximate 100 % of the dye is removed within 10 min. Results demonstrate that involving GO into the system remarkably increases the photocatalytic activity of Ag_3PO_4 under visible light irradiation. As the photocatalytic decontamination of the low-concentration dye solution follows a pseudo-first-order reaction (Yu, Yu et al. 2003), the corresponding

degradation of bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites is estimated to be $(6.40 \pm 0.16) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.92$) and $(1.09 \pm 0.05) \times 10^{-1} \text{ min}^{-1}$ ($R^2 = 0.98$), respectively. This result indicates that involving GO into the Ag_3PO_4 photocatalyst system may significantly enhance (almost doubling) the total photocatalytic activities of the system.

To investigate the stability of Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites, the author repeated the photodegradation of AO7 dye with the photocatalysts five times. Corresponding results are shown in Figure 7.7. Figure 7.7a illustrates that there are obvious decreases of photocatalytic degradation activity of bare Ag_3PO_4 toward AO7 in every repeated cycle. During the last cycle, only 50 % of the dye could be removed within 40 min, which represents a significant loss of photocatalyst activities compared to that of the first cycle. However, when involving GO sheets into the system, as shown in Figure 7.7b, the photocatalytic efficiency of $\text{GO-Ag}_3\text{PO}_4$ nanocomposites displays only slight decreases (constant rate decreasing of $(2.80 \pm 0.05) \times 10^{-2} \text{ min}^{-1}$) without significant loss of activities after the reaction is performed consecutively five times. The morphology of catalysts after repeated reaction was evaluated by SEM. An obvious particle aggregation and corrosion of bare Ag_3PO_4 was observed after the photocatalysis process as shown in Figure 7.7c. Figure 7.7d illustrates that the morphology of the $\text{GO-Ag}_3\text{PO}_4$ nanocomposites do not significantly change after repeated reactions. These results indicate that bare Ag_3PO_4 photocatalyst is not stable during photocatalytic process and a loss in its activity under visible light irradiation is expected. The reason for this has been demonstrated that the photo-excited electrons of Ag_3PO_4 may simultaneously reduce the photocatalyst if no sacrificial reagent is involved in the system (Yi, Ye et al. 2010). The process can be represented as:

However, GO may effectively enhance the stability of Ag_3PO_4 during the photocatalytic process. The slight decrease of the activity of $\text{GO-Ag}_3\text{PO}_4$ nanocomposites during the recycling reactions may be attributed to the loss of some catalysts during photocatalytic performance, due to the even dispersibility of GO-

Ag_3PO_4 nanocomposites in aqueous solutions which may facilitate catalysts removal during the experimental procedure (Dreyer, Park et al. 2010; Zhu, Chen et al. 2011). This slight decrease in GO- Ag_3PO_4 nanocomposites activity may also be due to the slight solubility of Ag_3PO_4 in aqueous solutions resulting in the catalyst loss (Bi, Ouyang et al. 2011). Figure 7.7d indicates that the GO- Ag_3PO_4 nanocomposites may be rejected by membrane filtration (with pore size of $0.45\ \mu\text{m}$). However, corroded Ag_3PO_4 particles having small size may pass through the membrane filter, as shown in Figure 7.7c. These results indicate that involving large GO sheets into the system could facilitate material recovery by simple filtration which is beneficial for the water purification applications.

Figure 7.7 Five consecutive cycling photodegradation curves of AO7 dye over Ag_3PO_4 (a) GO- Ag_3PO_4 nanocomposites (b), SEM images of Ag_3PO_4 (c) and GO- Ag_3PO_4 nanocomposites (d) after decontamination experiments, respectively. Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

The photocatalytic performance of bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites was also evaluated by the photodegradation of phenol in aqueous solution under visible-light irradiation as shown in Figure 7.8. Prior to irradiation, the adsorption rates of phenol to bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites were about 6 % and 10 %, respectively. The high adsorption capability of composite material to phenol may be attributed to the hybridization of GO sheets, which is in agreement with the results of dye adsorption.

