Visible light driven heterojunction photocatalysts for removal of organic contaminants and bacterial inactivation

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**NANYANG
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UNIVERSITY**

SINGAPORE

**VISIBLE LIGHT DRIVEN HETEROJUNCTION
PHOTOCATALYSTS FOR REMOVAL OF
ORGANIC CONTAMINANTS AND BACTERIAL
INACTIVATION**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2017

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PHOTOCATALYSTS FOR REMOVAL OF
ORGANIC CONTAMINANTS AND BACTERIA
INACTIVATION**

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ABSTRACT

The presence of various antibiotics and their residues in aquatic systems has become one of the emerging environmental issues. Heterogeneous photocatalysis, one of advanced oxidation process driven by solar energy, has been regarded as a promising technology to eliminate antibiotics as well as other refractory organic contaminants. Under proper light irradiation, different reactive oxygen species such as hydroxyl, superoxide and hydroperoxyl radicals can be generated which will subsequently lead to the degradation of organic matters. Currently, research focused on applying heterogeneous photocatalysis to treat antibiotics is still rare, and most studies used TiO_2 with a wide band gap as candidate. Therefore, the major objective of this study is to explore other kinds of semiconductor-based heterojunctions to photodegrade recalcitrant organic compounds.

In the first part of this study, 2D BiOCl nanodiscs were prepared via one-step solvothermal method. To enhance its photocatalytic activity, Ag nanoparticles (Ag NPs) were deposited on the surface of BiOCl to form BiOCl-Ag heterostructured composites as photocatalysts to eliminate sulfanilamide (SAM) which is the precursor of sulfonamide group under visible light irradiation. The photo-degradation efficiency of SAM was improved by 71.7% using BiOCl-Ag compared to pristine BiOCl , indicating that Ag deposition is effective to augment the photocatalytic activity of BiOCl . Furthermore, the existence of Ag NPs also endowed BiOCl-Ag composites significant and enhanced antimicrobial ability as verified by the disinfection effect on *Escherichia Coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*).

In the second part of this study, by optimizing the synthesis conditions, WO_3 nanoplates with uniform size were obtained by a facile one step hydrothermal method while different amounts of Ag NPs were loaded onto WO_3 nanoplates using

a photo-reduction method to generate $\text{WO}_3\text{-Ag}$ composites. The performance of pure WO_3 and $\text{WO}_3\text{-Ag}$ composites as visible light driven photocatalysts was estimated by degradation of SAM and inactivation of *E. coli* and *B. subtilis*. The operation conditions were carefully optimized and the results illustrated that $\text{WO}_3\text{-Ag}$ composites showed remarkably better photocatalytic efficiency than that of pure WO_3 while their performance was found to be closely related to the amount of Ag deposited.

In the third part of this study, two kinds of semiconductors, WO_3 and $\text{g-C}_3\text{N}_4$, were combined together to construct different $\text{WO}_3\text{-g-C}_3\text{N}_4$ heterojunctions via a facile hydrothermal method. Sulfamethoxazole (SMX), one of the most commonly utilized antibiotics from sulfonamide class, was adopted as a model organic contaminant to evaluate the degradation performance of as-prepared $\text{WO}_3\text{-g-C}_3\text{N}_4$ composites under visible light illumination. In particular, SMX removal efficiency can be raised up largely to 91.7% when optimized $\text{WO}_3\text{-g-C}_3\text{N}_4$ composites with initially 8 mg $\text{g-C}_3\text{N}_4$ being applied at a dosage of 1.0 g L^{-1} . Such enhanced photocatalytic activity can be ascribed to the formation of direct solid-state Z-scheme heterojunctions between $\text{g-C}_3\text{N}_4$ and WO_3 , which could improve the photogenerated electron-hole pairs separation efficiency as well as the redox capability. At the same time, the larger surface area and extended visible light absorption capability can also contribute to the enhanced efficiency.

In the last phase of this study, efforts were made to fabricate reduced graphene oxide- WO_3 (RGO- WO_3) composites to explore their potential degradation feasibility towards SMX as visible light driven photocatalysts. Significantly improved SMX degradation ($> 98\%$) was obtained by two as prepared RGO- WO_3 composites. Moreover, these composites presented good stability and reusability making them promising candidates towards elimination of SMX. Furthermore, the

photocatalytic intermediates of SMX were analyzed and the photodegradation pathway was proposed accordingly.

Overall, the major contribution of this study is the successful construction of various highly efficient visible light driven heterogeneous composites; in particular, WO₃ based composites were the most efficient. Moreover, the outstanding performance for sulfonamides degradation and excellent stability make them promising candidates in practical application to remove refractory organic pollutants from water systems.

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LIST OF SYMBOLS AND ABBREVIATIONS

Λ	Wavelength
k_{app}	Pseudo first-order rate constant
pH_{zpc}	pH of the point of zero charge
pK_a	Acid dissociation constant
Ag NPs	Silver nanoparticles
AOP	Advanced oxidation process
BET	Brunauer-Emmett-Teller
CAS	Chemical Abstract Service
CASP	Conventional activated sludge process
CB	Conduction band
C_3N_4	Carbon Nitride
CNT	Carbon nanotube
DRS	Diffuse-reflectance spectra
EDX	Energy-dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
E_F	Fermi level
FTIR	Fourier-transform infrared spectroscopy
GAC	Granular activated carbon
GO	Graphene oxide
HPLC	High performance liquid chromatography
H_2O_2	Hydroperoxide
LC/MS/MS	Liquid chromatography tandem mass spectrometry
LSPR	localized surface plasmon resonance
NF	Nanofiltration

-OH	Hydroxyl
OH ⁻	Hydroxide ion
·OH	Hydroxyl radicals
·OOH	Hydroperoxyl radicals
O ₂ ^{-·}	Superoxide radicals
PL	Emission photoluminescence spectrum
RGO	Reduced graphene oxide
RO	Reverse osmosis
ROS	Reactive oxygen species
SA	Sulfonamide
SAM	Sulfanilamide
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman scattering
SMX	Sulfamethoxazole
SPR	Surface plasmon resonance
TEM	Transmission electron microscopy
THM	Trihalomethane
TOC	Total organic carbon
UV	Ultraviolet light
VB	Valence band
VLD	Visible light driven
WWTP	Waste water treatment plant
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF PUBLICATIONS

Part of the findings in the thesis has been published in the following papers:

1. **Zhu, W.**, Sun, F., Goei, R., & Zhou, Y. Construction of WO₃-g-C₃N₄ composites as efficient photocatalysts for sulfamethoxazole degradation under visible light. *Catalysis Science & Technology*, Just Accepted.
2. **Zhu, W.**, Sun, F., Goei, R., & Zhou, Y. (2017). Facile fabrication of RGO-WO₃ composites for effective visible light photocatalytic degradation of sulfamethoxazole. *Applied Catalysis B: Environmental*, 207, 93-102.
3. **Zhu, W.**, Liu, J., Yu, S., Zhou, Y., & Yan, X. (2016). Ag loaded WO₃ nanoplates for efficient photocatalytic degradation of sulfanilamide and their bactericidal effect under visible light irradiation. *Journal of Hazardous Materials*, 318, 407-416.
4. **Zhu, W.**, Li, Z., Zhou, Y., & Yan, X. (2016). Deposition of silver nanoparticles onto two dimensional BiOCl nanodiscs for enhanced visible light photocatalytic and biocidal activities. *RSC Advances*, 6(69), 64911-64920.

CHAPTER 1 INTRODUCTION

1.1 Background

With rapid industrialization, many hazardous contaminants have been released to the environment which has become one of the biggest challenges in 21st century. The elimination of hazardous substances (such as organic pollutants, inorganic pollutants and microorganisms) is thereafter one major issue that needs to be solved from the aquatic environments including not only wastewater but also surface water and ground water. Among various kinds of contaminants, the emergence of antibiotics and their residues in various aquatic systems has drawn intensive attention because of the potential threats to both human health and aquatic ecosystems.

It is estimated that every year the global usage of antibiotics is about 100,000 to 200,000 tons, therefore, a large amount of antibiotics as well as their residues can find their ways into the environment (Shi, Yang et al. 2014, Song, Yang et al. 2016). Though the concentration of antibiotics observed in the water bodies is usually low, they can cause the occurrence of acute and chronic toxic effects as well as antibiotic resistance among microorganisms (Bonvin, Omlin et al. 2013, Song, Yang et al. 2016). Nevertheless, many studies have proved that conventional water treatment which involves physical, chemical and biological oxidation processes cannot efficiently remove antibiotics as well as other recalcitrant organics. Consequently, it is still urgent to develop highly efficient, stable, and eco-friendly “green” methods to achieve the elimination of antibiotics and their residues from aquatic systems (Michael, Rizzo et al. 2013, Cao, Low et al. 2015).

In recent decades, the improvement of nanotechnology has provided a promising pathway to environmental remediation. Nanomaterials with attractive physical and chemical properties are excellent adsorbents, catalysts and sensors due to their large specific surface areas and high reactivity. Therefore, increasing efforts have been devoted to utilize nanomaterials to achieve the “green” and efficient treatment goal. Among potential solutions, one of advanced oxidation processes (AOPs), semiconductor-based photocatalysis has emerged with inestimable superiority since it is considered to be an economic, renewable, clean, and safe technology, which requires only the inexhaustible solar light as driving force, and suitable semiconductors as photocatalyst to conduct catalytic reactions for a variety of applications including decomposition of organic pollutants (Cao, Low et al. 2015).

Solar energy is a clean energy source which can provide ultimate renewable energy. However, the challenge lies in its effective harvesting, conversion and storage of solar energy. In recent years, semiconductors with nanostructures have attracted a lot of attention and they can be applied as photocatalysts driven by solar energy. At ambient temperature and pressure, when irradiated by solar light or other artificial lights, photocatalysts are able to be excited and generate electron-hole pairs which can further trigger the production of active radicals like hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\cdot-}$) and hydroperoxyl radicals ($\cdot\text{OOH}$). These radicals can have synergistic photo-oxidation effect which is effective in enhancing the degradation and mineralization of organic pollutants in water (Li and Qu 2009). At the same time, these photocatalysts also present antimicrobial effect due to the inactivation on the microorganisms by the radicals. Therefore, photocatalysis shows the capability to treat water contaminated by both organic pollutants and microbiological contamination, simultaneously.

Currently, the development of highly efficient semiconductor-based photocatalysis has become a topic of significant interest. However, studies proved

that quite a lot of single phase semiconductors, such as titanium dioxide (TiO_2), can only be photo-excited by near-ultraviolet (UV) band of the solar spectrum which severely limits their efficiency of harvesting solar energy. Furthermore, the rapid electron-hole recombination rate is regarded as another essential factor that hinders the overall photocatalytic efficiency. One popular route to overcome the aforementioned limitations is to fabricate heterogeneous photocatalysts. Such heterojunctions with proper design can have the possibility to utilize not only UV light but also visible light as energy source and to have reduced electron-hole recombination rate. Thereafter, it is highly possible that they have much enhanced photocatalytic ability compared their single phase semiconductors. Consequently, such heterogeneous photocatalysts driven by sustainable solar energy may potentially become an efficient way to eliminate recalcitrant organics from the aquatic environment.

1.2 Knowledge gap and research motivation

The application of photocatalysis process in practice is now still in the initial stage as a variety of limitations and challenges from different aspects still exist. From the industrialization and commercialization points of view, the realization of photocatalysis process should address challenges from material development, engineering, economic points of views (Qu, Alvarez et al. 2013). However, this requires the cooperation of researchers from various disciplines, while in this thesis, main efforts will be devoted to work on the challenges raised from material development since exploration and construction of suitable catalysts is believed to be one of the main challenges to overcome. Up to date, TiO_2 is one of the most widely studied semiconductor photocatalysts with a wide band gap of 3.2 eV. Due to the wide band gap, bare TiO_2 can only be photo-excited by UV light irradiation which strongly restricts its photocatalytic performance. In order to strengthen its

photocatalytic efficiency, many researchers chose to fabricate TiO_2 -based heterojunctions to shift its optical response from UV to the visible light range and to reduce the electron-hole recombination rate. Especially, some of them were found to be quite effective in degrading refractory organic compounds such as various antibiotics under UV light and/or visible light illumination (An, Yang et al. 2010, Wang, Yap et al. 2011, Chen and Chu 2012).

In addition, new semiconductors with narrower band gaps that can be powered by visible light, namely, visible light driven (VLD) photocatalysts, have attracted lots of attention as well. In particular, tungsten trioxide (WO_3), Bismuth oxychloride (BiOCl) and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) have been recognized as promising candidates due to their specific physical and chemical properties. Furthermore, it is important to note that the heterogeneous composites of the above three semiconductors may possess even better photocatalytic ability. However, unlike TiO_2 -based heterostructures which have been extensively explored, the construction of efficient heterojunctions of WO_3 , BiOCl and $\text{g-C}_3\text{N}_4$ is still at the early stage. Hence, though there are many approaches to fabricate different types of heterojunctions, when it comes to the above three candidates, very limited systematic studies focused on the development of their heterogeneous composites, especially those can be driven by visible light, are available.

As mentioned earlier, photocatalysis may be a promising solution to water pollution caused by antibiotics and other recalcitrant organic matters. Nevertheless, non- TiO_2 composites used as photocatalysts to eliminate antibiotics is rare. The operating parameters optimization, possible reaction mechanism, and the intermediates identification during the photocatalytic process are even less. Therefore, it is of significant importance to search suitable co-catalysts to design effective heterojunctions of non- TiO_2 materials like WO_3 , BiOCl and $\text{g-C}_3\text{N}_4$ to act as VLD photocatalysts. It is also essential to systematically evaluate their potential

application to remove antibiotics as well as other organic compounds from water environments.

1.3 Objectives and scope of study

The aim of this thesis is to develop highly efficient photocatalytic heterojunctions based on three types of semiconductors, namely WO_3 , BiOCl , and $\text{g-C}_3\text{N}_4$. To achieve this goal, different strategies have been used to fabricate various heterogeneous composites while their specific photocatalytic performance was evaluated by two kinds of most commonly used antibiotics namely SAM and SMX. Particularly, silver nanoparticles (Ag NPs) were firstly applied as co-catalyst to modify both WO_3 and BiOCl . Compared to BiOCl , WO_3 presented advantages like a narrower band gap, a simpler synthesis method, easily controlled morphology and crystallinity, and more importantly, higher photocatalytic ability towards sulfanilamide (SAM) under visible light irradiation. Thus, in the later stage, WO_3 was chosen as main catalysts, while $\text{g-C}_3\text{N}_4$ and reduced graphene oxides (RGO) were utilized as co-catalysts. The photocatalytic performance of the as-prepared RGO-WO_3 and $\text{WO}_3\text{-g-C}_3\text{N}_4$ was then evaluated by Sulfamethoxazole (SMX). The specific scopes of this work are as follows:

1. Synthesis of BiOCl-Ag heterogeneous composites and evaluation of their photocatalytic performance as VLD photocatalysts.
 - a. To optimize the synthesis method to prepare two dimensional (2D) BiOCl nanodiscs.
 - b. To deposit Ag NPs on the surface of BiOCl nanodiscs forming BiOCl-Ag heterogeneous composites
 - c. To evaluate and optimize the photocatalytic performance of BiOCl-Ag composites for SAM degradation.
 - d. To investigate the antimicrobial effect of BiOCl-Ag composites.

2. Fabrication of WO_3 -Ag heterogeneous composites and estimation of their photocatalytic performance towards SAM degradation under visible light illumination.

a. To optimize the synthesis process to prepare well crystallized WO_3 nanoplates.

b. To load various amount of Ag NPs on the surface of WO_3 nanoplates generating various WO_3 -Ag composites

c. To characterize the as-prepared WO_3 -Ag composites, and to evaluate as well as optimize their photocatalytic performance towards SAM degradation.

d. To study the antimicrobial effect of different WO_3 -Ag composites.

e. To quantify Ag leaching and to evaluate the potential effect to the environment.

3. Construction of WO_3 -g- C_3N_4 heterojunctions and evaluate their performance for elimination of SMX.

a. To synthesize and characterize various WO_3 -g- C_3N_4 composites.

b. To evaluate and optimize the photocatalytic performance of different WO_3 -g- C_3N_4 composites for SMX degradation.

4. Preparation of RGO- WO_3 heterostructures and estimation of their photocatalytic performance towards SMX under visible light irradiation.

(a) To synthesize RGO- WO_3 composites with various RGO loading.

(b) To characterize the as-prepared RGO- WO_3 composites.

(c) To evaluate and optimize the photodegradation ability of different RGO- WO_3 composites towards SMX degradation.

(d) To determine the degradation byproducts generated during the photocatalytic process.

1.4 Organization of thesis

This thesis consists of seven chapters. Specifically, **Chapter 1** shows a brief background, knowledge gap and research motivation, objectives and the scope of this study, and the organization of this thesis. **Chapter 2** provides an up-to-date literature review of current water contamination caused by antibiotics, limitation of current treatment methods, types of photochemical AOPs and their limitations, the possible application of photocatalysis as an alternative solution, and the possible challenges of photocatalysis process in the water treatment process. From **chapter 3** to **6**, various kinds of heterojunctions were fabricated and their photocatalytic performance under visible light was evaluated and optimized. In particular, **Chapter 3** illustrates the optimized method to synthesize BiOCl nanodiscs, while Ag NPs were used as co-catalysts to prepare BiOCl-Ag heterogeneous composites. The photodegradation ability of SAM and the antimicrobial ability were carefully evaluated. Since results show that BiOCl has a relatively wide band gap and complex synthesis method, it may be not a suitable candidate as photocatalyst driven by visible light irradiation. Therefore, in the next chapter, WO₃ with a narrower band gap and simply synthesis method was selected to explore its potential as VLD photocatalyst. To further enhance the photocatalytic performance of WO₃, different materials were employed as co-catalysts. In **chapter 4**, Ag was used to modify WO₃ nanoplates, where WO₃-Ag composites with different loading amounts of Ag were prepared. Subsequently, the photocatalytic performance of these catalysts was evaluated. **Chapter 5** describes the construction of WO₃-g-C₃N₄ heterojunctions and their photodegradation performance towards SMX. **Chapter 6** presents the fabrication of RGO-WO₃ composites as well as their photodegradation performance for SMX. The degradation byproducts were also investigated in **chapter 6**. Lastly, **Chapter 7** summarizes all the major findings in this thesis, at the

same time, four recommendations were proposed which aim to figure out the challenges and limitations that photocatalysis process are now facing.

In brief, the original research contributions of this study lie in the simple preparation of different WO_3 based heterogeneous composites to explore the influence of different co-catalysts on their photocatalytic performance. Moreover, efforts were devoted to exploration the possibility of applying these heterogeneous composites to eliminate emerging organic contaminants which posing threats to the environment and human health.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Since the discovery of penicillin in 1928, various kinds of natural or synthetic antibiotics, which can be defined as chemotherapeutic compounds capable of restraining or regulating the growth of microorganisms, have been used world widely (Li 2014, Gothwal and Shashidhar 2015). Though there is no accurate data, it is estimated that the global antibiotic consumption is around 100,000 to 200,00 tons every year (Kümmerer 2009, Manzetti and Ghisi 2014). The excessive use and high consumption of antibiotics in both human and veterinary medicines has resulted in the ubiquitous occurrence of antibiotics as well as their residues in various water bodies (Watkinson, Murby et al. 2009, Manzetti and Ghisi 2014).

The emergence of antibiotic compounds in aquatic systems is now regarded as an emerging and serious environmental issue which has drawn increasing attention world widely (Homem and Santos 2011, Berendonk, Manaia et al. 2015, Ding, Wu et al. 2016). Existence of antibiotics and their residues in the environment can present adverse effects to not only the ecological system but also human health (Baran, Adamek et al. 2011, Homem and Santos 2011). Even at low concentrations, antibiotics are believed to be significantly toxic to bacteria and algae, and more importantly, they are able to spread and maintain antibiotic resistance genes and bacteria in different environmental compartments, which will consequently reduce the therapeutic potential of antibiotics towards human and animal pathogens. (Hernando, Mezcua et al. 2006, Huerta, Marti et al. 2013, Ho, Zakaria et al. 2014, Lu, Na et al. 2015, Sharma, Johnson et al. 2016).