Figure 7.8 Photocatalytic activities of control, Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites for photodegradation of phenol under visible light irradiation. (50 mg of sample, initial concentration of phenol 10 ppm) Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

As indicated by Figure 7, there was no phenol removal under visible light irradiation without photocatalysts, implying that the phenol has no photolysis. In the presence of bare Ag_3PO_4 particles, an approximate 100 % degradation of phenol is achieved within 30 min, with degradation rate constant $(2.70 \pm 0.11) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.87$). In the presence of $\text{GO-Ag}_3\text{PO}_4$ nanocomposites, an approximate 100 % of phenol is removed within 20 min, with a degradation rate constant $(3.80 \pm 0.26) \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.77$).

The GO-Ag₃PO₄ nanocomposites exhibit higher photocatalytic activity for the decomposition of phenol compared with bare Ag₃PO₄ particles, which further validates that involving GO into the system can remarkably increase the photocatalytic activity of Ag₃PO₄ under visible light irradiation. Moreover, the stability tests results shown in Figures 7.9a and 9b further confirm that GO-Ag₃PO₄ nanocomposites are also a stable and efficient visible light photocatalyst compared with bare Ag₃PO₄ particles.

Figure 7.9 Five consecutive cycling photodegradation curves of phenol over Ag₃PO₄ (a) GO-Ag₃PO₄ nanocomposites (b). Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

7.2.3 Antibacterial and photocatalytic disinfection evaluation of GO-Ag₃PO₄ nanocomposites under visible light irradiation

Ag and Ag-based composites are known to be effective biocides against numerous kinds of bacteria, fungi and virus (Marambio-Jones and Hoek 2010). Besides, the semiconductor-mediated photocatalytic disinfection has been considered as a promising and an effective alternative for microorganism removal (Malato, Fernandez-Ibanez et al. 2009). Thus it is reasonable to assume that the novel GO-Ag₃PO₄ nanocomposites may be suitable for disinfection application. Nevertheless, little is known about the

antibacterial performance of bare Ag_3PO_4 or Ag_3PO_4 -based composites. As a result, for the first time, this work will investigate the intrinsic antibacterial and photocatalytic disinfection of both Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites by using the model waterborne pathogen *E.coli*.

Figure 7.10 (a) Results of the antibacterial tests applying different samples: control, Ag_3PO_4 , and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites. (b) Images of *E.coli* colonies on an agar plate incubated with different samples: control, Ag_3PO_4 , and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites. (sample concentration: 20 mg/L, initial bacterial concentration: $\sim 10^7$ cfu/mL) Each data point and error bar represents the mean and the standard errors, respectively, of independent triplicates.

Figure 7.10a illustrates that 100 % bacterial cell removal occurred both in the presence

of bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposite system at sample concentrations of 20 mg/L. The bactericidal activities of the samples are further confirmed by the images of colonies incubated on an agar plate with and without samples. As shown in Figure 7.10b, *E.coli* can be completely killed in the presence of bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ nanocomposites. The previous work reported in Chapter 5 validated that large GO sheets synthesized have no obvious antibacterial activity toward *E.coli* cells within 100 mg/L of GO sheets. Therefore, the excellent antibacterial activities of bare Ag_3PO_4 and $\text{GO-Ag}_3\text{PO}_4$ composite are thought due to the intrinsic property of Ag_3PO_4 .

Figure 7.11 Image of *E.coli* colonies on an agar plate incubated with Ag^+ . (Ag^+ concentration: 4.5 ppm, initial bacterial concentration: $\sim 10^7$ cfu/mL)