Though conventional Wastewater Treatment Plants (WWTPs) are supposed to be the last places where antibiotics can be treated in the sewage disposal system, most of them are found to be not sufficient enough to eliminate antibiotics since they are not designed to eliminate emerging contaminants such as various antibiotics (Xu, Zhang et al. 2007, Homem and Santos 2011, Gothwal and Shashidhar 2015). This fact will subsequently lead to the leaching of antibiotics and their metabolites into surface waters as well as groundwater. Hence, WWTPs are considered to be the dominant anthropogenic sources for antibiotics into various environmental matrices, including soil, surface water, drinking water, groundwater, seawater, plants and aquatic organisms (Baran, Sochacka et al. 2006, Baran, Adamek et al. 2011, Homem and Santos 2011, Zou, Xu et al. 2011, González-Pleiter, Gonzalo et al. 2013, Huerta, Marti et al. 2013, Michael, Rizzo et al. 2013, Liu, Zhang et al. 2014, Gothwal and Shashidhar 2015, Ding, Wu et al. 2016). Moreover, due to the low elimination efficiency, the continuous release and accumulation of antibiotics originated from the extensive usage turn them into persistent or “pseudo-persistent” contaminants (Watkinson, Murby et al. 2009, Homem and Santos 2011, Gao, Mao et al. 2012, Liu, Zhang et al. 2014, Gothwal and Shashidhar 2015). Therefore, it is urgent to develop practical, economical and eco-friendly methods and technologies which are capable to effectively eliminate antibiotic pollutants.

2.1.1 Sulfonamides in the aquatic environment

According to the mechanism of action, antibiotics can be classified to 15 groups: tetracyclines, sulfonamides (SAs), β -lactams, polypeptides, rifamycin, monobactams, carbapenems, aminoglycosides, glycopeptides, lincomycin, macrolides, chloramphenicol, quinolones, and fluoroquinolones. Among the above groups, SAs have attracted extensive attention due to their widespread use. Basically, SAs are the synthetic derivatives of sulfanilic acid which contain the

sulfonamide groups with a free amino group ($-N^4H_2$) at one end of the molecular. To date, more than 150 kinds of SAs have been applied as antibacterial drugs and the commonly used SAs have been summarized in **Table 2.1** (Smith and Milward 1983, Baran, Adamek et al. 2011). **Fig. 2.1 (a), (b) and (c)** illustrate the general chemical structure of SAs, SAM and SMX, and SAM is the precursor of SA group and the simplest SA antibiotic.

In various countries, as a result of their relatively low cost and effectiveness, SAs have been listed as the second most commonly used antibiotics just behind tetracyclines for the treatment of bacterial, fungal as well as protozoal infections in both human and animal medicines (Sarmah, Meyer et al. 2006, Kim, Choi et al. 2007, García-Galán, Díaz-Cruz et al. 2008, Heuer, Solehati et al. 2011, Gao, Mao et al. 2012, Hsu, Chen et al. 2014). As polar and amphoteric substances, most members of SA group are water soluble which allows them to migrate easily in the environment (Kim, Choi et al. 2007, Baran, Adamek et al. 2009, Baran, Adamek et al. 2011). Specifically, the occurrence of SAs such as SMX and SDT have been frequently observed in almost all surface water (Kim, Choi et al. 2007). Thus, the overuse and good solubility of SAs have led to their high excretion rate and persistence in the surrounding environment posing threats to the aquatic environments as well as human health. More importantly, SAs can be accumulated in various organisms of a food chain, through which they can enter human bodies and raise potential risks to public health (Kümmerer 2008, Gao, Mao et al. 2012, Li, Yu et al. 2017). The existence of SAs may cause side effect such as allergic reactions in some hypersensitive individuals. Moreover, another direct consequence is that even when the concentrations of SAs and their metabolite residues are low, they are capable to induce high levels of pathogens resistant to clinical drugs in human (Neu 1992, Baran, Adamek et al. 2009, Adamek, Baran et al. 2012, Exall, Balakrishnan et al. 2013).

Table 2.1 Common names, CAS number and structure of commonly used SAs (Baran, Adamek et al. 2011).

Common names of SAs	CAS numbers	Abbreviation	-R
Sulfanilamide	63-74-1	SAM	-H
Sulfacetamide	144-80-9	SCT	-COCH ₃
Sulfacarbamide	547-44-4	SC	-CONH ₂
Asulam	3337-71-1		-COOCH ₃
Carbutamide	339-43-5		-CONH(CH ₂) ₃ CH ₃
Sulfathiourea	515-49-1	STU	-CSNH ₂
Sulfaguanidine	57-67-0	SGM	=C(NH ₂) ₂
Sulfathiazole	72-14-0	STZ
Sulfafurazole, sulfisoxazole	127-69-5	SSZ
Sulfamethoxazole	723-46-6	SMX
Sulfamoxole	729-99-7	SMM
Sulfapyridine	144-83-2	SPY
Sulfadiazine	68-35-9	SDZ
Sulfamethoxine, Sulfamethoxydiazine	651-06-9	SMO

Sulfamerazine	127-79-7	SMR
Sulfamethazine, Sulfadimidine	57-68-1	SDM
Sulfadimethoxine	122-11-2	SDT
Sulfamethoxypyridazine	80-35-3	SMP
Sulfachloropyridazine	80-32-0	SCP
Sulfadoxine	2447-57-6	SDX

Fig. 2.1 Chemical structure of SAs (a), SAM (b) and SMX (c).

2.2 Removal of antibiotics from water

2.2.1 WWTPs and their limitations

As mentioned above, most conventional WWTPs present very limited removal efficiency towards antibiotics as well as other micro-pollutants, while concurrently, the elimination efficiency varies notably among different kinds of antibiotics (Batt, Kim et al. 2007, Shi, Ma et al. 2014). In general, conventional WWTPs consist a primary, secondary and sometime a tertiary stage, where various biological and

physicochemical processes are involved and contributing to the removal of antibiotics in different stages, such as filtration, coagulation, flocculation, sedimentation and biological processes (Rizzo, Manaia et al. 2013).

Overall, the removal of antibiotics in conventional WWTPs is mainly achieved in the secondary stage by the biological treatment, of which Conventional activated sludge process (CASP) is the most commonly applied method. In a typical CASP, both biotic (biodegradation by bacteria and fungi) and non-biotic or abiotic processes (sorption, hydrolysis, photolysis) are involved. Therefore, during this treatment, the removal of antibiotics is achieved by their sorption as well as their further degradation and/or transformation on the activated sludge.

Since the concentrations of various antibiotics in the influents and effluents of WWTPs are generally different due to their consumption patterns, their physicochemical properties, the types of treatment processes adopted and the different operation conditions, the removal efficiency of various antibiotics may vary greatly. In the case of SAs, though different results were obtained, most of the previous studies revealed that they cannot be effectively eliminated via conventional WWTPs, which may be caused by their poor sorption on the active sludge and their semi-resistance against biological degradation (Braschi, Blasioli et al. 2010, Adamek, Baran et al. 2012). In addition, it is important to note that some SAs adsorbed by the biomass in WWTPs may be returned to the environment, making WWTPs a source of SAs pollution (Navalon, Alvaro et al. 2008).

2.2.2 Other methods and their limitations

The ineffectiveness of conventional WWTPs in eliminating antibiotics has promoted the intensive search for other effective solutions to remove antibiotics and their residues from water bodies (Michael, Rizzo et al. 2013). Consequently, various physical (adsorption process and membrane process), chemical

(chlorination and advanced oxidation processes) as well as some combined approaches have been explored.

2.2.2.1 Adsorption

Adsorption processes are common strategies to remove organic pollutants, in which adsorbents will be added to transfer the contaminants from the fluid phase to their solid surface. As a result, after an certain adsorption process, contaminants are not degraded but are concentrated and transferred to a new phase which means the appearance of new solid residues requiring further treatment (Homem and Santos 2011).

The most commonly used adsorbents are granular activated carbons (GACs), and they can be applied to remove hydrophobic and charged contaminants (Le-Minh, Khan et al. 2010, Gothwal and Shashidhar 2015). As investigated by various studies, GACs present quite limited removal efficiency towards SAs which may be caused by the low adsorption of SAs on the surface of GACs (Adams, Wang et al. 2002, Westerhoff, Yoon et al. 2005, Baran, Adamek et al. 2011, Mc Ardell, Kovalova et al. 2011). The drawback of adsorption process using GACs lies in the high investment due to their high cost and due to poor regeneration ability (Crisafulli, Milhome et al. 2008). Particularly, the cost of production of high quality GACs is quite high, while after usage, another important issue is that additional treatment is required to remove the adsorbed organic contaminants (Mohan and Pittman 2007, Vince, Aoustin et al. 2008).

The same problem appears for other kind of absorption media, which is the high cost of regeneration and reuse leading to the raise of the overall cost. Meanwhile, it is important to note that adsorption is usually a physical process which can only remove/concentrate rather than degrade/decompose pollutants. Additional cost is thereby needed to deal with such concentrated waste stream (Adeleye, Conway et al. 2016). Though efforts have been devoted to develop alternatives with relatively

lower cost, many of them are proved to possess lower adsorption capacity and quick clogging of the pores (Adeleye, Conway et al. 2016).

2.2.2.2 Membrane filtration

Currently, membrane filtration processes have been utilized as common elements in drinking water and wastewater treatment, and especially, nanofiltration (NF, pore size range $0.001\ \mu\text{m}$) and reverse osmosis (RO, pore size range $< 0.001\ \mu\text{m}$) are to be effective in removing organic micro-pollutants because of their lower pore sizes (Kimura, Iwase et al. 2009, Vergili 2013, Ganiyu, van Hullebusch et al. 2015). Koyuncu *et al.* applied NF to study the removal efficiency of several SA antibiotics, including SMX, SDT and SMR, and their results illustrated that the removal efficiency of these SA antibiotics was around only 11-20% after 90 min operation (Koyuncu, Arikan et al. 2008). While study of Košutić *et al.* found that SDZ and SDM were effectively removed ($> 90\%$) by a RO/NF system (Košutić, Dolar et al. 2007).

The application of membrane filtration faces several challenges. First, similar to adsorption process, the contaminants being treated are actually concentrated and transferred to a new phase rather than degraded (Homem and Santos 2011). As a result, proper method should be proposed to handle the concentrated stream which would increase the cost (Van der Bruggen, Mänttari et al. 2008). Another challenge lies in the high pressure that required during the operation of NF and RO which requires high energy input (Monteiro and Boxall 2010, Exall, Balakrishnan et al. 2013, Michael, Rizzo et al. 2013). More importantly, for all membrane separation, a non-negligible issue is membrane fouling which would affect not only the permeability but also membrane life time (Goosen, Sablani et al. 2005, Gao, Liang et al. 2011).

2.2.2.3 Chlorination

Chlorination is frequently used low cost technology in water treatment to decompose organic contaminants. In a typical chlorination process, chlorine gas (Cl_2) can hydrolyze to hypochlorous acid (HOCl) in water following **Eq (2.1)**, and HOCl as a weak acid can subsequently dissociate to hypochlorite (ClO^-) and H^+ . HOCl is the main reactive chlorine species involved in the water treatment to oxidize organic compounds like antibiotics (Acero, Benitez et al. 2010, Homem and Santos 2011). However, when chlorine species like HOCl and ClO^- are used to treat compounds with aromatic rings, neutral amines and double bonds, more toxic byproducts than the parent molecules may be generated, such as trihalomethanes (THMs) and haloacetic acids which present potentially dangerous carcinogenic activity (Navalon, Alvaro et al. 2008, Acero, Benitez et al. 2010). Another disadvantage of usage of Cl_2 is that the safety hazards associated with storage, transportation and handling of Cl_2 .

As an alternative to Cl_2 , chlorine dioxide (ClO_2) has also been studied to oxidize organic compounds (Kim, Panditi et al. 2015). Compared to Cl_2 , application of ClO_2 will not generate toxic THMs (Navalon, Alvaro et al. 2008, Homem and Santos 2011). However, in comparison to other oxidants, ClO_2 shows higher selectivity and cannot react with hydrocarbons, carbohydrates, aromatic as well as molecules containing aldehydes, ketones and primary and secondary amines. Hence these drawbacks strongly limit its application (Sharma 2008).

Adams *et al.*, Stackelberg *et al.* and other researcher have investigated the effect of various chlorination methods on some SA antibiotics, and their results found that though high removal was observed, the byproducts generated were believed to be more toxic than the original compounds (Adams, Wang et al. 2002, Stackelberg, Gibbs et al. 2007, Li and Zhang 2012, Li and Zhang 2013). Hence, increased concern

towards the formation of toxic halogenated byproducts has inspired the development of other alternative solutions like advanced oxidation processes.

2.2.2.4 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) operated at ambient temperature and normal pressure has drawn increasing attention as alternative solutions to eliminate antibiotics and their residues since they are quite efficient against many recalcitrant pollutants (Tambosi, De Sena et al. 2009, Zapata, Oller et al. 2010, Oller, Malato et al. 2011, Paul, Aravind et al. 2013, Lofrano, Libralato et al. 2015, Serna-Galvis, Silva-Agredo et al. 2016). Contrary to physical processes where organic contaminants are transferred to a new phase, AOPs appear to be more attractive since they show the possibility to oxidize a variety of organic compounds to less toxic and more biodegradable products, and sometime completely mineralization to CO₂ and H₂O can be realized (Esplugas, Bila et al. 2007, Monteiro and Boxall 2010). Usually, the destruction of organic contaminants in various AOPs is achieved by the chemical reactions based on in situ formation of powerful active species, especially ·OH, which is regarded as a powerful and non-selective/low selectivity oxidizing agents (such as chlorine, molecular ozone, *etc.*) (Akmehmet Balcioglu, Arslan Alaton et al. 2003, Lee and von Gunten 2010, Paul, Aravind et al. 2013, Zhang, Zhang et al. 2013).

After years of study, researchers are now quite clear about the possibilities and capability of various conventional treatment technologies (Oller, Malato et al. 2011). However, such information is still lacking for different AOPs, as a result, these AOPs faces challenges and barriers from various aspects which limit their practical application in the water treatment process. From engineering points of view, challenges such as the lack of the full-scale application of AOPs and appropriate integration with other technologies (process coupling) in the water treatment system need to be solved. At the same time, the application of various AOPs are limited by

the lack of operation experience, high investment, and technical feasibility (Matilainen and Sillanpaa 2010, Oller, Malato et al. 2011). Nevertheless, there are plenty of different AOP technologies, and their readiness for real application and industrialization is actually different from one to another. Therefore, the possible challenges and limitations lying ahead of individual technology need to be considered and addressed one by one.

Particularly, various AOPs can be generally divided into chemical AOPs (such as ozonation and Fenton method), photochemical AOPs (such as photolysis with UV, Photo-Fenton method, photocatalysis), electrochemical AOPs (EAOPs), as well as combined methods (Homem and Santos 2011). There have been many review papers that summarized the application of AOPs in water treatment, and here efforts will be mainly devoted to a brief summary of application of photochemical AOPs since they are suggested to be the most recent development in AOPs (Malato, Blanco et al. 2007). When sustainable solar energy is adopted as source of energy, it would be able to decrease the artificial energy consumption involved in these technologies (Malato, Blanco et al. 2007, Vilar, Pinho et al. 2011).

Every year, 3×10^{24} J of energy is delivered to the surface of the earth from the sun, which is about four orders of magnitude larger than the annual energy used by humans globally. It is worth noting that solar energy is an abundant source of energy, while it is also clean and safe (Chen, Ma et al. 2010). As a result, photochemical AOPs using solar light could be regarded as simple, clean, efficient and relatively inexpensive technologies (Oturán and Aaron 2014).

Fig. 2.2 Spectral distribution of the solar photon irradiation based on the AM1.5 global data (The curve is based on the American Society for Testing and Materials Terrestrial Reference (Gueymard 2004, Zhou, Qu et al. 2012)).

Nevertheless, one of the challenges that most photochemical AOPs facing now is that they can only utilize UV light which strongly limits their application. As illustrated by the spectral distribution of the solar photon irradiation based on the AM1.5 global data (**Fig. 2.2**), it is clear that the whole spectrum is composed by mainly three regions: ultraviolet (UV), visible and infrared. It is clear that UV light only occupies around 3 to 4% of the whole solar light spectrum, which is actually a very small portion in comparison to visible light ($\lambda > 400$ nm) accounting about 44% of the whole solar spectrum (Chen, Cai et al. 2010). Therefore, to overcome this shortcoming, more and more researchers are devoting increased effort to develop appropriate AOPs systems which can be powered by solar light (Adamek, Baran et al. 2012).

2.2.3 Application of photochemical AOPs and their limitations

The employment of photochemical AOPs to treat organic contaminants have been widely studied. For instance, UV/H₂O₂ photolysis and Photo-Fenton are suggested to be quite effective in application of decoloration of various dyes (Muruganandham and Swaminathan 2004, Arslan-Alaton, Tureli et al. 2009, Asghar, Raman et al. 2015). Nonetheless, when it comes to emerging trace organic

compounds like antibacterial drugs, the application of photochemical AOPs are still in the early stage. Consequently, here efforts will be mainly dedicated to underline the possible effect of several photochemical AOPs on SA group.

2.2.3.1 Direct UV Photolysis, UV/H₂O₂, and UV/O₃ photolysis

Photolysis is a process of which the target compounds are directly degraded under artificial or natural light as a result of photochemical reactions (Klavarioti, Mantzavinos et al. 2009). Though UV treatment is widely used for drinking water disinfection, it is found that when be adopted to degrade micropollutants, its efficiency varies among different pollutants. Specifically, both the physicochemical properties of the target compounds and the UV dose will affect the effectiveness of UV photolysis (Matilainen and Sillanpaa 2010). At the same time, many other factors like UV source, pH, temperature, turbidity water matrixes compositions can influence the efficiency of photolysis (Matilainen and Sillanpaa 2010, Fatta-Kassinos, Vasquez et al. 2011, Yang, Zhou et al. 2014).

It is pointed out that most micropollutants cannot be effectively decomposed under that the UV dose generally applied for disinfection purpose (Pereira, Weinberg et al. 2007, Yang, Zhou et al. 2014). To improve the photolysis efficiency, one widely utilized strategy is to combine irradiation with oxidants like hydrogen peroxide (H₂O₂) and ozone (O₃) to produce ·OH radicals (Toor and Mohseni 2007, Matilainen and Sillanpaa 2010, Oturan and Aaron 2014).

In the case of photolysis under UV, the removal efficiency of SA antibiotics varied, where the elimination of SMX was quite weak without addition of H₂O₂ (Kim, Yamashita et al. 2009, Zuccato, Castiglioni et al. 2010, Ryan, Tan et al. 2011). Sudha *et al.* studied the degradation of several kinds of SA antibiotics under both simulated UV light (254 nm and 350 nm) and natural sunlight, and they found that the degradation rates were quite low with a half-lives from 1 to 9 days when no H₂O₂ was added (Batchu, Panditi et al. 2014). J. T. Wu *et al.* investigated the

degradation of four kinds SA antibiotics under various UV/oxidant systems, finding that with the existence of oxidants like H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$ or NaBrO_3 , the photolysis of these antibiotics was largely promoted and SDZ was the most difficult to mineralize (Wu, Wu et al. 2015). While in the study of Wanqian Guo *et al.*, UV/ O_3 process was proved to be more efficient in degrading SDZ than bare O_3 or UV process (Guo, Yang et al. 2016).

As mentioned earlier, the effectiveness of UV photolysis would be affected by many parameters which consequently limit its application. Since direct UV photolysis is usually not efficient, oxidants like H_2O_2 and O_3 are required. However, the dosage of H_2O_2 would affect the photolysis efficiency as well, where excess H_2O_2 is found to be detrimental as it would act as $\cdot\text{OH}$ scavenger (Song, Ravindran et al. 2008, Matilainen and Sillanpaa 2010). The addition of H_2O_2 and O_3 would lead to higher cost. At the same time, the transport and handling of H_2O_2 is still challenging nowadays (Fu, You et al. 2010, Nidheesh, Gandhimathi et al. 2013). Moreover, UV-lamps that currently used need high energy input, this would increase the overall cost as well. Another issue that cannot be neglected is that both H_2O_2 and O_3 are actually toxic and they can generate toxic byproducts. Therefore, photolysis is usually suggested to be not effective in the long term (Adeleye, Conway et al. 2016).

2.2.3.2 Photo-Fenton

Conventional Fenton process is a metal-catalyzed oxidation reaction, in which oxidizing agents like H_2O_2 and a catalyst (metal salts or oxides, like iron) will be employed, and these Fenton reagents would produce radicals such as $\cdot\text{OH}$ via a free radical chain reactions to degrade organic compounds in water (Park and Yoon 2007). Fenton process has been widely applied because it presents good efficiency in removing of recalcitrant compounds (Poyatos, Muño et al. 2010). For conventional Fenton process, one major disadvantage is that large amount of

metal-containing sludge would be produced. Such sludge not only leads to the loss of catalysts but also has negative effect on the environment. Photo-Fenton is a combination process of Fenton reagents with light irradiation. Studies confirm that the use of UV light can decrease the generation of sludge meanwhile remarkably enhance the degradation efficiency due to the promoted generation of radicals $\cdot\text{OH}$ (Poyatos, Muño et al. 2010, Umar, Aziz et al. 2010, Nidheesh, Gandhimathi et al. 2013).

Several studies reported the degradation of SAs employing Photo-Fenton process. Batista *et al.* investigated the degradation of SDZ and STZ (25.0 mg L^{-1}) under Photo-Fenton process, and they found that the degradation efficiency was largely enhanced with the existence of Fe(III)-oxalate than free iron and complete degradation could be achieved within 8 min at the pH 2.5 and a H_2O_2 concentration of 5.0 mM (Batista and Nogueira 2012). Similarly, in the study of Pérez-Moya *et al.*, effective degradation of SMT was observed by adjusting the reaction conditions such as pH and catalyst dosage of the Photo-Fenton process (Pérez-Moya, Graells et al. 2010).

Though Photo-Fenton is regarded to be quite efficient, the performance of Photo-Fenton process strongly depends on many operational parameters like pH, temperature, dose of Fenton reagents, composition of reaction medium, presence of chelating agents (Pouran, Aziz et al. 2015). More importantly, it suffers from several drawbacks like requirement of power and labor input, and more importantly, cost of recovery of iron species (Herney-Ramirez, Vicente et al. 2010). Therefore, how to reduce the cost is one of the major concerns about its real application, and hence further study is needed.

2.2.3.3 Heterogeneous Photocatalysis

Heterogeneous photocatalysis which usually employs semiconductors as catalysts is believed to be one of the most promising AOPs in the past several decades.

Photocatalysis based on semiconductors can use either UV light or sunlight. Semiconductor photocatalysis has become a topic of significant interest due to its promising potential to solve the emerging energy shortage and environmental issues. Specifically, when illuminated by appropriate light source, semiconductor photocatalysts are capable to split water into hydrogen (H_2) and oxygen (O_2), to decompose organic pollutants, as well as to inactive microorganisms (Hoffmann, Martin et al. 1995).

However, as mentioned above, one of the major challenges that photochemical AOP processes faces is that they can only be driven by UV light rather than solar light. On the contrary, when semiconductor photocatalysts are well designed they are capable to be powered by visible light making it the most attractive AOP technology in the past decades. Even though, only very few single semiconductors are found to present the capability to efficiently utilize solar energy till now, while a large variety of them can only be excited under the ultraviolet (UV) light irradiation.

Taking TiO_2 as an example, though it is recognized to be one of the most studied semiconductor photocatalyst, it can mainly be excited by UV light because of its wide band-gap of 3.2 eV (Fujihira, Satoh et al. 1981). Hence, if visible light can be successfully used by semiconductor photocatalysts as driving force, it is highly possible that the photocatalytic efficiency will be largely improved. Inspired by this idea, more and more researchers are now paying attention to construct VLD photocatalysts, which can be photo-excited under not only UV light but also visible light. Up to now, various VLD photocatalysts have been reported, ranging from simple oxides (Bi_2O_3 (Zhang, Wang et al. 2006) and WO_3 (Chen and Ye 2008)), sulfides (CdS (Bao, Shen et al. 2007)), nitrides (C_3N_4) (Wang, Maeda et al. 2009), oxyhalides ($BiOCl$) (Xiao, Liu et al. 2012, Zhang, Liu et al. 2012, Yu, Cao et al.

2014), to complex oxides (Bi_2WO_6 (Zhang, Wang et al. 2011) and $\text{Zn:In(OH)}_y\text{Sz}$ (Zhang, Wong et al. 2009)).

Compared to photolysis under UV, enhanced removal of SAs were observed by photocatalysis (e.g. TiO_2 and ZnO as photocatalysts), and round 90% SMX, SMT (sulfamethazine) were removed under UV irradiation (Kaniou, Pitarakis et al. 2005, Nasuhoglu, Yargeau et al. 2011, Xekoukoulotakis, Drosou et al. 2011).

Overall, as a promising AOP technology, photocatalysis based on semiconductors has rapid oxidative ability to effectively eliminate recalcitrant organic compounds from the polluted water bodies. Up to date, development of appropriate photocatalytic systems is drawing increased attention among researchers. Thus, in the following sections, the mechanism of and possible applications of semiconductor photocatalysis will be further elaborated.

2.3 Semiconductor photocatalysts

2.3.1 Basic reaction mechanism of semiconductor photocatalysis

In a typical photocatalytic process, mainly three important steps occur and contribute to the photocatalytic ability of the catalyst: photon absorption, electron-hole-pair generation and separation, and catalytic surface reaction (Cao, Low et al. 2015). When the photos with energy equal or larger than the band-gap of a semiconductor are absorbed (**Eq (2.2)**), photoinduced electron-hole pairs will be generated, and these electron-hole pairs will subsequently initiate or accelerate the specific reduction and oxidation (redox) reactions. Specifically, when being irradiated, an electron (e_{cb}^-) will be firstly promoted from the valence band (VB) into the conduction band (CB), and correspondingly a hole (h_{vb}^+) will be left behind (Hoffmann, Martin et al. 1995). After that, the excited electrons and holes will move to the surface of the semiconductor. Since the electrons produced possess a strong reduction capacity and the holes exhibit a strong oxidative capacity, they can

act as reductant and oxidant to respectively react with suitable electron donors (D) and acceptors (A) adsorbed on the surface of the semiconductor or existed within the electrical double layer surrounding the charged particles. At the same time, the electrons and holes can also recombine when migrating to the surface. In this context, the input energy will dissipate in the form of heat or emitted light instead of causing redox reactions. Moreover, such recombination is usually related to the existence of scavengers or defects of the crystalline where the electrons and holes can be trapped. It is believed that recombination of electrons and holes can result in decrease of the photocatalytic efficiency. Therefore, a better crystallinity with fewer defects of a semiconductor can inhibit the occurrence of the trapping states as well as recombination sites, which will then lead to improved photocatalytic efficiency (Wang, Zhang et al. 2014).

2.3.2 Photodegradation of organic pollutants

During photocatalytic process, the electrons generated will be passed to electron acceptor. If organic contaminants in polluted water are the target, the electron acceptor is normally assumed to be O_2 where $O_2^{\cdot-}$ will be produced firstly and then turned to $\cdot OH$ eventually. Simultaneously, the photogenerated holes will oxidize the organic molecules to relevant products. If complete degradation of the targeted organic molecules is achieved, final products will be CO_2 , H_2O and ionized halides, and then this oxidation process is called mineralization.

Specifically, once the electrons and holes are generated under illumination, the holes will migrate to the surface of the photocatalyst. Next, they will be transferred directly to the pollutants absorbed on the surface leading to the direct oxidation of the pollutants as illustrated in **Eq (2.3)**. This usually happens when the pollutants can be strongly absorbed on the surface of the photocatalyst, where a good

electronic contact is established. Another mechanism is that the holes will firstly move to the water molecules absorbed on the surface of the photocatalyst generating $\cdot\text{OH}$ radicals. These $\cdot\text{OH}$ will then react as oxidants to oxidize the contaminant molecules (indirect oxidation) as displayed in **Eq (2.4)**. This occurs in the systems in which pollutants are weakly absorbed on the surface of photocatalysts. Hence, the oxidation rate relies on how long or how fast the $\cdot\text{OH}_s$ can move to reach the pollutant molecules. Here, the suffix “s” indicates the formation of surface groups which can be regarded as surface trapped holes. In summary, the $\cdot\text{OH}$ radicals generated can work via two pathways, on one hand, they can absorb on the surface to react with pollutants (**Eq (2.5-1)**), and on the other hand they can desorb into water to work as free radicals ($\cdot\text{OH}_{\text{free}}$) as shown in **Eq (2.5-2)**.

In addition, the reductive pathway can produce $\cdot\text{OH}$ following **Eq (2.6)** (Bahnmann, Bockelmann et al. 1991). Here, oxidant species like O_2 are converted to H_2O_2 by photogenerated electrons. Then, H_2O_2 produced will be further reduced to $\cdot\text{OH}$.

The above equations may take place separately in different systems or may happen concurrently in some systems (Robertson, Robertson et al. 2012). No matter in which way the reactions may occur, they will lead to a complex set of subsequent reactions contributing to the semiconductor photocatalytic activity. Besides the degradation of organic pollutants, semiconductor photocatalysts can also convert inorganic pollutants into less toxic or less dangerous compounds through oxidation

and reduction (Litter 1999, Litter, Morgada et al. 2010). Analogously, such photocatalytic ability can also kill or remove the biological entities in the aquatic environments, such as macromolecules, bacteria, and viruses (Robertson, Robertson et al. 2012).

2.3.3 Photocatalytic inactivation of microorganisms

It is very important to ensure the microbiological safety of drinking water, and this requires good protection of water resource, effective water treatment process and good maintenance of distribution system. Many studies have demonstrated that photocatalysis shows destructive effect on a wide range of microorganisms, including bacteria, viruses, fungi and protozoa (Robertson, Robertson et al. 2012). Therefore, this disinfection effect of photocatalysis can work as an additional barrier in water treatment process to ensure the microbiological safety of drinking water.

Fig. 2.3 Schematic illustration of using photo-excited TiO_2 to inactivate *E. coli* (Sunada, Watanabe et al. 2003, Byrne, Dunlop et al. 2015).

The mechanism of photocatalytic disinfection is similar to the elimination of organic pollutants where reactive oxygen species (ROS) generated by surface redox reactions play the main role. In particular, $\cdot OH$ radicals are believed to be the primary species responsible for the inactivation of microorganisms, while $O_2^{\cdot-}$,

·OOH as well as H_2O_2 can also contribute to the disinfection process (Cho, Chung et al. 2004). ROS produced during the photocatalytic process can attack a wide range of pathogens since they are not specific to only one site or an individual pathway, which implies that the possibility is very low for microorganisms to develop resistance towards photocatalysis (Goulhen-Chollet, Josset et al. 2009). When interacting with microorganism cells, ROS attack will take place firstly on the out layers of the cell. After the out layers are damaged, ROS will enter the cell and detriment the sensitive metabolic processes as well as genetic materials within the cells. Sunada, Watanabe *et al.* described the inactivation process of *E. coli* using photo-excited TiO_2 thin film as displayed in **Fig. 2.3**, illustrating that after the cell membrane is broken, ROS will enter the cell.

Though photocatalysis can affect a wide range of microorganisms, different microorganisms show different response times to the photocatalytic inactivation due to the cell wall complexity. According to the report of Malato, Fernández-Ibáñez *et al.*, protozoa exist the strongest resistance towards photocatalytic process, followed by bacterial spores, mycobacteria, viruses, fungi and bacteria. In the case of bacteria, gram positive and gram negative bacteria have very different cell wall structures, and such differences are suggested to be able to affect their response times against photocatalytic process. Usually, gram positive bacteria have a thick cell wall (20 to 80 nm) with many layers (up to 25) of peptidoglycan and teichoic acids as shown in **Fig 2.4 (a)**. By contrast, gram negative bacteria only have two distinct membranes of which a thin peptidoglycan layer (7 to 11 nm) is encapsulated by a lipid membrane consisting of lipopolysaccharides and lipoproteins as presented in **Fig. 2.4 (b)**. It is clear that the wall structure of gram positive bacteria is more complicated but much thinner compared with that of gram positive bacteria. Lydakís-Simantiris, Riga *et al.* reported that compared to gram negative bacteria like coliforms, gram positive bacteria such as enterococci show longer response

times to photocatalytic process and therefore they need longer time to obtain effective inactivation.

Besides cell walls, other factors can also influence the response of microorganisms to photocatalytic disinfection. For example, some surface structures and enzymes can affect the response time. More notably, some disease causing bacterial species can produce structures called endospores with strong resistance, making them to be able to undergo unfavorable conditions. Generally, because of the complexity of microorganisms, it is hard to fully understand the mechanism of photocatalytic inactivation or to build an exact mode to illustrate the mechanism. Similar to the steps described in **Fig. 2.2**, the inactivation of microorganisms is achieved by the prolonged ROS attack on the cell wall at first, resulting in the damage of the out layer of the cell, and after that the cytoplasmic membrane will be compromised allowing the following direct attack on the intracellular components (Byrne, Dunlop et al. 2015).

Fig. 2.4 Outer layer of (a) gram positive bacteria and (b) gram negative bacteria (Dalrymple, Stefanakos et al. 2010).

2.3.4 Limitations of semiconductor photocatalysts

Though semiconductor photocatalysis is recognized as a promising method to solve energy and environmental issues, their practical application is still largely limited by some drawbacks. For a typical photocatalytic process, mainly two factors can limit its efficiency. First, semiconductor photocatalysts can only absorb the

photons with energy above its band-gap. Therefore, strategies are needed to maximize the total light absorption efficiency. Second, the charge separation process will compete with the charge recombination process which will decrease the overall photocatalytic efficiency. Hence, better electron-hole separation rate and quick transportation to the active redox sites are required. As mentioned earlier, improving the crystallinity with less defects can reduce the electron-hole recombination rate and thereafter enhance the photocatalytic efficiency. Additionally, photocatalysts with smaller size (or in porous and hollow structures) can reduce the distance between the chargers and reaction sites and subsequently lead to lower recombination rate (Zhou, Qu et al. 2012). In brief, limited visible light absorption and short lifetime of the photogenerated electron-hole pairs are two factors that detriment the performance of semiconductor photocatalysts.

Tremendous efforts have been devoted to search effective methods to improve the photocatalytic efficiency of semiconductors, including textural design, and construction of various heterogeneous photocatalysts. Especially, the construction of semiconductor heterojunctions is suggested to a promising strategy to effectively enhance the photocatalytic ability by improving the photoinduced charges separation efficiency and extend the light absorption ability. Therefore, compared to simple individual component, such composites or heterojunctions consisting of two or more building blocks usually show significantly enhanced photocatalytic ability.

2.4 Semiconductor heterojunction photocatalysts

Up to date, a large number of studies have been conducted to synthesize various heterojunctions with improved photocatalytic efficiency (Xiang, Yu et al. 2012). An efficient photocatalyst is supposed to have the ability to utilize wider light range of the solar spectrum, to enhance the separation of electron-hole pairs, to provide enough active sites, and finally to promote the overall photocatalytic efficiency. To

realize these requirement, one promising strategy is to adopt appropriate co-catalysts (Coronado, Fresno et al. 2013, Qu and Duan 2013). Hence, the selection of proper co-catalysts is of great importance for efficient photocatalysis process (Tong, Ouyang et al. 2012). It is proved that the loading of appropriate co-catalysts on semiconductors is an effectual measure to improve the electron hole separation efficiency and surface reaction and thus promote the photocatalytic activity (Yang, Yan et al. 2013, Bai, Yin et al. 2016, Rahman, Ran et al. 2016). As a consequence, extensive attention is now being paid on the development and selection of suitable co-catalysts to construct effective and stable heterogeneous photocatalysts. Currently, the mechanisms of how co-catalysts accelerate the photocatalytic process are still ambiguous and unsatisfactory, and further study is therefore necessary (Tong, Ouyang et al. 2012).

There have been numerous and various semiconductor heterojunction photocatalysts with improved photocatalytic performance in comparison to relevant single semiconductors, they can be classified to four types according the review of Wang *et. al.*: (1) the semiconductor-semiconductor (S-S) heterojunctions; (2) the semiconductor-metal (S-M) heterojunctions; (3) the semiconductor-carbon group (S-C) heterojunctions (carbon group: activated carbon, carbon nanotubes (CNTs) and graphene); (4) the multicomponent heterojunctions (Wang, Zhang et al. 2014). In particular, the design principle of each type will be elaborated in the following sections.

2.4.1 S-S heterojunctions

An S-S heterojunction system is composed by two different semiconductors. If it is a combination of one p-type and one n-type semiconductor, then it is called a p-n heterojunction. On the other hand, other combination style of two semiconductors is named *non-p-n* heterojunction. It is suggested that p-n heterojunction is a kind of

effective architecture. When p-type and n-type semiconductors are coupled together, the heterojunctions would be able to more effectively separate the charges and quickly transfer the charges to the surface resulting in a longer life time of the charge carriers when compared to pure single semiconductor. The transfer and separation of electron and hole would lead to a formation of a built-in electrical potential driven by which the electron and hole would move in the opposite directions. Particularly, electrons would be transferred to the CB of the n-type semiconductor while holes to the VB of the p-type one. Moreover, a p-n heterojunction can separate the locally incompatible redox reactions in nanospace. These advantages can significantly improve the photocatalytic activity of p-n heterojunctions.

For *non*-p-n heterojunction, the two semiconductors are supposed to generally have matched band gap structures and are bonded tightly. In this system, one semiconductor has a lower level of CB and VB than those of the other. When being irradiated, electrons would move from the lower CB to the higher one, while holes transfer from the lower VB to the higher one as well. This would lead to the separation and transportation of charges which would be further enhanced by internal field. Moreover, large amounts of electrons on the surface of one semiconductor and large amounts of holes on the surface of the other can be involved in the redox reactions, resulting promotion of photocatalytic activity.

2.4.2 S-M heterojunctions

In a S-M heterojunction system, electrons migrate from the material with higher Fermi level to the other one with lower Fermi level to align the Fermi energy levels at the interface of two materials. For example, when the S-M heterojunction is composed of an n-type semiconductor and a metal, the electrons migration direction will start from the n-type semiconductor to the metal forming a space-charge

separation region which is named as the Schottky barrier. As a result, excessive negative charges will accumulate on the metal while excessive holes will accumulate on the semiconductor at the same time. Schottky barrier can decrease the electron-hole recombination rate and thereafter improve the photocatalytic efficiency by acting as an effective electron trap.

2.4.2.1 Surface Plasmon Resonance in S-M heterojunctions

(1) Surface plasmon Resonance

The collective oscillations of free charges in a conducting material (such as metals) are called plasmons. If the oscillations of conduction electrons are coupled to an electromagnetic field of incident light, then such oscillation modes are called surface plasmons. Surface plasmons can interact strongly with light. When the frequency of incident photon is resonant with the collective oscillation, an absorption band will occur, and such resonances are acknowledged as surface plasmon resonance (SPR) effect (Link and El-Sayed 1999, Ghosh and Pal 2007). Take metal as an example, when the metal nanoparticles are irradiated by light at their plasmon frequency, intense electric fields will be generated on the surface of the nanoparticles. The resonance frequency of SPR could be adjusted by many factors including size, shape, interparticle interactions, materials and proximity to other nanoparticles (Mock, Barbic et al. 2002, Atay, Song et al. 2004, Kolwas, Derkachova et al. 2009, Kim, Husakou et al. 2010).