It is generally accepted that Ag^+ at high concentrations exhibits bactericidal activity (Pal, Tak et al. 2007; Kim, Baek et al. 2011). The Ag^+ of the sample solution was monitored by inductively coupled plasma (ICP) measurements. The bare Ag_3PO_4 solution contains 4.9 ppm (mg/L) Ag^+ , while the $\text{GO-Ag}_3\text{PO}_4$ composite solution contains 4.6 ppm Ag^+ . The high level of Ag^+ in sample solution is due to the slight solubility of Ag_3PO_4 (Stumm and Morgan 1996). A control experiment shows that total

bacterial removal was observed in the presence of 4.5 ppm Ag^+ (in the form of AgNO_3), as shown in Figure 7.11. These facts suggest that the antibacterial activity of Ag_3PO_4 and GO- Ag_3PO_4 nanocomposites may have resulted from dissolved Ag^+ . It is worth mentioning that the relatively high level of Ag^+ depends on the solubility of the Ag_3PO_4 . Nearly 6 mg/L of Ag_3PO_4 (in terms of 4.6 ppm Ag^+) dissolved under these experiment conditions which led to the complete removal of *E.coli* cells. As a result, a study on the relationship between sample concentration and disinfection efficiency is out of discussion for this particular system. A low concentration of 20 mg/L of sample was used in all the disinfection experiments.

The SEM was used to investigate the morphology changes of *E.coli* cells after disinfection reaction. *E.coli* cells remained in good state in the absence of samples as shown in Figures 7.12a and 12b. However, in the presence of Ag_3PO_4 and GO- Ag_3PO_4 nanocomposites, obvious cell damages were observed as shown in Figures 7.12d, 12e, 12g and 12h. These results imply that Ag^+ can react with some membrane proteins to damage the cell membrane and its relative function. This is in good agreement with previous research (Marambio-Jones and Hoek 2010). Moreover, in the presence of GO- Ag_3PO_4 nanocomposites, most of the cells were gathered on GO sheets in Figures 7.12g and 12h. This implies that the water soluble GO sheets may adsorb and gather the bacteria onto the surface, which was also observed in Chapter 5 (Liu, Liu et al. 2011; Liu, Liu et al. 2011). This sorption may enhance the interaction between bacteria and materials on GO sheets. Unfortunately, the Ag_3PO_4 crystals were destroyed during the disinfection process in both Ag_3PO_4 and GO- Ag_3PO_4 systems, as shown in Figures 7.12e and 7.12h, although it is much better in GO- Ag_3PO_4 system than Ag_3PO_4 . This may be due to the interaction between Ag_3PO_4 and bacteria or bacterial secretion containing other ions like chloride ions and thiol groups, as the solubility of Ag_3PO_4 is higher than some other silver compounds such as AgCl (stumm and Morgan 1996). Therefore the reusability of Ag_3PO_4 -based composite in disinfection process may be affected. Future work should be focused on finding methods to control the solubility of Ag_3PO_4 -based materials.

Figure 7.12 SEM images of *E.coli* cells after treated with different samples for 2 h: control (a) (b) without and (c) with visible light irradiation, Ag_3PO_4 (d) (e) without and (f) with visible light irradiation, GO- Ag_3PO_4 nanocomposites (g) (h) without and (i) with visible light irradiation, respectively. (sample concentration: 20 mg/L, initial bacterial concentration: $\sim 10^7$ cfu/mL).

The photocatalytic disinfection of the novel GO- Ag_3PO_4 nanocomposites was further investigated by SEM measurements after visible-light irradiation. No obvious change of bacterial cells was observed after 2 h visible-light irradiation in the absence of catalysts, as shown in Figure 7.12c. This implies that short time visible-light irradiation has no obvious effects on bacteria damage. However, in the presence of Ag_3PO_4 photocatalysts, most of the bacterial cells were damaged, as shown in Figure 7.12f. Some cell degradation was observed in Figure 7.12f, compared with Figure 7.12e. In the presence of GO- Ag_3PO_4 nanocomposites, bacterial cells were enwrapped by GO

sheets, and obvious cell degradation was observed under visible-light irradiation as shown in Figure 7.12i. These results indicate that the photocatalytic degradation capability of bacterial cells in GO-Ag₃PO₄ nanocomposite system was enhanced in comparison with that in the bare Ag₃PO₄ system under visible light irradiation. The enhanced photocatalytic disinfection property of GO-Ag₃PO₄ nanocomposites may be due to the good adsorption ability of GO for bacteria, facilitating the interaction between bacterial cells and catalysts. It may also be due to the enhanced photocatalytic activity of GO-Ag₃PO₄ nanocomposites as compared with bare Ag₃PO₄, which has been proved in photocatalytic organic pollutant degradation experiments.

7.2.4 Mechanism of photocatalytic decontamination/disinfection activities of GO-Ag₃PO₄ nanocomposites under visible light irradiation

As is well known, an efficient charge separation/transfer is crucial for the enhancement of the photocatalytic activities (Hoffmann, Martin et al. 1995; Chen, Ma et al. 2010; Zhang, Lv et al. 2010). GO has been shown to be an effective electron transportation and acceptor in the system of GO/TiO₂, GO/ZnO, Ag/AgX/GO (X= Br, Cl) (Liu, Bai et al. 2010; Zhang, Lv et al. 2010; Du, Lai et al. 2011; Yoo, Cuong et al. 2012; Xu, Yan et al. 2013). The GO sheets can facilitate charge transfer and suppress the recombination of electron-hole pairs of the GO-based photocatalysts. Thus it is reasonable to assume that a reinforced charge separation/transfer may be achieved in our GO-Ag₃PO₄ nanocomposite system, where GO could act as electron acceptor and Ag₃PO₄ as electron donor. Moreover, recent research indicates that AgX, Ag nanoparticles and CQDs can act as electron acceptors to facilitate the photoexcited electrons transfer from Ag₃PO₄, and effectively protect Ag₃PO₄ from photocorrosion (Bi, Ouyang et al. 2011; Liu, Fang et al. 2012; Liu, Fang et al. 2012; Zhang, Huang et al. 2012). On the basis of the experimental facts and analysis, a proposed explanation for the enhanced photocatalytic activity and stability observed from our GO-Ag₃PO₄ nanocomposite system, as shown in Figure 7.13 follows. When the GO-Ag₃PO₄ nanocomposites are irradiated with visible light, the photogenerated electrons may be transferred to the GO

sheets, thus inhibiting the charge recombination and promoting photocatalytic activity. The efficient electron transfer from Ag_3PO_4 to GO sheets also sustains the stability of GO- Ag_3PO_4 nanocomposites by shielding electrons from the Ag_3PO_4 . Also the photogenerated holes on Ag_3PO_4 may oxidize polluted dyes, while the electrons on GO adsorb surface O_2 to form various reactive oxygen species (ROSs) and thus assist in the degradation of organic pollutants. In addition to enhanced charge separation, the photocatalytic reaction also involves the transportation of contaminant molecules over the catalyst surface. Previous reports have shown that GO sheets have relatively high adsorption ability towards some organic pollutants including methylene blue, rhodamine B and acid orange (Xiong, Zhang et al. 2010). Depending on different properties of the organics, the adsorption abilities of GO to organics are different. The high adsorption abilities of organic pollutant on the catalyst surface can enhance the electron transfer efficiency and contact opportunity with photogenerated active species. As a result, the observed high photocatalytic activity towards our GO- Ag_3PO_4 nanocomposite system may also be due to the adsorption ability of GO to organics.

Figure 7.13 Schematic drawing showing the process of the photocatalytic dye degradation and disinfection over GO- Ag_3PO_4 nanocomposites.

As for the mechanism of antibacterial and photocatalytic disinfection activity of GO-Ag₃PO₄ nanocomposite system, an explanation is illustrated by Figure 7.13. Firstly, the excellent intrinsic antibacterial activity of GO-Ag₃PO₄ nanocomposites is mainly caused by the high level of soluble Ag⁺ due to the slight solubility of Ag₃PO₄. The water soluble GO sheets adsorb and gather the bacteria onto the surface, which may enhance the interaction between bacterial cells and Ag₃PO₄ photocatalysts on GO sheets. Eventually the bacterial cell degradation is achieved by Ag₃PO₄ photocatalysts under visible light irradiation, which is similar to the photocatalytic degradation of organic dye. The synergetic effects of high level of Ag⁺ release, good adsorption capability of GO to bacterial cells, and enhanced photocatalytic activity of GO-Ag₃PO₄ nanocomposites are attributed to the excellent antibacterial and photocatalytic disinfection activity of this novel composite.