(2) SPR in S-M heterojunctions

Noble metals are often used to modify semiconductors forming so called plasmonic photocatalysts, where SPR effect provides the possibility to enhance the photocatalytic efficiency of these S-M heterojunctions. Three mechanisms have been proposed to explain the enhancement of photocatalytic activity caused by SPR. The first one is the charge transfer mechanism where charge carriers generated from photo-excited metal are induced to transfer to the semiconductor by SPR. In the

near-field electromagnetic mechanism, SPR could lead to intense electromagnetic fields near the plasmonic nanostructures. When interact with the electromagnetic fields, the electron-hole pair formation efficiency will be highly promoted (Awazu, Fujimaki et al. 2008, Christopher, Ingram et al. 2010, Hou, Liu et al. 2011, Ingram, Christopher et al. 2011, Kumar, Krishnamoorthy et al. 2011, Liu, Hou et al. 2011). The other mechanism suggests that such heterojunctions are able to have longer optical path lengths for photons due to efficient scattering of resonant photons. Consequently, excited charge carriers will be produced at a higher efficiency (Ingram, Christopher et al. 2011).

Many studies have reported the enhanced photocatalytic performance of semiconductors when noble metals are used as co-catalysts to form S-M heterojunctions. It is believed that such enhancement may actually be caused by both plasmonic enhancement and/or simply self-catalysis.

2.4.2.2 Silver nanoparticles (Ag NPs) and their antimicrobial mechanism

Silver is an important member of noble metals, and it is used widely in many areas like catalysis, biological labeling, photonics, photography, optoelectronics as well as surface-enhanced Raman scattering (SERS) detection (Kearns, Foster et al. 2006, Smith, Duan et al. 2006). More importantly, Ag NPs have been highly commercially applied in many areas ranging from disinfection medical devices and home appliances to water treatment (Vigneshwaran, Kathe et al. 2007, Tolaymat, El Badawy et al. 2010). The SPR absorption of silver is in the UV range, however, research shows that the frequency of resonance can shift to the visible light range when the nanoparticles are very small in size (Hou and Cronin 2013). When being applied as a co-catalyst, the electrons generated under light irradiation will transfer to Ag NPs since they have a better electron attracting ability (Katsumata, Oda et al. 2013). This would lower the recombination rate of the electron-hole pairs, and consequently improve the photocatalytic activity.

Moreover, another important fact of silver and its compounds is that they have been proved to be excellent antimicrobial agents against a broad spectrum (Berger, Spadaro et al. 1976, Zhao and Stevens Jr 1998). However, the antimicrobial mechanisms of silver and Ag NPs have not been fully understood yet. Previous studies found that both metallic silver and silver ions (Ag^+) have disinfection activity (Holt and Bard 2005, Lok, Ho et al. 2006), and three mechanisms have been raised to elaborate the disinfection activity of Ag NPs.

a. Direct contact with cell membranes

Ag NPs can contact cell membranes directly. In one hypothesis, positively charged Ag NPs can interact with negatively charged bacterial cells through electrostatic attraction (Raffi, Hussain et al. 2008). While another theory suggests that the sulfur containing proteins may be the preferential sites for Ag NPs to attach with cell membranes. This is similar to the mechanism of the interaction with thiol groups of respiratory chain proteins and transport proteins to inactivate them (Morones, Elechiguerra et al. 2005). Moreover, studies have shown that when Ag NPs are attached to the cell membranes of the bacteria, they can increase permeability of the cell and subsequently affect respiration.

b. Release of Ag^+

Ag NPs can dissolve and release Ag^+ in the aqueous phase. Ag^+ is useful and effective in bactericidal applications. Ag^+ has high affinity with thiol groups of some protein with cysteine residues. Specifically, Ag^+ can react with enzymes in the respiratory chain such as NADH dehydrogenase, and this will disturb the ATP synthesis of the cell. Similarly, Ag^+ can also attack transport proteins resulting in proton leakage and finally collapse of the proton motive force (Dibrov, Dzioba et al. 2002, Holt and Bard 2005, Lok, Ho et al. 2006). Ag^+ is reported to be able to hinder the uptake and exchange of phosphate in *E. coli*, and this can subsequently lead to the efflux of intracellular phosphate, mannitol, succinate, glutamine, and proline

(Schreurs and Rosenberg 1982). In addition, Ag^+ is recognized to be a strong nucleic acid binder which can thereafter form complexes with DNA and RNA causing the condensation of DNA and the loss of replication ability (Arakawa, Neault et al. 2001).

c. Produce reactive oxygen species

Ag NPs are able to produce free radicals, especially ROS in water. The disinfection mechanism of ROS has been discussed in the section 2.3.3.

Fig. 2.5 Summarized diagram of nanoscale silver interaction with bacterial cells (Marambio-Jones and Hoek 2010).

Overall, the antimicrobial mechanism of Ag NPs is not clearly known, but many studies have observed the excellent antimicrobial effect of Ag NPs suggesting that they are able to detriment cell viability, inhibit population growth, and finally lead to the death of the cells. For example, **Fig. 2.5** summarizes the antibacterial mechanisms of nanoscale silver where these three mechanisms may work separately or simultaneously to achieve effective antibacterial performance (Marambio-Jones and Hoek 2010). Nevertheless, the application of Ag NPs has some limitations. One issue to be solved is that compared to larger-size particles, nanoparticles show a strong potential to agglomerate which influences their interaction with cells

(Lankoff, Sandberg et al. 2012). Therefore, suitable dispersion approaches should be adopted to avoid or release the formation of agglomeration.

2.4.3 S-C heterojunctions

Inspired by the recent important awards such as the 1996 Nobel Prize in chemistry (fullerenes), the 2008 Kavli Prize in Nanoscience (carbon nanotubes), and the 2010 Nobel Prize in Physics (graphene), study towards carbon-based materials has become a very important research topic (Titirici, White et al. 2015). As a consequence, in the area of photocatalysts, there have been a lot of reports using carbon materials to fabricate so called S-C heterojunctions to achieve improved photocatalytic performance.

Various carbon types used such as activated carbon, carbon nanotubes (CNTs) and graphene have been applied to construct S-C heterojunctions with good photocatalytic activity. In particular, when activated carbon with very high specific surface area is used to modify semiconductors, the photocatalytic activity will be largely enhanced because of the significant increase in surface area which can increase the amount of pollutants adsorbed on the surface. CNTs can also supply a notable increase of surface area like activated carbon when combined with semiconductors. More importantly, CNTs exist properties that activated carbon lacks. Specially, CNTs possess metallic conductivity, and can form Schottky barrier junctions just like the S-M system. At the same time, CNTs can work as electron acceptors to hinder the recombination in the system due to their excellent electron-storage capacity. In addition, graphene, a 2D material, has attracted remarkable attention due to its outstanding properties, and it is regarded to be a very promising component in the heterogeneous photocatalysis systems.

2.4.3.1 Graphene-based semiconductor photocatalysts

Graphene is a single layer of sp^2 bonded carbon atoms arranged in a two dimensional honeycomb fashion (Kamat 2010, Xiang, Yu et al. 2012, Titirici, White et al. 2015). Graphene possesses excellent properties like excellent thermal conductivity ($\sim 5,000 \text{ W m}^{-1}\text{K}^{-1}$), superior electron mobility ($200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) at ambient temperature and extremely high theoretical specific surface area ($\sim 2600 \text{ m}^2\text{g}^{-1}$) (Schedin, Geim et al. 2007, Dato, Radmilovic et al. 2008, Xiang, Yu et al. 2012, Fu, Xia et al. 2015, Hajishafiee, Sangpour et al. 2015). Thereby, these outstanding properties make graphene and reduced graphene oxide (RGO) to be excellent candidates serving as co-catalysts in efficient heterogeneous photocatalysts (Kamat 2010, Xiang, Yu et al. 2012, Zhang, Yang et al. 2013).

In the graphene-based semiconductor composites, graphene or RGO can firstly work as superior supporting matrixes to bond functional components and to disperse catalyst nanoparticles. At the same time, with the larger surface/interface, they can both increase the adsorption capacity for reactants and also supply more active sites for the photocatalytic reactions. Moreover, they can also work as excellent electron mediators to adjust electron transfer leading to improved electron-hole separation efficiency (Xiang, Yu et al. 2012, Huang, Yue et al. 2013, Yang and Xu 2013). Together with the extended photoresponding range as well as enhanced visible light absorption intensity, these graphene-based semiconductors will therefore show improved photocatalytic activity.

In previous studies, researchers have fabricated various graphene/RGO-based semiconductors and applied them to treat various antibiotics. Compared to original semiconductors, such graphene/RGO composites presented remarkably improved photocatalytic efficiency. Yan, Sun *et al.* found that RGO-BiVO₄ heterogeneous composites degraded 68.2% ciprofloxacin within 1 h under visible light, which was two times higher than bare BiVO₄. Dong, Sun *et al.* evaluated the photocatalytic

performance of ZnSnO₃/RGO with metronidazole under both visible light and UV light, and the efficiency was significantly enhanced where nearly 100% removal was achieved within 1 h under UV light illumination. The modification of TiO₂ with different amounts of RGO could increase the degradation efficiency of norfloxacin to more than 90% within 3 h ($\lambda > 320$ nm) (Li, Xiong et al. 2013). In the case of SA groups, BiOCl/RGO composites could reach to a SAM removal efficiency of 88.35% in 5 h under visible light irradiation (Dong, Pi et al. 2016). Our recent studies presented the similar result, in which the removal efficiency of SMX was raised to more than 90% within 3 h by RGO-WO₃ composites (Zhu, Sun et al. 2017).

2.4.4 Multicomponent heterojunctions

A typical multicomponent heterojunction contains at least three components where two or more components can be activated by visible light and the other is an electron transfer system (metal) (Liu, Li et al. 2015). Since the semiconductors may have different photo-absorption ranges, such combination could subsequently broaden the absorption range of the whole system. More notably, metal in the system can promote the electron-hole separation process and enhance the interfacial charge transfer as well. As a consequence, broader absorption range and better electron-hole separation can work together leading to the improvement of photocatalytic efficiency (Qu and Duan 2013, Wang, Zhang et al. 2014).

In brief, co-catalysts are vital for promoting the overall efficiency of photocatalysis process. However, the understanding towards the mechanisms of co-catalysts affecting the photocatalytic process are still limited. The selection of suitable co-catalysts to modify certain semiconductors requires systematic study to figure out the properties of co-catalysts, their relationship with the semiconductors and the desired effects brought along the co-catalysts. However, since there are

numerous materials which could be adopted as co-catalysts, there may be no universal role to decide which one is the best for a certain semiconductor. Therefore, for a certain semiconductor, various co-catalysts could be employed in the first stage to select the most appropriate one. Moreover, future study is necessary to achieve better understanding towards the possible mechanism of improved photocatalytic performance caused by co-catalysts

2.5 Examples of potential semiconductors

2.5.1 p-type BiOCl

BiOCl as a p-type semiconductor belongs to main group multicomponent V-VI-VII semiconductors. BiOCl has a tetragonal layered structure comprising of [Cl-Bi-O-Bi-Cl] sheets which are combined together by the nonbonding interaction through the Cl atoms along the c-axis (Zhang, Liu et al. 2006). Its unique electrical, catalytic and optical properties make it a very promising catalyst, ferroelectric material and pigment (Shen, Zhou et al. 2015). Hence, it has attracted wide interests. Size, shape and morphology are very important for the properties of nanomaterials, therefore BiOCl with various structures including nanobelts (Deng, Wang et al. 2005), nanofibers (Wang, Shao et al. 2008), nanoplates (Deng, Chen et al. 2008, Ma, Liu et al. 2010) , nanosheets (Geng, Hou et al. 2005, Ye, Zan et al. 2011), nanoflakes (Ma, Liu et al. 2010, Li, Liu et al. 2011), and 3D hierarchical nanostructures (Zhang, Ai et al. 2008, Lei, Wang et al. 2009, Song, Mao et al. 2010, Zhu, Liao et al. 2010) have been developed through different methods. Among so many BiOCl structures, 2D nanostructures like nanoplates and nanosheets can be further used as building units in constructing of advanced materials and devices (Xiong, Cheng et al. 2011). To date, even though there is a huge desire, it is still hard to produce BiOCl with well-defined 2D morphology and well crystallization.

When being applied in the photocatalytic process, BiOCl has a wide band gap of 3.19-3.44 eV (Gondal, Chang et al. 2010) which limits its photo-absorption mainly in the UV region of the solar spectrum. Another limitation is caused by the high electron-hole recombination rate at or near the surface which leads to the low overall quantum efficiency during the photocatalytic reaction (Liqiang, Xiaojun et al. 2003). Hence, it is necessary to modify BiOCl to improve its activity. An effective way is to combine with metals like Ag and Pt to form S-M heterojunctions, and some studies have investigated the direct combination with co-catalyst nanoparticles like Ag, Au, and Pt (Yu, Cao et al. 2013, Kim, Pradhan et al. 2014, Lin, Ding et al. 2014).

2.5.2 n-type WO₃

WO₃ is an n-type semiconductor, and wide investigations suggest that WO₃ presents great potential in various applications, such as lithium-ion batteries (Li and Fu 2010), gas sensors (Ma, Zhang et al. 2011, Zhang, Boudiba et al. 2013), photocatalysts (Chen and Ye 2008, Zhang, Tang et al. 2011, Luo, Cao et al. 2013), photoelectrodes (Bignozzi, Caramori et al. 2013), photochromic and electrochromic devices (Zhu, Wei et al. 2010, Dalavi, Devan et al. 2013, Zhang, Duan et al. 2013), field-emission devices (Liu, Zhao et al. 2005) and solar energy devices (Zheng, Tachibana et al. 2010). Especially, monoclinic WO₃ (m-WO₃) is the most stable phase of WO₃ structures (Fleig and Maier 1997, Li, Zhang et al. 2006, Bathe and Patil 2008, Chen, Gao et al. 2008, Chen, Wang et al. 2008, Ham, Phuruangrat et al. 2010) with a low band gap energy (2.4 to 2.8 eV). It is regarded as a promising photocatalyst in treating organic pollutants under solar irradiation (Bamwenda and Arakawa 2001, Zhao and Miyauchi 2008, Cabrera, Latimer et al. 2012).

Since particle morphology, including shape and size will significantly influence the photocatalytic activity of a particular photocatalyst (Li and Haneda 2003), many

efforts have been devoted to synthesize WO_3 with different nanostructures like nanowires (Polleux, Gurlo et al. 2006, Phuruangrat, Ham et al. 2010, Su, Feng et al. 2011), nanorods (Lee, Seo et al. 2003, Zhu, Wei et al. 2010, Zhu, Wang et al. 2011, Kalanur, Hwang et al. 2013), nanotubes (Hara, Zhao et al. 2011, Schieder, Lunkenbein et al. 2013), nanoplates (Oaki and Imai 2006, Chen, Gao et al. 2008, Kalantar-zadeh, Vijayaraghavan et al. 2010, Ma, Zhang et al. 2011, Chen, Zhou et al. 2012, Zhang, Duan et al. 2012, Zou, Li et al. 2012), porous structure (Xie, Zhu et al. 2011), nanoparticles (Le Houx, Pourroy et al. 2009, Heidari, Marzbanrad et al. 2010), and thin film (Wang, Lindgren et al. 2000, Ahmed, Hassan et al. 2013). Generally, WO_3 with different morphologies has been synthesized by diverse methods including inorganic-organic hybrid method (Chen, Gao et al. 2008, Chen, Wang et al. 2008), hydrothermal reaction (Kominami, Yabutani et al. 2001, Li, Zhang et al. 2006), thermal oxidization (Siciliano, Tepore et al. 2008), pulsed spray pyrolysis deposition technique (Bathe and Patil 2008) and wet chemical precipitation (Wolcott, Kuykendall et al. 2006). Among those methods, hydrothermal method is capable to well control the size and shape of the products at relatively low temperature and low cost making it a promising approach in synthesizing WO_3 (Rao, Deepak et al. 2003, Byrappa and Adschiri 2007).

Pure WO_3 as photocatalyst is not good enough because of its low CB level which restricts its capability to react with electron acceptors like O_2 (Miyauchi 2008), while concurrently increases the electron-hole recombination rate (Katsumata, Oda et al. 2013). Thus, to improve its photocatalytic efficiency, the recombination rate should be reduced. Generally, two strategies are widely used, namely, nanostructuring the morphology and modifying the surface of WO_3 with semiconducting or metal nanoparticles (Zhang, Wang et al. , Liu and Xue 2008, Paramasivam, Nah et al. 2010, Sun, Wang et al. 2010, Kong, Huang et al. 2012). With smaller particle size, it would be easier for the electrons and holes to reach the

surface of WO_3 , and thus decreases the volume of recombination (White, Jang et al. 2010). Furthermore, formation of WO_3 -based heterojunctions will lead to a better charge separation between electrons and holes and thereafter decreases the electron-hole recombination rate while increases the photocatalytic efficiency (Armelao, Barreca et al. 2007).

2.5.3 g- C_3N_4

Carbon nitrides are a class of polymeric materials composed by mainly two elements which are carbon and nitrogen (Wang, Blechert et al. 2012, Zhu, Xiao et al. 2014). In particular, graphitic carbon nitride (g- C_3N_4) is the most stable allotrope of carbon nitrides at ambient atmosphere. As a kind of π -conjugated semiconductor, g- C_3N_4 has a narrow band gap of around 2.7 eV (Xiang, Yu et al. 2011, Katsumata, Motoyoshi et al. 2013, Chen, Hu et al. 2014). Due to its low density, super hardness, non-toxicity, reliable chemical inertness, unique optical and electronic properties, low cost and large scale productivity, it has drawn wide attention in various applications such as photoelectric nanodevices, photovoltaic solar cell, chemical sensors, and photocatalysis (Zhang, Pan et al. 2013, Jiang, Zhu et al. 2016, Xiong, Cen et al. 2016). Though its rich surface properties as well as the presence of basic surface sites have drawn wide attention to its application as photocatalyst, the limited delocalized conductivity, high recombination rate and low specific surface area restrict the overall photocatalytic efficiency of bare g- C_3N_4 (Li, Zhang et al. 2014, Ong, Tan et al. 2016).

To increase the photocatalytic activity of g- C_3N_4 , a co-catalyst or other semiconductor materials can be loaded on its surface forming heterogeneous composites. Since they have differentiated band positions, such combinations can improve the electron-hole separation efficiency as well as photostability of these g- C_3N_4 composites (Zhu, Xiao et al. 2014).

2.6 Challenges in the application of semiconductor photocatalysis for the water treatment process

As stated earlier, though semiconductor photocatalysis shows great application potential in the water treatment process, there are several gaps needing further exploration, including catalyst development, reactor design and process optimization (Chong, Jin et al. 2010). Specifically, Meng Nan Chong *et al.* summarized five points that desire further study to promote the performance of photocatalysis in the water treatment, including (1) fabrication of photocatalysts with high photo-efficiency and capability to use broader light range; (2) development of cost effective as well as efficient catalyst immobilization methods; (3) optimization of operation parameters; (4) design of effective photocatalytic reactor system; and (5) design of efficient integrated or coupling systems (Chong, Jin et al. 2010).

The need to explore new photocatalysts has been illustrated in section 2.3.4, while the rest technical barriers will be simply illustrated as below. First of all, most current photocatalysts are used in a slurry form. This enables the catalysts to well expose their active sites on the surface, and then results in a high volumetric generation rate of ROS. Nevertheless, in order to recycle or reuse the catalysts in the slurry form, additional post-recovery process is demanded (Klavarioti, Mantzavinos et al. 2009, Byrne, Fernandez-Ibañez et al. 2011). This post-recovery process is crucial, in addition to recycle the catalysts, this process is supposed to prevent the introduction of new contaminants which is the polluted catalysts themselves as well (Yang and Li 2007). However, such post-recovery process implies that more investment will be needed (Byrne, Fernandez-Ibañez et al. 2011).

Instead of the slurry form, another way is to select a suitable way to immobilize the catalysts. Immobilization of catalysts can effectually inhibit the loss of catalysts during the reaction. Nevertheless, catalysts fixation would not only affect the mass

transfer of reactant to the catalyst surface but also decrease the surface area as well as the amount of active sites exposed to the light (McMurray, Byrne et al. 2004). As a result, the overall efficiency will decline compared to that in the slurry form (Chan, Yeong Wu et al. 2011). Moreover, the fixation of catalysts would raise up the cost from an economic point of view. Hence, to overcome these drawbacks, it is urgent to develop approaches which can provide large surface for catalysts fixation and be cost effective (Matilainen and Sillanpaa 2010).

The photocatalytic performance can be affected by many operating parameters, including catalyst dosage, light wavelength and intensity, solution pH, temperature and water matrix, as briefly summarized as followed. When the quantum yield increases, the photocatalytic reaction rate will subsequently increase. Catalyst dosage is a critical factor affecting photocatalytic efficiency. When the catalysts are used in the slurry form, the efficiency firstly raises with the increase of dosage, and then declines when the dosage is over a certain amount which may be caused by the particles agglomerate, decreased light penetration, and poor dispersion. The influence of pH and temperature on photocatalytic performance is widely reported, where studies found that by optimizing reaction pH and temperature, a better overall efficiency can be achieved. The composition of the water is also an important factor altering the overall efficiency. The presence of humic substances, bicarbonates or dissolved gases and other components are widely investigated showing their influence on the photocatalysis efficiency (Fujishima, Rao et al. 2000, Klavarioti, Mantzavinos et al. 2009, Chong, Jin et al. 2010, Matilainen and Sillanpaa 2010, Ahmed, Rasul et al. 2011, Spasiano, Marotta et al. 2015). Therefore, when being applied in practice, it is crucial to study the water properties and to optimize the operating parameters.

To successfully apply the photocatalysis process at an industrial level, the design of suitable photocatalytic reactor and design of efficient integrated or

coupling systems are quite essential. Such design should be capable to effectually harvest light, immobilize or recycle the catalysts, collect reaction products, and at the same time, be economic (Lazar, Varghese et al. 2012, Dong, Feng et al. 2015). So far, most studies are still limited to laboratory or pilot plant scale, therefore, it is necessary to establish effectual and economical reactors and systems in large scale to realize the commercial application of photocatalysis process (Comninellis, Kapalka et al. 2008, Stasinakis 2008, Chong, Jin et al. 2010, Qu, Alvarez et al. 2013).

At the same time, another key technical issue to be solved is to figure out a suitable “position” for photocatalysis process in the water treatment process. Photocatalysis process as well as other AOPs can be applied either alone or coupled with other physicochemical and biological processes (Klavarioti, Mantzavinos et al. 2009). To achieve best treatment performance, process coupling is more preferable. For example, when being combined with biological process, photocatalysis can be employed as a pre-treatment or post-treatment method depending on the properties of the water to be treated (Klavarioti, Mantzavinos et al. 2009, Chong, Jin et al. 2010). When it is adopted as a pre-treatment method which is followed by biological post-treatment, photocatalysis process would be beneficial to convert initially biorecalcitrant contaminants to more biodegradable intermediates (Matilainen and Sillanpaa 2010). When the pollutants to be treated in the water are biodegradable, photocatalysis process can be employed as post-treatment after biological pre-treatment, which is suggested to be less costly (Klavarioti, Mantzavinos et al. 2009). Nevertheless, the integration of photocatalysis process into the water treatment process is depend on the purpose as well as composition of each specific case. Till now, there is no universal strategy to locate the photocatalysis in the water treatment, and it is necessary to carry out further studies as well as to establish a globally database in the future.

In addition to the above points, another concern now drawing increased attention is the possible impacts on the environment due to leaching of catalysts. Though numerous kinds of newly created nanoparticles have been widely applied in various areas, their environmental fate and behavior, their possible adverse effects on the environment as well human health are still lacking (Dreher 2004, French, Jacobson et al. 2009, Keller and Lazareva 2013, López-Serrano, Olivas et al. 2014). Some previous studies illustrated that nanoparticles may possess potential harmful effects on the environmental and health due to their unique properties (Donaldson, Stone et al. 2004, López-Serrano, Olivas et al. 2014). Therefore, it is of great importance to understand the potential risks of the nanoparticles released into the environment (Lazareva and Keller 2014). In particular, studies pointed out that the exposure assessment and the toxicology of the nanoparticles should be studied; at the same time, the environmental and biological behavior and fate of the nanoparticles as well as their recyclability and overall sustainability should be investigated (Dreher 2004, Nowack and Bucheli 2007, Griffitt, Luo et al. 2008). Currently, research focusing on the possible adverse effects of nanoparticles on the environmental and human health is still in the initial stage, and systematic study is thereafter required.

2.7 Summary of literature review

The existence of various antibiotics as well as other organic pollutants are now one of the main environmental issues that human beings are now facing. Take SAs as an example, the abuse and uncontrolled usage of these antibiotics has resulted in their existence in various kinds of water bodies, posing threats to not only the environment but also human health. However, current WWTPs are not efficient enough in dealing with water polluted by antibiotics, which consequently triggers the need for other promising technologies. In particular, AOPs are suggested to be most promising approaches which have the potential to treat water contaminated by

various organic pollutants including antibiotics. Therefore, more and more researchers are now turning their interest to AOPs. There are plenty of various AOP technologies, and they may face different challenges when being applied in the water treatment process. In particular, researchers suggested that among various AOPs, semiconductor photocatalysis is a promising approach to solve the current environmental issues such as water contamination by all kinds of emerging organic pollutants.

When being irradiated by appropriate light source, these photocatalysts can be excited to generate electron-hole pairs which can trigger the generation of various active radicals. Subsequently, these radicals can lead to the occurrence of a series of redox reactions to photodegrade the organic compounds in the water. Nevertheless, it is worth noticing that application of photocatalysis in the water treatment still faces many challenges from different aspects, including material science, engineering and economic points of view. Thereafter, in order to overcome these shortcomings and challenges, considerable effort and further study are strongly needed in the future. In particular, the construction of efficient photocatalysts is one of the most important issues to be addressed when using photocatalysis process. Thus, in this study, main efforts were firstly devoted to construction of efficient heterogeneous photocatalysts. This is because, the photocatalytic efficiency of the majority of single phase semiconductor photocatalysts is strongly limited by the poor light absorption ability and quick electron-hole recombination. Moreover, it is believed that by choosing suitable co-catalysts and forming heterogeneous photocatalysts, the photocatalytic efficiency can be significantly promoted. In particular, the aforementioned fabrication of S-S, S-M and S-C heterogeneous composites are very promising ways to significantly improve photocatalytic ability under visible light as a result of their much broader light absorption range and remarkably reduced charges recombination rate. In the following chapters, three

promising semiconductors, namely WO_3 , BiOCl , $\text{g-C}_3\text{N}_4$, as well their heterojunctions were thoroughly studied to explore their potential application as VLD photocatalysts to eliminate antibiotics from SA group.

CHAPTER 3 CONSTRUCTION OF Ag-BiOCl HETEROGENEOUS PHOTOCATALYST FOR SULFANILAMIDE REMOVAL AND BACTERIAL INACTIVATION

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3.1 Introduction

As illustrated in **Chapter 2**, antibiotics have been widely used all over the world. Due to the high consumption, antibiotics as well as their residues can easily find their way into the environment (Batt, Bruce et al. 2006, Watkinson, Murby et al. 2009, Díaz-Reyes, Delgado-Macuil et al. 2010, Fram and Belitz 2011, Rizzo, Della Sala et al. 2014, Shokri, Isapour et al. 2015). SAs are derivatives of sulfanilic acid which are extensively used as veterinary antibiotics (Dmitrienko, Kochuk et al. 2014, Yang, Huang et al. 2015). As relatively persistent antibiotics, SAs and their residues can accumulate in soil and may leach to the groundwater or surface water thus pose potential threats to human beings and aquatic organisms (Daughton and Ternes 1999, Kümmerer 2009, Munir, Wong et al. 2011, Wegst-Uhrich, Navarro et al. 2014). Hence, effective methods to remove SAs and their residues are desired. In particular, photocatalysis process based on semiconductors within nanoscale is

regarded as an efficient technology in degrading a wide range of organic pollutants. In order to successfully employ photocatalysis process to remove antibiotics like SAs, a main technique task is to find suitable semiconductor photocatalysts. Among numerous semiconductors, BiOCl, a typical p-type semiconductor with tetragonal crystal structure, has unique optical, electrical and catalytic properties making it a promising candidate as catalyst, ferroelectric material and pigment (Shen, Zhou et al. 2015).

However, just like many other semiconductor photocatalysts, pure BiOCl itself is not effective enough. That is because BiOCl has a wide band gap value of 3.19-3.44 eV (Gondal, Chang et al. 2010), which limits its photo-absorption in the UV region. Another limitation is the high recombination rate of photoinduced electron-hole pairs at or near the surface which leads to a low overall quantum efficiency during photocatalytic reaction (Liqiang, Xiaojun et al. 2003).

Therefore, to improve the photocatalytic efficiency, fabrication of multifunctional heterogeneous catalysts can be applied. For instance, decorating semiconductors with metal nanoparticles forming S-M heterojunctions is suggested to be an effective way to decrease charge carrier recombination rate during the photocatalytic process (Zhang, Yang et al. 2015). Such noble metals, as co-catalysts in heterogeneous photocatalysts, may serve as electron sinks/reservoirs which can separate electron-hole pairs more effectively and in turn to supply more active sites for the reduction reaction during photocatalytic process (Marschall 2014).

There have been previous studies attempting to modify BiOCl with co-catalyst nanoparticles like Ag, Au, Pt and other metals. However, in these studies, BiOCl used usually had a 3D structure (Chen, Zhu et al. 2014, Di, Xia et al. 2014, Gao, Wang et al. 2014, Kim, Pradhan et al. 2014, Lin, Ding et al. 2014, Nussbaum,

Shaham-Waldmann et al. 2014, Yu, Cao et al. 2014, Zhang, Zhou et al. 2015), and the synthesis of 2D BiOCl is still challenging. Compared with 3D structures, 2D BiOCl nanostructures have drawn great attention due to their high specific surface areas, more uncoordinated surface atoms, and excellent optical and catalytic properties (Xiong, Cheng et al. 2011, Zhang, Wang et al. 2014). More importantly, BiOCl with 2D nanostructures may have potential application as building blocks used in advanced materials and devices (Deng, Chen et al. 2008). Therefore, it is necessary to explore new environmental friendly and cost effective approaches to manufacture 2D BiOCl and further fabricate their co-catalyst heterogeneous composites with high yield and well-crystallized structure which could be used as efficient photocatalysts.

In this study, we developed a modified one-step solvothermal process to prepare 2D BiOCl, based on the methods of Yang, Ma *et al.* and Cheng, Shi *et al.* for 3D BiOCl synthesis. Ag NPs were adopted as co-catalyst and deposited on the surface of BiOCl by photo-reduction method to enhance its photocatalysis efficiency. SAM, a commonly used antibiotics and growth promoter was chosen as target pollutant to evaluate the photocatalytic ability of BiOCl and BiOCl-Ag composites (Kümmerer 2009). On the other hand, Ag is a well-known effective biocidal agent which has been used for a long history (Feng, Wu et al. 2000, Arakawa, Neault et al. 2001, Hu, Guo et al. 2007, Rai, Yadav et al. 2009, Li, Xie et al. 2010). However, Ag NPs tend to aggregate together in water resulting in the large detriment of its antibacterial efficiency since less surface area would be exposed to the bacterial cells (Lok, Ho et al. 2006, Lok, Ho et al. 2007, Marambio-Jones and Hoek 2010). Therefore, this study further explored the function of 2D BiOCl as supporter to allow proper dispersion of Ag NPs on its surface. The antibacterial performance of BiOCl as well as its Ag composites was investigated using *E. coli* and *B. subtilis* as model bacteria.

3. 2 Experimental part

3.2.1 Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), tungsten hexachloride (WCl_6), silver nitrate (AgNO_3), ethylene glycol ($((\text{CH}_2\text{OH})_2$, EG), urea ($\text{CO}(\text{NH}_2)_2$), ethanol, sulfanilamide (SAM), methanol, benzoquinone (BQ) and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich. All chemicals were analytical-grade reagents, and no further purification was required during the material preparation process.

3.2.2 Photocatalysts preparation

3.2.2.1 Synthesis of BiOCl nanodiscs

BiOCl nanodiscs were synthesized by a modified one-step facile solvothermal method. Briefly, 1 mmol WCl_6 and 1 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were separately dissolved in 15 mL EG before mixing together to form a uniform light green solution. Then, 6 mmol urea was dissolved into the mixed solution. The mixture was transferred into a 45 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 4 h. After cooling down to ambient temperature, the resulting white product was collected, centrifuged and washed by ethanol and distilled water for several times and finally dried by vacuum freeze drier for further modification or use.

3.2.2.2 Synthesis of Ag-doped BiOCl (BiOCl-Ag) composites

Ag doped BiOCl composites were produced by photo-reduction method. Briefly, 260 mg as-prepared BiOCl sample was evenly dispersed in 80 mL distilled water, and then 20 mL AgNO_3 solution (0.05 mmol L^{-1}) was slowly added with continuous stirring. The mixture was irradiated by a 200 W solar simulator (NEWPORT, USA) simulating AM 1.5 spectrum through a UV cut off filter ($\lambda < 420 \text{ nm}$) for 2 h. After

irradiation, the product was collected, centrifuged and washed by ethanol and distilled water for several times. Finally, the product was dried by vacuum freeze drier.

3.2.3 Characterization of catalysts

The obtained products were characterized by X-ray powder diffraction (XRD) using a D8-Advance Bruker-AXS diffractometer with Cu K α irradiation operated at 40 kV and 30 mA. The morphology of the samples was observed by a field-emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDX) of JOEL 6340 operated at 5 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were also applied with a JEOL 2010 microscope operated at 300 kV. Brunauer-Emmett-Teller (BET) surface area measurements were performed on a Quantachrome AUTOSORB sorption analyzer. X-ray photoelectron spectra (XPS) were measured by a Kratos Axis Ultra Spectrometer with a monochromic Al K α source at 1486.7 eV, a voltage of 15 kV and an emission current of 10 mA. UV-Vis diffuse reflectance spectra of powder samples were obtained with a Shimadzu UV-2600 UV-Vis spectrophotometer. Photoluminescence spectra (PL) were carried out with a PerkinElmer LS 55 Fluorescence spectrometer at 315 nm. Raman Spectra were tested by a Renishaw inVia Raman microscope with the excitation wavelength of 514.5 nm.

3.2.4 Photocatalytic activity test: Degradation of SAM

Photocatalytic activity of BiOCl and BiOCl-Ag composites was evaluated by the degradation of SAM using a 1.5 AM solar simulator (NEWPORT, USA) with a 200 W Xe arc lamp. Dichroic mirrors were utilized to control wavebands in specific

ranges 420-630 nm (visible light). In order to remove the UV residual, a polycarbonate filter was applied. Under dark condition, 50 mL suspension with photocatalyst dosage of 1.0 g L^{-1} and the initial SAM concentration of 10 mg L^{-1} was prepared and was then continuously stirred for 1 h to reach the adsorption equilibrium. The photocatalytic test was started by switching on the solar simulator. At certain time intervals, 3 mL sample aliquots were collected and immediately filtered through $0.45 \text{ }\mu\text{m}$ cellulose acetate syringe membrane filters. All the photodegradation experiments were conducted in triplicate. The concentration of SAM was measured by high performance liquid chromatography (HPLC) with a Spherisorb ODS-2 column ($150 \text{ mm} \times 4.6 \text{ mm I.D.}$, $5 \text{ }\mu\text{m}$) and an SPD-M20A diode array detector (DAD) using a Shimadzu LC system (LC-20AD). The operation parameters of HPLC is given in the APPENDIX A3.1. Ag ions (Ag^+) leaching from BiOCl-Ag composites during the photocatalytic reaction was determined by MP-OES (Agilent Technologies 4100). For the recycle test, after each test cycle, the catalysts were carefully collected, centrifuged and washed by water for three times before they were applied in the next cycle. In addition, the degradation intermediates were detected by LC/MS/MS and the analysis method is illustrated in the Appendix A3.2.

3.2.5 Antibacterial activity

Antibacterial ability of BiOCl and BiOCl-Ag against *E. coli* (ATCC 8739) and *B. subtilis* (ATCC 6633) was investigated under visible light irradiation. All glass apparatuses were autoclaved at $121 \text{ }^\circ\text{C}$ for 20 min before usage. The biocidal effect was evaluated by spread-plate method (Roberts, NESTER et al. 1998). *E. coli* and *B. subtilis* were firstly incubated in liquid Luria-Bertani (LB) nutrient medium at $37 \text{ }^\circ\text{C}$ for 20 h with continuous shaking at 200 rpm. The bacterial suspensions were then harvested and washed with 0.85% NaCl solution twice. The bacterial cells were

re-suspended in 0.85% NaCl solution and the cell density was adjusted to about 3×10^7 colony forming units per milliliter (cfu mL⁻¹). After that, 50 mg catalyst was then added with a final concentration of 1.0 g L⁻¹. At certain intervals, 2 mL of reaction mixture was sampled and immediately diluted with 0.85% NaCl solution. After appropriately dilution, 100 μ L of sample was spread on LB agar medium and incubated at 37 °C for 18 h. The number of colonies formed on the medium was carefully counted to determine the numbers of viable cells. The mixtures of bacterial cells and photocatalyst samples without light irradiation were prepared as control. All the above experiments were conducted in triplicates.

3.3 Results and discussion

3.3.1 Characterization of BiOCl and BiOCl-Ag

Fig. 3.1 Schematic diagram of the synthesis of BiOCl and BiOCl-Ag.

The schematic illustration of the BiOCl and BiOCl-Ag synthesis process is presented in **Fig. 3.1**. The possible growth mechanism of 2D BiOCl in EG solution has been proposed by other researchers and can be explained by Ostwald ripening where small BiOCl crystalline nuclei appeared in the EG solution at high

temperature and auto-generated vapor pressure followed the chemical reaction in **Eq (3.1)** (Zhu, Liao et al. 2010, Xiao, Hao et al. 2012, Ye, Xie et al. 2013). By Ostwald ripening, the small BiOCl nuclei aggregated together and grew into larger 2D BiOCl nanodisks as shown in Scheme S1.

Fig. 3.2 XRD patterns of BiOCl and BiOCl-Ag.

To study the phase purity and crystal structure of BiOCl before and after Ag loading, XRD was applied and the results are displayed in **Fig. 3.2**. All the detectable peaks from pure BiOCl were well indexed to the JCPDS Card No. 06-0249. No other peak was observed in this pattern indicating that BiOCl produced was of high purity. Additionally, the sharp diffraction peaks observed implies the good crystallinity of BiOCl. Similar XRD pattern was obtained after Ag was loaded on BiOCl except an additional peak related to metallic Ag located at 38.2° matching with (111) planes of the face-centered cubic structure Ag (JCPDS No. 04-0783) appeared. This indicates that the introduction of Ag NPs would not damage the crystal structure of BiOCl.

The shape and morphology of the as-synthesized BiOCl were firstly observed by FESEM where the synthesized BiOCl consisted of homogeneous, disc-like shaped structures with an average size of 100 to 300 nm and thickness of 20 nm as shown in **Fig. 3.3 (a)**. EDX result (**Fig. A3.1**) reveals that the product only contained the elements of Bi, O and Cl, confirming that the product was pure BiOCl. In the studies of Yang, Ma *et al.* and Cheng, Shi *et al.*, though they also used $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, WCl_6 and urea as precursors, their products were 3D flower-like BiOCl, Bi_2WO_6 and BiOCl- Bi_2WO_6 hierarchitectures other than pure 2D BiOCl. Here, we manipulated the precursors to successfully prepared pure BiOCl (BET surface area: $6.54 \text{ m}^2 \text{ g}^{-1}$, **Fig. A3.3**) with well-defined 2D disc-like nanostructures. Compared to BiOCl, small particles can be found on the surface of BiOCl-Ag sample under SEM observation (**Fig. 3.4 (b)**), and peaks around 3 KeV belonging to element Ag were observed in its EDX pattern (**Fig. A3.1**). Moreover, these small Ag NPs with a size around 15-30 nm could be more clearly seen under TEM (**Fig. 3.3 (d)**), and the lattices indexing to BiOCl and Ag NPs were observed under higher magnification as marked in **Fig. 3.3 (e)**. Specifically, the lattice fringe with a *d*-spacing of 0.275 nm was consistent with the (110) plane of tetragonal structure BiOCl and the lattice spacing of 0.236 nm was corresponded to the (111) face-centered cubic structure of Ag were observed. These lattice fingers matched well with the XRD results confirming the successful introduction of Ag in metallic form on BiOCl. At the same time, no significant size or morphology variation of BiOCl nanodiscs was found after Ag loading (**Fig. 3 (b) and (d)**), implying that photo-reduction is a suitable method to deposit Ag NPs on BiOCl without affecting its morphology.