7.3 Conclusion

This study has shown that a novel visible light induced GO-Ag₃PO₄ photocatalyst can be fabricated in the lab. The GO-Ag₃PO₄ nanocomposites exhibit high-performance photocatalytic degradation activity toward organic pollutants with enhanced efficiency and stability compared with bare Ag₃PO₄ particles. This novel composite also demonstrates excellent intrinsic antibacterial activity towards *E.coli*. Moreover, the GO-Ag₃PO₄/visible light system illustrates enhanced photocatalytic cell degradation compared with bare Ag₃PO₄, due to the synergetic effects of excellent antibacterial Ag⁺, good adsorption ability of GO toward bacterial cells and high-efficient photocatalytic activity of Ag₃PO₄. The recovery of GO-Ag₃PO₄ nanocomposites can be implemented by a simple filtration process due to the large GO sheets. It is worth mentioning that the photocatalytic degradation efficiency of GO-Ag₃PO₄ nanocomposites/visible light system toward dye and phenol is much higher than that of GO-TiO₂-Ag nanocomposite/solar irradiation system or Ag/TiO₂ nanofiber composites/solar irradiation system. As a result, the new GO-Ag₃PO₄ nanocomposites

may find promising applications in environmental remediation and water treatment. Results of this work also provides a methodology and demonstrates the feasibility of synthesis and applications of ternary GO-TiO₂-Ag₃PO₄ nanocomposites in the near future.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This work aimed to develop high-performance TiO₂ nanocomposite photocatalysts for water disinfection and decontamination under solar irradiation. The photocatalysts synthesized in this study all have important features: (1) high photocatalytic efficiency; (2) easy recovery from treated water; (3) sensitive to solar light; (4) long-term antibacterial activity even without solar light irradiation. As a result, a group of novel TiO₂ nanocomposite photocatalysts were developed by introducing Ag or/and GO sheets, silver-based nanomaterials to achieve these important features. The synthesis method and characteristics of the nanocomposite photocatalysts prepared were extensively investigated and the photocatalytic activities of the nanocomposites were also evaluated and discussed.

Firstly, electrospun TiO₂ nanofibers were incorporated with Ag nanoparticles as Ag/TiO₂ nanofiber composites for the subsequent fabrication of Ag/TiO₂ nanofiber membrane. Results showed that Ag nanoparticle deposition has significantly enhanced the photocatalytic activity of TiO₂ nanofibers under solar irradiation, as well as provided intrinsic antibacterial capability without solar irradiation. The Ag/TiO₂ nanofiber membrane achieved 99.9 % *E.coli* inactivation and 80.0 % dye (MB) degradation under solar irradiation within 30 min. Moreover, compared with commercial P25 deposited membrane, the water permeate flux of the Ag/TiO₂ nanofiber membrane was remarkably high. Such excellent performances of Ag/TiO₂ nanofiber composites/solar irradiation system will lead to extensive cost effective water purification applications in the near future.

To further improve the photocatalytic efficiency of TiO₂, the small-sized TiO₂ nanorods with high specific surface area were introduced to incorporate with GO sheets

and Ag nanoparticles as novel multifunctional nanocomposites (GO-TiO₂-Ag). GO-Ag nanocomposites were first synthesized through a facile two-phase (toluene-water) method. The nanocomposites exhibited a remarkably enhanced antibacterial activity compared with the original Ag nanoparticles, suggesting that they may be used as effective antibacterial materials. The GO-Ag nanocomposites also showed high-performance photodegradation of dye (AO 7) under visible light irradiation, illustrating electrons can be effectively transferred from the excited dye to GO, then to Ag nanoparticles. Secondly, based on this research of GO-Ag and GO-TiO₂ nanocomposites, novel GO-TiO₂-Ag nanocomposites have been synthesized via the two-phase method, and confirmed by TEM, EDS and XRD analysis. The GO-TiO₂-Ag nanocomposites demonstrate enhanced photocatalytic activities in degrading AO 7 and phenol under solar irradiation compared with GO-TiO₂ and GO-Ag. These also exhibit excellent intrinsic antibacterial activity toward *E.coli*, as well as enhanced photobiocidal capability as compared to GO-TiO₂ and GO-Ag. A systematically investigation of the influence of Ag nanoparticle content in the nanocomposites for their photocatalytic activity indicates that the optimal Ag content in the GO-TiO₂-Ag nanocomposites varies for dye degradation and for phenol/bacterial degradation under solar irradiation due to different mechanisms. Given the superior photocatalytic activities of GO-TiO₂-Ag nanoparticles toward organic pollutants and waterborne pathogen under solar irradiation and the fact that they could be easily recovered relying on the large GO sheets, results clearly indicate that the new GO-TiO₂-Ag nanocomposites offer promising opportunities in the applications of water purification.