Fig. 3.3 SEM images of BiOCl (a) and BiOCl-Ag (b); TEM and HRTEM images of BiOCl nanodiscs (c); BiOCl-Ag composites (d) and (e).

The elemental compositions and chemical states of BiOCl and BiOCl-Ag were analyzed with XPS. **Fig. 3.4** shows the survey scan spectra of BiOCl and BiOCl-Ag in the binding energy range of 0 to 1200 eV. Only the characteristic peaks of Bi, Cl and O with C as a reference at 285 eV were observed in the survey of BiOCl (**Fig. 3.4 (a)**), which is consistent with the result of EDX (**Fig. A3.1**) and further verifies the high compositional purity of BiOCl nanodiscs. In the case of BiOCl-Ag, peaks at around 360 to 380 eV in the survey scan spectrum belonging to Ag were also detected as labeled in **Fig. 3.4 (a)**. To identify the status of Ag NPs deposited on BiOCl, the high resolution scan of Ag 3d were conducted (**Fig. 3.4 (b)**). Two major peaks associated with the 3d doublet assigning to the binding energy of Ag 3d 5/2 and 3d 3/2 of metallic Ag at 368.1 and 374.1 eV, respectively, were detected (Cheng, Huang et al. 2011, Zhu, Chen et al. 2011, Zhu, Chen et al. 2011). Based on

the results of XPS, the Ag content in BiOCl-Ag composites was estimated to be 1.862 at. %.

Fig. 3.4 Full XPS spectra of BiOCl, and BiOCl-Ag (a); high-resolution XPS spectrum of Ag 3d of BiOCl-Ag (b).

To further probe the possible effect of Ag NPs introduction on the vibrational and structural properties of BiOCl crystals, Raman spectroscopy was applied and the results are displayed in **Fig. 3.5**. For pure BiOCl, two distinguishable bands located at 145 cm^{-1} and 199 cm^{-1} were observed, which can be ascribed to the A_{1g} and E_g internal Bi-Cl stretching modes, respectively (Shamaila, Sajjad et al. 2011, Tian, Guo et al. 2012, Zhang, Liang et al. 2012, Xia, Xu et al. 2013). Similar vibration modes were detected for BiOCl-Ag except that the peak intensity was remarkably higher. Such enhanced intensity is known as Surface Enhancement Raman Scattering (SERS) effect caused by the incorporation between Ag NPs and BiOCl. In particular, the surface plasmon resonance of Ag can lead to local electromagnetic field enhancement (Shan, Xu et al. 2007, Li, Hu et al. 2012), and this may be the major contributor to the SERS effect of BiOCl-Ag composites. The Raman spectra further confirmed that Ag NPs were closely bonded with BiOCl and the interaction between BiOCl and Ag NPs would strengthen the intensity of Raman peaks of BiOCl.

Fig. 3.5 Raman spectra of BiOCl and BiOCl-Ag.

3.3.2 Optical absorption property

The influence of Ag NPs on the optical properties of BiOCl was studied by UV-Vis DRS and Photoluminescence (PL) spectra. Pure BiOCl nanodiscs mainly showed absorption in the UV region with an absorption edge at around 350 nm as illustrated in **Fig. 3.6 (a)**. After being modified with Ag NPs, significant absorption in the visible light range from 420 to 600 nm was observed in BiOCl-Ag composites. Ag NPs have been proved to be capable to enhance the light absorption performance of semiconductors as a result of their localized surface plasmonic resonance (SPR) effect. Therefore, the observed new broad absorption in the range of 400-550 nm could be assigned to the SPR effect of Ag NPs which would provide BiOCl-Ag photoactivity in the visible light region and lead to an improved photocatalytic performance (Awazu, Fujimaki et al. 2008, Yu, Fan et al. 2011, Kong, Jiang et al. 2013, Liu, Tang et al. 2015, Zhang and Xu 2016). The band gap of BiOCl and BiOCl-Ag were calculated to be 3.53 and 3.40 eV, respectively, by the

UV-Vis spectra using Kubelka-Munk function proving that BiOCl-Ag had a smaller band gap due to the introduction of Ag NPs.

Fig. 3.6 UV-Vis DRS (a); Photoluminescence spectra (b) of BiOCl and BiOCl-Ag composites. Inset in (a) is the transformed Kubelka-Munk functions vs. photon energy.

The enhanced light absorption of BiOCl-Ag implies it would generate photoinduced electron-hole pairs more efficiently than BiOCl under UV and visible light illumination. However, the recombination of electron-hole pairs can significantly hinder the photocatalytic performance. Hence, it is essential to fabricate the heterogeneous composites which are capable to effectively separate, migrate and transfer charge carriers. PL spectrum is a useful method to study the fate of electron-hole pairs in semiconductor particles. As the PL spectra of BiOCl and BiOCl-Ag displayed in **Fig. 3.6 (b)**, it is clear that compared to BiOCl, BiOCl-Ag presented remarkably quenched intensity indicating a lower recombination rate between electrons and holes. Thus, loading of Ag NPs on BiOCl can efficiently inhibit the recombination of electron-hole pairs and achieve a higher charge separation efficiency which would also benefit the photocatalytic activity.

3.3.4 Photocatalytic degradation of SAM

Before applying visible light, SAM solution was continuously stirred for 5 h in dark without adding any photocatalyst. No obvious change of concentration was found indicating that the hydrolysis of SAM was negligible. When visible light was applied, 8.6% SAM was degraded without photocatalyst (**Fig. 3.6**). The degradation efficiency was increased to 82.4% when BiOCl-Ag presented which is almost twice higher than that of BiOCl (26.1%). TOC changes during the photo-degradation process can reveal the degree of mineralization of organic molecules. As shown in **Fig. 3.6** (inset), the TOC removal efficiency of SAM with BiOCl and BiOCl-Ag in 5 h reaction was 19.5% and 61.6%, respectively, indicating the better SAM mineralization performance of the latter. Meanwhile, the lower TOC removal efficiency compared with the degradation efficiency of SAM suggests the generation of intermediates during the photocatalytic process. In general, the remarkable improvement in degradation performance can be ascribed to the introduction of Ag NPs on the surface of BiOCl as illustrated by **Eqs (3.1) - (3.5)**. In brief, Ag NPs can strongly absorb visible light due to their SPR effect (Kamat 2002, Kelly, Coronado et al. 2003, Shan, Huang et al. 2014), and thereby generate photo-excited electrons and holes. The photoinduced electrons can rapidly transfer to the CB of BiOCl, which subsequently intensifies the separation rate of electron-hole pairs. Additionally, photo-excited Ag can shift to more positive potentials forming positively charged $\text{Ag}^{\text{n}+}$ as active species (Jiang, Wang et al. 2012), which also can degrade SAM. At the meantime, light irradiation can active BiOCl to produce holes in its VB and electrons in the conduction band. The photoinduced electrons can be trapped by electron acceptors like dissolved oxygen (DO) and subsequently produce superoxide ions ($\text{O}_2^{\cdot-}$) to attack SAM surrounded. Photoinduced holes can directly oxidize the adsorbed SAM on BiOCl-Ag surface and also can react with water forming $\cdot\text{OH}$ and H^+ . H^+ is able to interact with $\text{O}_2^{\cdot-}$.

creating $\cdot\text{OOH}$ and $\cdot\text{OH}$. After a chain of reactions, these active species would perform together leading to the enhanced degradation of SAM. The tentative photocatalytic mechanism is proposed in **Fig. 3.8**.

Fig. 3.7 Degradation of SAM under visible light by BiOCl and BiOCl-Ag (a); TOC removal efficiency of SAM with BiOCl, BiOCl-Ag after 5 h irradiation (inset (a)); degradation of SAM of BiOCl-Ag with different scavengers after 5 h irradiation under visible light (b), SAM = 10 mg L⁻¹, catalyst dosage = 1.0 g L⁻¹, initial pH = 7±0.2.

In order to verify the roles of different active species involved in the photocatalytic process of BiOCl-Ag composites, radical scavengers including methanol (h^+ scavenger), BQ ($\text{O}_2^{\cdot-}$ scavenger) and DMSO ($\cdot\text{OH}$ scavenger) were added. Results (**Fig. 3.7 (b)**) show that these scavengers could inhibit the degradation to different degrees. In comparison to the efficiency without any scavenger, BQ and methanol could remarkably suppress the degradation of SAM and the efficiency was respectively reduced by 54.9% and 48.2% which are more

than that of DMSO (25% reduction) indicating that $O_2^{\cdot-}$ and h^+ were the main active species participated in the photo-degradation of SAM.

Fig. 3.8 Photocatalytic mechanisms of SAM degradation (a) and bacterial inactivation (b) by BiOCl-Ag under visible light irradiation.

During the photocatalysis process, initial pH could affect the surface charging of photocatalysts and organic matters thus may influence the adsorption of organic matters on the catalysts. Meanwhile, pH level would affect the generation of radicals involving the participation of H^+ and/or OH^- as well. Therefore, the effect of initial pH on the degradation of SAM in the range of 5 to 9 was studied to optimize the reaction conditions (**Fig. 3.9 (a)**). Overall, slight increase of degradation efficiency can be found at lower pH for both BiOCl and BiOCl-Ag while higher pH showed marginally inhibition on the degradation performance. In particular, BiOCl-Ag degraded 91.7% SAM at pH 5 and this efficiency declined to 75.9% at pH 9 (82.4% at pH 7). Similar trend was observed for BiOCl where 33.2% SAM was degraded at pH 5 and 19.7% at pH 9 (26.1% at pH 7). Considering that adsorption of SAM on both catalysts was quite low (**Fig. A3.4**), the adsorption difference originated from pH changes was not the main factor affecting the degradation performance. Thus, the effect of initial pH on SAM degradation can be assigned to its influence on radical generation. Under acidic conditions, more h_{vb}^+

and more $\cdot\text{OH}$ may participate in SAM degradation as illustrated by **Eqs (3.3-3.5)**, which would subsequently improve the photocatalytic process.

Fig. 3.9 Degradation of SAM under visible light at different initial pH, SAM = 10 mg L⁻¹, catalyst dosage = 1.0 g L⁻¹ (a); five cycles of SAM degradation with BiOCl-Ag as photocatalysts under visible light for 5 h, SAM = 10 mg L⁻¹, catalyst dosage = 1.0 g L⁻¹, initial pH = 7±0.2 (b).

Good repeatability and stability of photocatalysts are of great importance in practical application. In this study, BiOCl-Ag remained vigorous photocatalytic activity even after five cycles as displayed in **Fig. 3.9 (b)**. Though slight loss of degradation efficiency was observed, this could be resulted from the unavoidable loss of BiOCl-Ag catalyst during the recovery process. The loss of Ag, mainly leaching as Ag⁺, during the usage would also affect the stability of BiOCl-Ag. More importantly, Ag⁺ is believed to be hazardous to aquatic ecosystems at high concentration (Benn and Westerhoff 2008, Arulraj, Devasenathipathy et al. 2015). Ag leaching during the BiOCl-Ag photocatalytic process was monitored by ICP to test the stability and possible hazard to water. According to the regulation established by USA Environmental Protection Agency (EPA), the secondary maximum contaminant level (SMCL) of Ag is 0.1 mg L⁻¹ (Tan, Teo et al. 2010, Westerhoff, Alvarez et al. 2016). The results are given in **Table 3.1**, where Ag leaching after 5 h reaction in all observed conditions was below 0.08 mg L⁻¹,

without risk to human health according to the WHO guideline (0.1 mg L^{-1}) (Organization 2004, Zodrow, Brunet et al. 2009). This means that Ag leaching from BiOCl-Ag within one cycle (5 h) would not be harmful to the environment or remarkably suppress its photocatalytic efficiency. However, it is worth pointing out that the prolonged reaction time Ag concentration would consequently increase and may be higher than the SMLC, which would thereafter pose threats to the environment and human health. Thus, it is of great importance to monitor Ag leaching when BiOCl-Ag is utilized in real.

Table 3.1 Ag leaching after 5 h visible light irradiation at different initial pH.

Initial pH (± 0.2)	Ag leaching (mg L^{-1})
5	0.08
7	0.06
9	0.06

Fig. 3.10 SEM image of BiOCl-Ag after 5 repeated cycles (a) and XRD patterns of fresh BiOCl-Ag and used BiOCl-Ag after 5 cycles.

After 5 cycles, the used BiOCl-Ag was observed by SEM as illustrated in **Fig. 3.10 (a)** where no significant morphology change was found. Meanwhile, the XRD pattern of the used BiOCl-Ag (**Fig. 3.10 (b)**) was well maintained compared to the

fresh BiOCl-Ag. Such results prove that the as-prepared BiOCl-Ag had high photostability and can be reused.

Fig. 3.11 Proposed pathway for SAM photocatalytic degradation by BiOCl-Ag.

The intermediate products generated during the photocatalytic process were analyzed by LC/MS/MS. As illustrated in the ES (+) mode (**Fig. A3.5**), three peaks at m/z 61.2, 158.1 and 173.2 could be observed. Specifically, compound 1 (C1) found at m/z 173.2 (Mw 172) could be assigned to SAM, while compound 2 (C2, Mw 157) observed at m/z 158.1 was stemmed from the cleavage of S-N bond due to radical attack. Compound 3 (C3, Mw 60) can be referred to Acetic acid, which indicates the bond cleavage of the benzene ring and the decomposition of SAM as well as other intermediates (Feng, Liao et al. 2016). Therefore, it is clear that the attack of radicals such like $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ would lead to the S-N bond cleavage and the ring open and thus result in the degradation of SAM under visible light. Here, as shown in **Fig. 3.11**, a degradation pathway was proposed based on the detected intermediates.

3.3.5 Antibacterial activity under visible light irradiation

BiOCl can produce active radicals like $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$ in aqueous conditions by direct absorption of photons under visible light irradiation (Chen, Liu et al. 2010, Pare, Sarwan et al. 2012, Wang, Hui et al. 2014, Podporska-Carroll, Panaitescu et al. 2015). These radicals are capable to attack bacterial cells and eventually lead to their death (Foster, Ditta et al. 2011). So far, there is no report exploring the antibacterial activity of BiOCl. In our study, results (**Fig. 3.12** and **Fig. A3.6**) demonstrate that pure BiOCl indeed carries antibacterial function and this effect can

be further improved under light irradiation which may result from radical formation as mentioned above. However, its antibacterial efficiency (1-log or 2-log reduction) was not high enough for disinfection purpose. On the other hand, BiOCl-Ag composites performed much better than BiOCl under both dark and visible light conditions. Specifically, BiOCl-Ag achieved 100% antibacterial efficiency against both *E. coli* and *B. subtilis* after 2 h irradiation with 7-log reduction.

Fig. 3.12 Log reduction of *E. coli* (a), and *B. subtilis* (b) by the as-prepared photocatalysts (1.0 g L^{-1}) in dark (D) and under visible light (L).

The higher antibacterial effect of BiOCl-Ag composites may be induced by several reasons as illustrated in **Fig. 3.8 (b)**. Firstly, the antibacterial effect of Ag can be one important contributor since Ag is a well-known and effective biocidal agent (Feng, Wu et al. 2000, Arakawa, Neault et al. 2001, Hu, Guo et al. 2007, Rai, Yadav et al. 2009, Li, Xie et al. 2010). Though the antibacterial mechanism of Ag NPs has not been thoroughly understood, three mechanisms have been proposed (Marambio-Jones and Hoek 2010). (1) Ag NPs can directly contact with bacterial cell membranes leading to the increase of cell permeability, change of cell structure and subsequently loss of cell viability (Amro, Kotra et al. 2000, Hu, Guo et al. 2007, Zhang and Chen 2009). (2) Ag NPs can release Ag^+ in the aqueous phase. Ag^+ can react with some proteins with cysteine due to its high affinity with thiol groups and some enzymes in the respiratory chain and detriment their functions (Feng, Wu et al.

2000, Rai, Yadav et al. 2009). Moreover, Ag^+ acts as strong nucleic acid binder to DNA and RNA which would cause the densation of DNA and loss of replication ability (Arakawa, Neault et al. 2001). (3) Ag NPs are able to generate free radicals which could attack and inactivate bacterial cell (Kim, Kuk et al. 2007, Choi and Hu 2008). Secondly, active radicals generated in the photocatalytic reactions of BiOCl-Ag can effectively inactive bacterial cells by decomposing their cell walls and membranes which would lead to the leakage of intracellular molecules and finally death of cells (Foster, Ditta et al. 2011, Podporska-Carroll, Panaitescu et al. 2015). In brief, the excellent antibacterial performance of BiOCl-Ag under visible light irradiation comes from two parts: (i) inactivation effect originated from metallic Ag and Ag^+ ; (ii) antibacterial effect of active radicals. This study proves that BiOCl-Ag composites can be a good candidate for disinfection purpose.

3.4 Conclusions and challenges

In this study, 2D BiOCl nanodiscs with good crystallinity were successfully synthesized via a modified facile solvothermal method. After that, BiOCl-Ag nanocomposites were prepared by a simple photo-reduction method. Ag NPs formed on the surface of BiOCl nanodiscs can be clearly observed by TEM, and were proved to be metallic Ag by both XRD and XPS analysis. Moreover, the introduction of Ag NPs demonstrated remarkable influence on the properties of BiOCl, including a shift on absorption edge towards visible region, the appearance of SERS effect, and significantly reduced recombination rate of electron-hole pairs. All these changes indicate that BiOCl-Ag has the potential to possess largely improved photocatalytic activity than bare BiOCl under visible light irradiation. In particular, SAM was utilized to evaluate the photocatalytic performance of BiOCl and BiOCl-Ag under visible light illumination, and the results well confirmed that BiOCl-Ag presented remarkably promoted photocatalytic activity where it showed

approximately twice higher degradation efficiency as compared to that of BiOCl. Additionally, the influence of initial reaction pH was thoroughly investigated, finding that acidic condition would be more beneficial to SAM degradation. Further study verified that the main active species playing a role during the photocatalytic process can be ascribed to $O_2^{\cdot-}$ and h^+ . By employing LC/MS/MS to analyze the intermediates generated during the photocatalytic reactions, the possible SAM degradation pathway was accordingly proposed. At the same time, the existence of Ag NPs can facilitate the antibacterial performance of BiOCl, evidenced by 100% inactivation efficiency over *E. coli* and *B. subtilis* under visible light irradiation. This is because not only Ag with antibacterial ability but also the various active species generated during photocatalytic process played the crucial roles and therefore contributed to the overall antibacterial performance. This study shows that BiOCl-Ag composites can be a promising photocatalyst in degradation of organic pollutants as well as removal of pathogens in water treatment with visible light from sunlight as energy source.

Nevertheless, it is vital to mention that the synthesis process of 2D BiOCl was found to be quite sensitive, and even a slight change of reaction conditions would affect the final products. Specifically, quite a lot of factors were found to be able to affect the generation of final products, such as $Bi(NO_3)_3 \cdot 5H_2O$ to WCl_6 ratio, and addition of water.

In the preliminary study, the possible influence of $Bi(NO_3)_3 \cdot 5H_2O$ to WCl_6 ratio on the final products was studied by varying the ratios. In particular, when 0.5 mmol WCl_6 and 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ were used as precursors, results showed that BiOCl- Bi_2WO_6 microflowers (**Fig. A3.7**) rather than pure BiOCl were produced, and this finding is in corresponding with previous reports (Yang, Ma et al. 2013, Cheng, Shi et al. 2015, Cui, Zhou et al. 2015).

At the same time, results proved that when preparing the samples, the addition of water would affect the final products significantly even at very low amount. XRD was applied to characterize the products obtained from different synthesis conditions as presented in in **Fig. A3.8**. From the XRD result, it is clear that when the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to WCl_6 ratio was kept at 1:1 and different volume of water (1mL and 5 mL) was added, the final products were pure Bi_2WO_6 rather than bare BiOCl since no peak belonging to BiOCl was observed. Moreover, the XRD patterns were found to be well matched with the orthorhombic structure of Bi_2WO_6 (JCPD file No. 39-0256) further proving the generation of Bi_2WO_6 . Therefore, it is clearly that water can be regarded as an important factor influencing the formation process of BiOCl and Bi_2WO_6 .

Thus, the controlled synthesis of BiOCl is still quite challenging, and this would affect their scale-up production when talking about its application in real. At the same time, BiOCl has a wide band gap (~ 3.53 eV in this study) which strongly limits their light response capability. Though the combination of Ag NPs forming heterostructures could narrow its band gap to some degree, the wide band gap is still one of the major factors affecting the photocatalytic performance of BiOCl under visible light illumination.

In consideration of the wide band gap and the difficulty of scale-up synthesis of BiOCl , it is of great importance to explore other kinds of semiconductor which have narrower band gap and simpler synthesis method. Moreover, in order to further improve their photocatalytic performance under visible light irradiation, one effective strategy is to find their appropriate co-catalysts generating heterostructure as efficient photocatalysts. Therefore, in the following study, main efforts were devoted to search new semiconductor material as more promising candidate as effectual photocatalysts which can be driven by visible light. After that, the

possibility of various materials working as co-catalysts was investigated to enhance its photocatalytic ability under visible light irradiation.

CHAPTER 4 FABRICATION OF WO₃-Ag PHOTOCATALYTIC COMPOSITES FOR SULFANILAMIDE REMOVAL AND BACTERIAL INACTIVATION

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4.1 Introduction

As stated in Chapter 3, the application of BiOCl as photocatalyst driven by visible light can be limited by its wide band gap and synthesis method. Therefore, the exploration of other promising candidates was needed. After through consideration, m-WO₃ with a low band gap energy (2.4 to 2.8 eV) was selected as a potential candidate for photocatalysis process. This is because WO₃ is suggested to be low cost and harmless materials which is also stable in acidic and oxidative conditions (Dong, Hou et al. 2017). Moreover, WO₃ is regarded as a promising photocatalyst to treat organic pollutants under solar irradiation (Fleig and Maier 1997, Bamwenda and Arakawa 2001, Li, Zhang et al. 2006, Bathe and Patil 2008, Chen, Gao et al. 2008, Chen, Wang et al. 2008, Zhao and Miyauchi 2008, Ham, Phuruangrat et al. 2010, Cabrera, Latimer et al. 2012).

Nevertheless, it is worth noting that pure WO_3 as photocatalyst has a relatively low efficiency due to its low CB level which not only limits its ability to react with electron acceptors like O_2 but also increases the recombination rate of the photogenerated electron-hole pairs (Miyauchi 2008, Katsumata, Oda et al. 2013). To address this obstacle, one strategy is to combine with suitable materials (co-catalysts) forming heterogeneous composites to achieve better charge separation efficiency and subsequently to increase photocatalytic efficiency (Zhang, Wang et al. , Armelao, Barreca et al. 2007, Liu and Xue 2008, Paramasivam, Nah et al. 2010, Sun, Wang et al. 2010, Kong, Huang et al. 2012, Acharyya, Ghosh et al. 2015, Momeni 2015, Xu, Yao et al. 2015, Momeni 2016, Momeni and Nazari 2016).

As pointed out in **Chapter 2**, the combination with suitable co-catalysts such as metals, other semiconductors and carbon materials forming S-M, S-S, and S-C heterojunctions are regarded as effective strategies to improve the photocatalytic performance of a certain semiconductor (Coronado, Fresno et al. 2013, Qu and Duan 2013) (Wang, Zhang et al. 2014). Therefore, in the following chapters, various co-catalysts including metals, semiconductors and carbon materials would be employed to construct heterogeneous composites, while their photocatalytic performance would be thoroughly studied.

In this chapter, the possibility to use metal as co-catalyst to improve the photocatalytic performance of WO_3 was explored. In particular, the combination of metal nanoparticles is suggested to be able to achieve better charge separation efficiency, and subsequently to increase photocatalytic efficiency (Zhang, Wang et al. , Armelao, Barreca et al. 2007, Liu and Xue 2008, Paramasivam, Nah et al. 2010, Sun, Wang et al. 2010, Kong, Huang et al. 2012, Acharyya, Ghosh et al. 2015, Momeni 2015, Xu, Yao et al. 2015, Momeni 2016, Momeni and Nazari 2016). Especially, when metal nanoparticles like Pt, Au and Ag are introduced, visible

light absorption of WO_3 would be broadened (Liu, Wang et al. 2013, Xu, Yao et al. 2015). Among these different metals, Ag NPs have received extensive attention because of its relatively low price and attractive enhancement of photocatalytic and antimicrobial performance. However, the aggregation trend of Ag NPs can cause efficiency loss limiting their potential large-scale applications in reality (Jana, Dandapat et al. 2010). Hence, on the other hand, WO_3 can act as suitable supporter for Ag NPs to achieve a high-loading and well dispersed Ag nanoclusters (Zhang and Chen 2009).

Though some researchers have reported Ag NPs modified WO_3 to investigate their various applications as catalysts, sensors, photoelectrochemical materials and photocatalysts (Liu, Wang et al. 2013, Acharyya, Ghosh et al. 2015, Ghosh, Acharyya et al. 2015, Ghosh, Saha et al. 2015, Xu, Yin et al. 2015), studies toward exploring the possible application of Ag modified WO_3 composites as photocatalysts to treat antibiotic contaminated water remains scarce. In this work, we firstly used a facile one pot hydrothermal method to achieve bulk synthesis of well morphology-controlled m- WO_3 nanoplates with uniform and smaller size compared to previous study (Ma, Zhang et al. 2011, Liu, Wang et al. 2013, Acharyya, Ghosh et al. 2015, Ghosh, Saha et al. 2015, Xu, Yin et al. 2015). Then, Ag NPs were anchored on WO_3 nanoplates to form WO_3 -Ag composites by simple photo-reduction method. A systematic characterization was carried out for WO_3 and WO_3 -Ag composites and laboratory-scale batch experiments were conducted to evaluate their photocatalytic activity under visible light by degradation on SAM: SAs, and the inactivation of *E. coli* and *B. subtilis*. To the best of our knowledge, it is the first time to apply WO_3 nanoplates and WO_3 -Ag composites to degrade SAM. Moreover, a plausible charge-transfer mechanism is tentatively proposed for the photocatalytic process.

4.2 Experimental Part

4.2.1 Materials

Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), hydrochloric acid (35% HCl), ethanol, SAM, BQ and DMSO were purchased from Sigma Aldrich Company. Methanol (HPLC-grade) was purchased from Merck Company.

4.2.2 Synthesis of WO_3 nanoplates under different temperatures

The synthesis of WO_3 nanoplates was carried out by a facile one pot hydrothermal method (Zhang, Yang et al. 2014). Typically, 3.0 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was firstly dissolved in 30 mL DI water and then transferred to a 120 mL Teflon-lined stainless-steel autoclave. At room temperature, 15 mL 35% HCl was gradually added into the autoclave under vigorous magnetic stirring with light yellow precipitate appeared. Finally, the autoclave was put into the oven to undergo a heating process for 8 hours at different temperatures (80 °C, 120 °C, 160 °C, 180 °C and 200 °C). After cooling down naturally, the products were collected and washed with ethanol and DI water for several times before being dried by vacuum freeze drier at -105°C. In particular, WO_3 synthesized at 180 °C (WO) was chosen for the following synthesis of WO_3 -Ag composites (WA) as a result of its better crystallinity as verified by XRD result.

4.2.3 Synthesis of WO_3 -Ag (WA) plasmonic composites

WA plasmonic composites were synthesized through a simple photo-reduction method. Briefly, 100 mg WO nanoplates was firstly dispersed into 60ml DI water in the quartz capsule of 120mL. Then, 20mL AgNO_3 solution (10 mmol L^{-1}) was added with continuously stirring under dark. Subsequently, the mixture was irradiated by a 500 W Xe lamp (wavelength range: 380-800 nm) for certain time (1

h, 2 h and 3 h, respectively) to control the amount and size of Ag NPs deposited on the surface of WO₃. The distance between the light source and the solution surface was carefully adjusted to make sure the measured light intensity was 100 mW cm⁻². After rinsing with ethanol and water for several times, the products were dried by vacuum freezer drier. The samples prepared at 1 h, 2 h and 3 h, were named as WA1, WA2 and WA3, respectively.

4.2.4 Materials Characterization

XRD, SEM, TEM, XPS, UV-Vis, BET, and Raman were conducted as illustrated in Chapter 3. PL spectra was recorded on a PerkinElmer LS 55 Fluorescence spectrometer at 325 nm.

4.2.5 Photocatalytic activity test for SAM degradation

Photocatalytic activity of WO₃ and WA composites (0.5 g L⁻¹) was evaluated by degradation of SAM (10 mg L⁻¹) using a 1.5 AM solar simulator (NEWPORT, USA) with a 200 W Xe arc lamp. Dichroic mirrors were utilized to control wavebands in specific ranges 420-630 nm (visible light). To remove the UV residual, a polycarbonate filter was applied. The vessel was firstly stirred for 1 h in the dark to reach the adsorption equilibrium. The photocatalytic test was initiated by switching on the solar simulator. Sampling of the solution was carried out at various time intervals and were filtered with 0.45 µm cellulose acetate syringe membrane filter before the SAM concentrations were determined via high performance liquid chromatography (HPLC) (seen in the APPENDIX A3.1). The effect of initial pH (5.0-9.0) was studied, and the pH was adjusted with 0.5 M NaOH and 0.25 M HCl. All the photodegradation experiments were conducted in triplicate. To investigate the formation of different ROS during the photocatalytic process, methanol, BQ and DMSO were chosen as scavengers. The total organic carbon (TOC) remaining in

the solution was measured with a TOC analyzer (Analytikjena multi N/C 2100). Ag leaching from WA composites during the photocatalytic reaction was determined by MP-AES (Agilent Technologies 4100). The degradation intermediates were detected by LC/MS/MS and the analysis method is illustrated in the APPENDIX A3.2.

4.3 Results and discussion

4.3.1 Morphology and crystal structure characterization

Results show that uniform WO_3 nanoplates can only be produced at $\text{pH} < 1$ (**Fig. A4.1 (b) and (c)**). The schematic illustration of various synthesis conditions is presented in **Fig. 4.1**. When $\text{pH} < 1$, temperature would influence the crystal phase and morphology of WO_3 as depicted **Fig. 4.2 (a)**. At low temperature (80°C), the XRD pattern is in agreement with the standard JCPDS NO: 18-1418 of orthorhombic $\text{WO}_3 \cdot \text{H}_2\text{O}$ (Ma, Zhang et al. 2010). At higher temperature, WO_3 was generated by dehydration of $\text{WO}_3 \cdot \text{H}_2\text{O}$ (**Eq (4.2)**) and the products shared similar XRD patterns that indexed to pure m- WO_3 (PDF NO: 01-083-0951) (Xiao, Wang et al. 2014). No additional peak was detected illustrating that WO_3 obtained was of high purity. Sharper peaks indicating better crystallinity were achieved at high temperature ($160, 180$ and 200°C) which may be attributed to the better dehydration of $\text{WO}_3 \cdot \text{H}_2\text{O}$.

Fig. 4.2 (b-e) displays TEM images of $\text{WO}_3 \cdot \text{H}_2\text{O}$ and WO_3 . $\text{WO}_3 \cdot \text{H}_2\text{O}$ (**Fig. 4.2 (b)**) showed obvious twist in shape and the particle sizes were in the range of 40-60 nm. By contrast, WO_3 produced at higher temperatures had good rectangular-like shape with sizes around 60-80 nm (**Fig. 4.2 (c) and (d)**). With further magnification,

the lattices spacing of 0.376 nm corresponding to (020) m-WO₃ could be clearly observed (**Fig. 4.2 (e)**).

Fig. 4.1 Schematic illustration of the synthesis condition of WO₃ nanostructures and their morphological results.

WA samples were also studied by XRD (**Fig. 4.3 (a)**). No significant signal of Ag phase was detected, which is possibly due to the relatively low deposition amount of Ag (Samerjai, Liewhiran et al. 2014). Additionally, their diffraction angles showed no obvious change compared to those of WO proving that modification with Ag would not change the high crystalline of WO₃. Ag NPs were observed on the surface of WO₃ by TEM (**Fig. 4.3 (c), (d), and (e)**) after visible light irradiation. However, if irradiation time was short (1 h), Ag NPs was too small to be clearly observed. (**Fig. 4.3 (b)**). The average size of Ag NPs increased slightly with the extension of irradiation duration and the lattices of 0.236 nm and 0.204 consisting with (111) and (220) face-centered cubic structure of Ag were observed (**Fig. 4.3 (e)**). Ag NPs were more frequently found on the edges of the WO₃ nanoplates which may be assigned to relatively higher surface energy there.

Fig. 4.2 XRD patterns of WO_3 synthesized at 80 °C, 120 °C, 160 °C, 180 °C and 200 °C for 8 h (a); TEM images of WO_3 synthesized at 80 °C (b), 120 °C (c), 180 °C (d) for 8 h, and HRTEM image of WO_3 synthesized at 180 °C (e).

Fig. 4.3 Comparison of XRD patterns of WO, WA1, WA2 and WA3 (a); TEM images of WA1 (b), WA2 (c), WA3 (d), and HRTEM image of WA2 (e).

Fig. 4.4 (a) displays the HAADF STEM image of the WA composites, and it clearly shows that a small nanoparticle was found on the edge of WO_3 nanoplate. To further prove that the small nanoparticle was Ag, the line scan EDX was applied along arrow region (**Fig. 4.4 (a)**). As shown in **Fig. 4.4 (b)**, the EDX spectrum of

across the arrow confirms the existence of element W, O and Ag. In addition, the intensity of the Ag signals only appeared when scanned across the small nanoparticle. After the probe moved away from this region, only W, O were detected.

Fig. 4.4 A HAADF-STEM image of WA2 with an arrow indicating the EDX line scan position (a), and the corresponding EDX line scan profiles with element W, O and Ag (b).

Raman spectra were conducted to further identify the phase of the products and the evolution of bonds upon Ag deposition as presented in **Fig. 4.5**. For WO, four typical peaks locating at 134, 274, 715 and 805 cm^{-1} were detected, which are highly close to the wavenumbers of m-WO₃ (Tägtström and Jansson 1999, Bittencourt, Llobet et al. 2004). Peak located at 134 cm^{-1} is assigned to the lattice vibration of WO₃ and the peak at around 274 cm^{-1} is attributed to $\delta(\text{O-W}^{6+}\text{-O})$ bending mode (Tägtström and Jansson 1999, Gouma and Kalyanasundaram 2008, Bai, Zhang et al. 2014). The rest two peaks at 715 and 805 cm^{-1} are originated by the $\nu(\text{O-W}^{6+}\text{-O})$ vibrational stretching mode of the W-O-W bridging oxygen in WO₆ octahedral units (Daniel, Desbat et al. 1987, Santato, Odziemkowski et al. 2001, Su, Lin et al. 2009, White, Jang et al. 2010, Xu, Yin et al. 2014).

Fig. 4.5 Raman Spectra of WO, WA1, WA2, and WA3.

Compared to WO_3 , all WA composites presented much stronger Raman intensities which could be caused by SERS due to Ag deposition (Thi 1985, Bittencourt, Llobet et al. 2004). More importantly, two more peaks emerged at 327 and 910 cm^{-1} . Band at 327 cm^{-1} is correspond to $\delta(\text{O}-\text{W}^{6+}-\text{O})$ bending vibration. Though it could be clearly observed in WO_3 Raman spectra due to its low intensity, the enhanced intensity caused by SERS effect made it observable in WA samples. The new band peaking at 910 cm^{-1} does not belong to m- WO_3 , and its intensity increased in direct proportion to Ag contents. The appearance of this new peak reveals a slightly distortion of WO_6 octahedral units as Ag atoms intercalate into WO_3 tunnels at the interface forming new tungsten bronze (Eq (4.3)). Subsequently, the number of W^{5+} , W^{4+} ions with lower oxidation state would increase. Even though, it is hard to observe peaks associated to the presence of W atom in lower oxidation state indicating that the extent of distortion is not significant due to the low dosage of Ag.

XPS spectra were conducted to study the elemental compositions and chemical states of WO_3 and WA composites. **Fig. 4.6 (a)** displays the XPS survey scan spectra of WO and three WA composites in the binding energy range from 0 to 1200 eV. For WO, only the characteristic peaks of W and O with C as a reference were observed, indicating the high compositional purity of WO_3 . In addition to W, O and C peaks, Ag peaks in the range from 360 to 380 eV were found in all WA samples as marked in **Fig. 4.6 (a)**. High resolution scan spectra of Ag 3d (**Fig. 5.6 (b)**) shows that two main peaks associated with the 3d doublet at 367.6 and 373.6 eV assigning to the binding energy of Ag 3d $5/2$ and 3d $3/2$ of metallic Ag were detected (Cheng, Huang et al. 2011, Zhu, Chen et al. 2011, Zhu, Chen et al. 2011), confirming the existence of Ag as metallic status. Based on XPS results, Ag contents (at. %) of WA composites were calculated to be 1.60%, 2.08%, and 3.32% for WA1, WA2 and WA3, respectively.

Fig. 4.6 XPS survey spectra of WO, WA1, WA2 and WA3 (a); high resolution Ag 3d band of WA1, WA2 and WA3 (b).

4.3.2 Optical properties

The optical properties of WO_3 and WA composites were studied with UV-Vis absorption spectra (**Fig. 4.7 (a)**) and PL spectra (**Fig. 4.7 (b)**). WO_3 showed weak visible light absorbance with the absorption on-set at 450 nm, which was in

accordance with the band gap of about 2.7 eV of m-WO₃ as reported previously (Iwu, Galeckas et al. 2012, Tanaka, Hashimoto et al. 2014, Zhan, Yang et al. 2016). By comparison, WA composites presented wider and broader absorption spectra. Additionally, the absorption on-set was red-shifted gradually with the increase of Ag amounts due to localized surface plasmon resonance (LSPR) originated from the metallic Ag NPs on WO₃ nanoplates (Roberts, NESTER et al. 1998, Daughton and Ternes 1999, Li, Xu et al. 2009, Munir, Wong et al. 2011, Samerjai, Liewhiran et al. 2014, Xiao, Wang et al. 2014, Zeng, Li et al. 2014). WA3 presented identically higher intensity, implying larger and higher amount of Ag NPs anchored on WO₃ nanoplates. Such high absorbance of WO₃-Ag composites demonstrate that they may have higher photocatalytic activity (Du, Zhang et al. 2005, White, Jang et al. 2010, Liu, Fang et al. 2012). Based on the UV-vis result, the band gaps for WO, WA1, WA2 and WA3 were calculated to be 2.73, 2.66, 2.44 and 2.31 eV indicating that loading of Ag NPs on WO₃ can result in narrowing of band gap energy.

Fig. 4.7 UV-vis absorption spectra of WO, WA1, WA2 and WA3 (a); PL spectra of WO, WA1, WA2, and WA3 (b).

PL spectrum is an effective method to study the surface processes involving photogenerated electron-hole pairs and the intensity of PL spectrum is directly proportional to electron-hole recombination rate. As displayed in **Fig. 4.7 (b)**, WO had the highest PL emission intensity in the range from 350 to 500 nm. Though all

WA samples presented similar emission profiles as WO₃, the intensities quenched significantly implying that they may be able to suppress the electron-hole pair recombination and/or to extend the reactive electron-hole lifetime compared to WO₃. Especially, Ag NPs can provide additional pathway for electrons to transfer, where they can move from the CB of excited WO₃ to Ag NPs leading to remarkably decrease of electron-hole pair recombination rate. Meanwhile, the introduction of Ag NPs may also cause some changes in the electron structures due to its ability of trapping electrons which would contribute to the photocatalytic performance of WA composites.