To further enhance the solar utilization of the TiO₂ nanocomposite photocatalysts, this author synthesized a novel multifunctional nanocomposite GO-TiO₂-Ag₃PO₄. Novel visible light induced photocatalyst Ag₃PO₄ instead of Ag nanoparticles were introduced to provide visible light photocatalysts and antibacterial properties. Firstly, binary GO-Ag₃PO₄ nanocomposites as visible light induced photocatalysts were fabricated through an ion-exchange method. Results indicate that the novel GO-Ag₃PO₄ nanocomposites exhibited significantly higher photocatalytic activities and improved stability under

Nano-composites	<i>E.coli</i> *	MB*	AO 7*	Phenol*
Ag-TiO ₂	70 min; 100 mg as membrane; 100%; ~10 ⁷ cfu/mL; 3.42×10 ⁻² min ⁻¹	80 min; 100 mg as membrane; 80%; 10 ppm; 2.11×10 ⁻² min ⁻¹	Nil	Nil
GO-Ag	120 min without solar ; 100 µg/mL; 100%; 10 ⁷ -10 ⁸ cfu/mL; 1.25×10 ⁻² min ⁻¹	Nil	120 min; 400 µg/mL; 40%; 10 ppm	Nil
GO-TiO ₂ -Ag-1	120 min; 100 µg/mL; 7.15 log; 1.75×10 ⁸ cfu/mL; 5.96×10 ⁻² min ⁻¹	Nil	120 min; 400 µg/mL; 99.3%; 10 ppm; 7.30×10 ⁻³ min ⁻¹	240 min; 1000 µg/mL; 99.3%; 10 ppm; 3.70×10 ⁻³ min ⁻¹
GO-TiO ₂ -Ag-2	90 min; 100 µg/mL; 8.24 log; 1.75×10 ⁸ cfu/mL; 9.85×10 ⁻² min ⁻¹	Nil	120 min; 400 µg/mL; 99.3%; 10 ppm; 1.33×10 ⁻² min ⁻¹	240 min; 1000 µg/mL; 100%; 10 ppm; 3.80×10 ⁻³ min ⁻¹
GO-TiO ₂ -Ag-3	120 min; 100 µg/mL; 8.24 log; 1.75×10 ⁸ cfu/mL; 7.16×10 ⁻² min ⁻¹	Nil	80 min; 400 µg/mL; 100 %; 10 ppm; 1.58×10 ⁻² min ⁻¹	240 min; 1000 µg/mL; 99.5 %; 10 ppm; 3.70×10 ⁻³ min ⁻¹
GO-Ag ₃ PO ₄	within minutes without solar; 20 µg/mL; 100 %; ~ 10 ⁷ cfu/mL;	Nil	10 min; 400 µg/mL; 100 %; 50 ppm; 1.09×10 ⁻¹ min ⁻¹	20 min; 1000 µg/mL; 100 %; 10 ppm; 3.8×10 ⁻² min ⁻¹

Table 8.1 Summary on disinfection and decontamination of pollutants by synthesized nanocomposites (reaction time; sample concentration; pollutant removal rate; initial pollutant concentration; constant rate /min⁻¹).

visible light irradiation compared with bare Ag_3PO_4 . Moreover, the $\text{GO-Ag}_3\text{PO}_4$ nanocomposites showed both excellent intrinsic antibacterial and visible light induced photocatalytic disinfection activities toward *E.coli* cells. It is worth mentioning that the photocatalytic degradation efficiency of $\text{GO-Ag}_3\text{PO}_4$ nanocomposites/visible light system toward dye and phenol is much higher than that of the $\text{GO-TiO}_2\text{-Ag}$ nanocomposite/solar system or the Ag/TiO_2 nanofiber composites/solar system. As a result, the new $\text{GO-Ag}_3\text{PO}_4$ nanocomposites may be promising for environmental applications and water treatment. This work also provides for the feasibility of synthesis and applications of ternary $\text{GO-TiO}_2\text{-Ag}_3\text{PO}_4$ nanocomposites in the near future.

These results are summarized in Table 8.1 in which relative efficiency of different nanocomposites under similar condition(s) are presented.

Besides the results mentioned above, it is worth to highlight that this research resulted in many novel approaches in the field of environmental science and engineering. These include:

- (1) First-time polyol synthesis has been used for deposition of Ag nanoparticles on TiO_2 nanofibers. The polyol synthesis is a soft and environmental friendly fabrication of Ag nanostructures with controlled shapes and properties (Wiley et al., 2007). Previous work applied co-electrospinning to the deposition of Ag nanoparticles on TiO_2 nanofibers (Jin et al., 2007). However, Ag ion is easily oxidized to Ag_2O rather than desired Ag nanoparticles during calcinations at high temperature. For this study, the in-situ polyol synthesis was used for the deposition of Ag nanoparticles on TiO_2 nanofibers. It can provide an environmental friendly method for the synthesis of metal- TiO_2 nanocomposites.
- (2) It's the first report on synthesis of multifunctional $\text{GO-TiO}_2\text{-Ag}$ nanocomposites, using the two-phase method. It can provide a universal approach for the synthesis of high quality GO-based metal/metal oxide nanocomposites.

- (3) It is the first-time evaluation of the intrinsic antibacterial and photocatalytic disinfection of Ag_3PO_4 crystals and Ag_3PO_4 -based nanocomposites for *E.coli*. Therefore, this work can provide the feasibility of environmental applications of Ag_3PO_4 crystals and Ag_3PO_4 -based nanocomposites.

8.2 Recommendations

In this work, the author developed a group of novel TiO_2 nanocomposite photocatalysts for water disinfection and decontamination under solar irradiation including mechanism studies. However, in order to expand these materials/processes to practical water treatment applications, future work is needed to complement this research topic. Recommendations are as follows:

- (1) As for the Ag/TiO_2 nanofiber membrane/solar irradiation system, studies of various Ag contents to evaluate its stability and long-term silver ion release of the Ag nanoparticles are important for practical water treatment purposes.
- (2) As for the GO-Ag and GO- TiO_2 -Ag nanocomposites/solar irradiation system, studies on the stability and long-term silver ion release of the Ag nanoparticles are also essential for practical water treatment applications. The monitoring of nanocomposites change in repeated cycles should be included. Moreover, the nanocomposites recovery evaluation by membrane filtration is highly recommended for future work.
- (3) As for the GO- TiO_2 - Ag_3PO_4 nanocomposites, the synthesis and applications of the ternary nanocomposites should be investigated based on results of the present study of binary GO- Ag_3PO_4 nanocomposites. A study of the optimal ratio of TiO_2 and Ag_3PO_4 to achieve highest photocatalytic performance of the

GO-TiO₂-Ag₃PO₄ nanocomposites should be included. Further studies should also be made to improve the photocatalytic stability of the Ag₃PO₄ semiconductor by preventing material photocorrosion.

- (4) Before practical application of these systems, the disinfection evaluation of other microbial pathogens and viruses besides *E.coli* should be investigated in the near future. Moreover, the decontamination of other organic pollutants which may be more resistant than organic dyes such as Persistent Organic Pollutants (POPs) should also be investigated.
- (5) All the works were done in lab at “bench scale”. Therefore, further testing to evaluate scale-up effects should be included for practical water treatment application.

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