4.3.3 Photocatalytic activity towards SAM

4.3.3.1 Photodegradation of SAM by different catalysts

Before applying visible light, SAM solution of 10 mg L⁻¹ was continuously stirred without adding any photocatalyst for 5 h in dark. No clear change of the concentration was observed indicating that the hydrolysis of SAM under dark is negligible. Additionally, preliminary study showed that adsorption of SAM on catalysts was less than 6% (**Fig. A4.2**) without irradiation, suggesting that SAM removal due to adsorption is minimal and photocatalytic degradation is the main contributor to SAM removal. Therefore, the SAM concentration after 1 h adsorption in dark was chosen as the initial concentration (C_0) to study the photodegradation of SAM due to WO₃ and WA composites. **Fig. 4.8 (a)** illustrates comparison of SAM degradation results by different catalysts. Without any catalyst, only 7.4% of SAM was degraded over 5 h. However, SAM degradation was largely enhanced after adding catalysts in the order of WA2 > WA3 > WA1 > WO. TOC tests were conducted after 5 h irradiation to provide preliminary investigation on the degree of SAM mineralization (Inset of **Fig. 4.8 (a)**), and the highest TOC removal efficiency was achieved by WA2 to 54.6% in consistent to the SAM degradation efficiency.

The possible mechanisms for the improved photocatalytic efficiency of WA composites under visible light are proposed in Fig. 4.9.

Fig. 4.8 Photodegradation of SAM under visible light by WO, WA1, WA2, and WA3 at different pH: pH = 7.0±0.2 (a), pH = 5.0±0.2 (b) and pH = 9.0±0.2 (c). Conditions: catalyst = 0.5 g L⁻¹, SAM = 10 mg L⁻¹. Inset is the corresponding removal efficiency of SAM and TOC at 5 h. SAM degradation by WA2 with the presence of different scavengers of ROS after 5 h irradiation under visible light. Conditions: pH = 7±0.2, catalyst = 0.5 g L⁻¹, SAM = 10 mg L⁻¹ (d).

Ag NPs on the surface of WO₃ exhibit excellent light absorption capability and thus expand their response range to the visible light region. Ag NPs also can enhance the local inner electromagnetic field due to LSPR effect (Liu, Fang et al. 2012). Therefore, when visible light is applied, the incident photons will be firstly absorbed by WO₃ forming electrons and holes. Since Ag NPs have a better electron attracting ability, the photogenerated electrons will then transfer to Ag NPs (Katsumata, Oda et al. 2013), which would lower the recombination rate of the

electron-hole pairs. These electrons will transfer rapidly to the O_2 adsorbed on WA surface, producing superoxide radical anions, $O_2^{\cdot-}$. $O_2^{\cdot-}$ will then turn to $\cdot OOH$ radicals which may react with the trapped electrons to generate H_2O_2 , and finally to produce $\cdot OH$ radicals (Wu, Liu et al. 1998). Such radicals will attack, degrade and mineralize SAM in the close vicinity. The proposed initial ROS reactions during the photocatalytic process are listed in **Eqs (4.4) to (4.9)**.

Fig. 4.9 Schematic illustration of the mechanisms of WA composites of SAM degradation and microbe inactivation.

To investigate the responsible ROS during the photocatalytic process of WA composites, different scavengers, like methanol (h^+ scavenger), DMSO ($\cdot OH$ scavenger) and BQ ($O_2^{\cdot-}$ scavenger) were applied. The SAM degradation by WA2

as an example was investigated, and results (**Fig. 4.8 (d)**) indicate that the addition of methanol had quite limited effect on SAM degradation. By contrast, DMSO and BQ notably inhibited the photocatalytic performance of WA2 suggesting that reduction of O_2 is the main pathway to generate ROS like $\cdot OH$ and $O_2^{\cdot -}$ which contributing to effective photocatalysis.

4.3.3.2 Effects of initial pH

The effect of initial solution pH on SAM degradation is illustrated by **Fig. 4.8 (b)** and **(c)**. By comparing the degradation results obtained at three initial pH values (5, 7 and 9), it can be found that SAM tends to be more degradable in acidic conditions. In particular, after 5 h irradiation at pH 5, 96.1% of SAM was degraded by WA2, which is much higher than those of pH 7 (72.7%) and 9 (63.6%). The similar trend can be discovered for the other two WA composites. At low pH, **Eq (4.4)** to **Eq (4.7)** are dominant reactions that related to the photocatalytic reactions, however, OH^- would hinder these reactions and inhibit photocatalytic performance at high pH. Overall, WA2 performed better than WA1 and WA3 at different pH, and the larger amount of Ag in WA3 could not further improve its photocatalytic activity. This may be due to the excessive loading of Ag which reduces the number of active sites capturing the photoinduced electrons and thereby leading to the decrease of photocatalytic efficiency.

4.3.3.4 Proposed pathways for SAM degradation

LC/MS/MS was applied to study the degradation intermediate products of SAM, and four compounds located at m/z 173.2, 158.1, 91.6 and 61.2 were observed in the ES (+) mode. The peak at m/z 173.2 represents SAM (C1, Mw 172), and after S-N cleavage, compound 2 (C2, Mw 157) could be detected. Such S-N cleavage could be caused by the radical attack such as $\cdot OH$ and $O_2^{\cdot -}$, and when C2 were further attacked, the generation of compound 3 (C3, Mw 90) and 4 (C4, Mw 60) which were Oxalic acid and Acetic acid were observed. Such results reveal the occurrence of the ring

open under radical attack, and such intermediates can be eventually mineralized to CO_2 and H_2O . According to the detected intermediates, a degradation pathway of SAM is proposed in **Fig. 4.10**.

Fig. 4.10 Proposed SAM degradation pathway by WA composites under visible light irradiation.

4.3.3.4 Stability and reusability of WA composites

Table 4.1 BET surface areas of four photocatalysts and Ag leaching after 5 h visible light irradiation.

Composite 0.5 g L ⁻¹	S_{BET}^a (m ² g ⁻¹)	Ag leaching (mg L ⁻¹)		
		pH = 5±0.2	pH = 7±0.2	pH = 9±0.2
WO	19.32	—	—	—
WA1	20.02	0.06	0.05	0.05
WA2	20.29	0.08	0.07	0.05
WA3	21.93	0.26	0.17	0.14

^aBET surface area.

As there is dissolved oxygen (DO) in water, Ag NPs may release small amount Ag^+ which would affect the stability and reusability of Ag-doped materials. Hence, MP-AES was employed to monitor Ag^+ concentration leached from WA samples after 5 h photocatalytic reaction. As shown in **Table 4.1**, Ag releasing is closely

associated with initial pH and could be suppressed by increasing pH values (Liu and Hurt 2010). Take WA3 as example, the final Ag^+ concentration was 0.260 mg L^{-1} at pH 5 while only 0.14 mg L^{-1} of Ag^+ was detected at pH 9 after 5 h reaction. In addition, dissolution result is proportional to the amount of Ag loaded on WO_3 as WA3 released more Ag^+ than others. BET results (**Fig. A4.4**) show that S_{BET} of WA3 was slightly larger than WA1 and WA2, and TEM images also prove Ag NPs on WA3 had larger sizes. These indicate that more Ag would be exposed to the air and water which would accelerate Ag dissolution. Generally, Ag^+ concentration was relatively low revealing the good stability of all WA composites. However, WA3 released more Ag^+ and exceeded 0.1 mg L^{-1} , the SMCL of silver established by US EPA, meaning that it may propose potential adverse effects to aquatic ecosystems. Therefore, WA3 is not suitable for practical application, and it is critical to carefully control the Ag content in composites when being used. For WA2, under all three pH conditions, the Ag^+ released was lower than the SMCL (0.1 mg L^{-1}), making it an efficient and environmental friendly candidate for practical application.

Fig. 4.11 Recycled photocatalytic degradation rate of SAM by WA2, Conditions: pH = 5 ± 0.2 , catalyst = 0.5 g L^{-1} , SAM = 10 mg L^{-1} (a); XRD patterns of fresh WA2, and used WA2 after 5 cycles photocatalytic experiment (b).

To further investigate the stability and reusability of WA composites (WA2 as an example), the photocatalysts were reused by simple washing and centrifuging

procedures for five cycles (**Fig. 4.11 (a)**). At pH 5, WA2 still performed vigorously even after five successful cycles. Slight reduction of photocatalytic activity was found which could be assigned to unavoidable loss of the photocatalysts in recycling process. The crystallinity of the used WA2 after five cycles was compared with the fresh WA2 by XRD patterns in **Fig. 4.11 (b)**. No notable difference in crystallinity structure was observed indicating that WA2 was quite stable through the whole photocatalytic process. This result also verifies that though Ag^+ would be released and lost, this proportion is relatively low showing no obvious influence on SAM degradation. Hence, it can be concluded that WA composites have high stability and reusability which are essential for their actual application.

4.3.3.5 Antibacterial activity under visible light irradiation

Fig. 4.12 Log reduction of *E. coli* by the as-prepared photocatalysts (0.5 g L^{-1}) in dark and under visible light (a), inset is the inactivation efficiency within 2 h; Log reduction of *B. subtilis* by as-prepared photocatalysts (0.5 g L^{-1}) in dark and under visible light (b), inset is the inactivation efficiency within 2 h.

Ag NPs possess excellent antibacterial effects in inactivating many pathogens (Lee, Yeo et al. 2003, Lok, Ho et al. 2006). However, the aggregation trend of pure Ag NPs (Fig. S8) will reduce their efficiency in application (Lok, Ho et al. 2006, Lok, Ho et al. 2007, Marambio-Jones and Hoek 2010). Here we used WO₃ nanoplates as supporter of Ag NPs to assure their well dispersion and for the first

time we explored the photocatalytic antibacterial performance of WA samples as comparison to WO_3 .

The log reduction results of *E. coli* and *B. subtilis* are illustrated in **Fig. 4.12**. Briefly, pure WO_3 showed weak antibacterial efficiency (< 2 -log reduction) even under light irradiation. After Ag NPs were loaded, the growth of *E. coli* and *B. subtilis* was significantly inhibited. Complete suppression was observed for all WA samples after 2 h irradiation confirming that Ag NPs were able to effectively enhance their antibacterial performance with small loading amounts. On the other hand, light irradiation also can remarkably improve the antibacterial performance suggesting that photocatalytic antibacterial effect is another contributor to the disinfection performance of WA composites.

Fig. 4.13 SEM images of *E. coli* cells treated by light control (a), WA3 for 2h (b and c); *B. subtilis* cells treated by light control (d), WA3 for 2h (e and f).

After treating, the surface structure and morphology of *E. coli* and *B. subtilis* were observed by SEM. Without any catalyst, the cells of *E. coli* and *B. subtilis* still kept their normal intact shape (**Fig. 4.13 (a)** and **(d)**). By contrast, after treating by WA3 for 2 h, both *E. coli* and *B. subtilis* cells showed obvious shape changes (**Fig. 4.13 (b), (c), (e)** and **(f)**). The cells shrank greatly indicating the walls and

membranes of these cells were seriously damaged, and the intracellular molecules were leaked out. This leakage is fatal which is supported by the cell viability.

The huge difference in antibacterial activity between WO_3 and WA composites could be ascribed to their different antibacterial mechanisms as illustrated in **Fig. 4.9**. For WO_3 , photocatalytic property may be the only contributor to its sterilizing capability. WO_3 could spontaneously generate electron (e^-) and cavity (h^+) under visible light illumination. The cavities formed are capable to oxidize the OH^- and H_2O absorbed on WO_3 to $\cdot\text{OH}$. Then the $\cdot\text{OH}$ attacks and decomposes the cell wall and membrane of the bacteria around the WO_3 nanoplates (Pathway ③ in **Fig. 4.9**), leading to the leakage of intracellular molecules and subsequently the death of cells (Shi, Zhang et al. 2011). However, the low light absorption ability in visible light range would significantly limit its photocatalytic antibacterial activity and would decrease drastically when light source is removed.

For WA composites, two factors will co-contribute to their antibacterial performance. One is the antibacterial effect of Ag NPs. Both metallic Ag (pathway ① in **Fig. 4.9**) and Ag^+ released by metallic Ag (pathway ② in **Fig. 4.9**) are excellent antibacterial agents (Lehninger, Nelson et al. 1993, Feng, Wu et al. 2000, Holt and Bard 2005, Lok, Ho et al. 2006). Additionally, antibacterial efficiency caused by Ag and Ag^+ can be further enhanced by the photoactive of Ag^+ and the photochemical reaction of the Ag-cysteine complex under irradiation, which would inhibit the enzymatic function of related proteins. Another factor is the radical attacking generated by their photocatalytic ability (Kim, Lee et al. 2008, McEvoy and Zhang 2014) just like WO_3 , where radicals ($\text{O}_2^{\cdot-}$, $\cdot\text{OOH}$, H_2O_2 , and $\cdot\text{OH}$) can be efficiently produced and attack bacterial cells.

4.4. Conclusions

WO₃ nanoplates with uniform size were synthesized using one step hydrothermal method. After modifying WO₃ with Ag NPs, enhanced SAM degradation efficiency was achieved under visible light irradiation. Such improved photocatalytic performance can be assigned to the LSPR effect of Ag NPs by broadening the absorption range extensively to the visible light region. In addition, Ag NPs on the surface of WO₃ can play as electron trapping centers which could improve the charge separation in photocatalytic process. However, this does not mean that the more Ag NPs loaded, the higher efficiency would be achieved. Excessive loading of Ag may inhibit the photocatalytic efficiency just like WA3 had lower degradation efficiency compared to WA2. Moreover, LC/MS/MS was employed to detect the degradation intermediates generated during the photocatalytic process under visible light irradiation, and a possible SAM degradation pathway was consequently proposed. In addition to SAM photodegradation, WO₃-Ag composites were found to present good antibacterial performance towards *E. coli* as well as *B. subtilis* compared with pure WO₃ under visible light irradiation. In particular, the antibacterial effect of metallic Ag and Ag⁺ and the photocatalytic antibacterial activity of WO₃-Ag composites may be the two important factors leading to the significantly enhanced antibacterial activity under the visible light irradiation. This work shows that various WO₃-Ag composites with different Ag loading contents could be simply synthesized and they present potential as photocatalysts in treating wastewater contaminated by SAs as well as pathogens.

Nevertheless, even though the introduction of Ag could remarkably improve that photocatalytic performance of WO₃, it is also important to point out that the employment of Ag into the system may pose potential threats to the environment if the reaction time is extended. Such prolonged reaction time may result in the continuous accumulation of Ag⁺ in the environment, and may eventually exceed the

SMCL standard. Therefore, take this into consideration, it is necessary to search for other kinds of materials to act as efficient co-catalysts while would not have negative effect to the environment.

CHAPTER 5 PERFORMANCE OF WO₃-g-C₃N₄ COMPOISTES FOR SULFAMETHOXAZOLE ELIMINATION VIA PHOTODEGRADATION

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5.1 Introduction

From **Chapter 3** and **4**, it is worth noting that WO₃ can be regarded as a more promising photocatalyst candidate as a result of its narrow band gap, simple synthesis method, and better light absorption capability. In **Chapter 4**, Ag NPs were proved to be able to significantly promote the photocatalytic performance of WO₃. However, an unavoidable issue that cannot be neglected is the stability of the photocatalysts considering the fact of Ag⁺ leaching. Though by controlling the reaction time, the concentration of Ag detected was below the SMCL standard, the potential threat still exists if the reaction time was prolonged. Thereby, it is critical to search other kinds of more desirable co-catalysts generating more active, stable and less hazardous heterogeneous photocatalysts.

In the following work, efforts were devoted to seeking an appropriate semiconductor to work as co-catalyst of WO₃ to construct a Z-scheme photocatalytic system. Z-scheme photocatalytic system was considered because it is suggested to possess not only high charge carrier separation efficiency but also strong redox ability in comparison to typical heterojunctions (Hong, Jiang et al. 2016, Ye, Fang et

al. 2016, Cui, Ding et al. 2017). In particular, direct solid-state Z-scheme system is usually composed by two semiconductors where the photo-excited electrons of the semiconductor with a lower CB could recombine with the holes of the other semiconductor with a higher VB at the solid heterostructure surface (Li, Zhou et al. 2015).

Therefore, to successfully construct a WO_3 -based Z-scheme photocatalytic heterostructure, one of the most important issues is to search suitable semiconductor materials which could form WO_3 -based Z-scheme photocatalytic heterostructures driven by visible light. As mentioned earlier, g- C_3N_4 is a kind of π -conjugated semiconductor with a narrow band gap (2.7 eV) (Xiang, Yu et al. 2011, Katsumata, Motoyoshi et al. 2013, Chen, Hu et al. 2014). More importantly, previous studies verified that g- C_3N_4 has suitable band edges which well match with those of WO_3 to form direct solid-state Z-scheme photocatalytic system (Chen, Hu et al. 2014, Jin, Murakami et al. 2014, Katsumata, Tachi et al. 2014, Cui, Ding et al. 2017), where the photogenerated electrons in CB of g- C_3N_4 will exhibit strong reducibility and the holes in VB of WO_3 will present strong oxidizability. Meanwhile, with a 2D nanosheets structure, g- C_3N_4 can provide larger surface area for pollutants adsorption as well as more active sites for redox reactions.

Till now, several studies have reported construction of WO_3 -g- C_3N_4 heterojunctions as photocatalysts with improved photocatalytic performance towards dye degradation, CO_2 reduction and water splitting could be achieved (Huang, Xu et al. 2013, Katsumata, Motoyoshi et al. 2013, Aslam, Cao et al. 2014, Chen, Hu et al. 2014, Katsumata, Tachi et al. 2014, Ohno, Murakami et al. 2014, Yang, Hu et al. 2014, Li, Wei et al. 2016, Wang, Qin et al. 2017). Nevertheless, to the best of our knowledge, there is no previous study focusing on the possible application of WO_3 -g- C_3N_4 composites for antibiotic elimination. Hence, here another typical antibiotic from SA class, namely SMX, was chosen as the degradation target to

evaluate the photocatalytic performance of the as-prepared $\text{WO}_3\text{-g-C}_3\text{N}_4$ composites.

SMX is one of the top-selling antibiotics in both human and veterinary medicine (Collado, Buttiglieri et al. 2013). As a result, SMX is frequently detected in the water cycle including wastewater, surface water as well as drinking water posing threats to both human health and the environment (Ji, Ferronato et al. 2014, Li 2014, Schaider, Rudel et al. 2014, Liu, Zhang et al. 2016). More importantly, SMX presents high concentration among the existing pharmaceuticals classes and has been listed as among the 30 most frequently detected organic wastewater contaminants as reported by the US Geological Survey (Schaider, Rudel et al. 2014) as well as the top 10 high priority pharmaceuticals identified in a European assessment of pharmaceutical and personal care products (PPCPs) (Lin, Yu et al. 2016).

In addition, SMX is reported to one of the most refractory pharmaceuticals in estuarine and coastal surface water samples and it as a long half-life of 85 to more than 100 days (Straub 2015, Kassotaki, Buttiglieri et al. 2016). SMX has two dissociation constant (pK_a) values at 1.6 and 5.7, therefore, SMX is able to exist in a cationic, neutral or anionic form (Scheme S1) depending on the pH range (Hou, Zhang et al. 2013, Dlugosz, Zmudzki et al. 2015). Between $\text{pK}_{a,1}$ and $\text{pK}_{a,2}$, SMX exists mainly in the form of neutral molecules, hence, the predominant form is non-protonated SMX at pH 3.0 and the negatively charged component of SMX accordingly increased when the pH was elevated to 5.2. Subsequently, at higher pH such as 7.0 and 10.0, deprotonated form of SMX will correspondingly become the predominant species.

Fig. 5.1 The SMX structures at different pH values: $\text{pK}_{a1} = 1.7$ and $\text{pK}_{a2} = 5.6$.

However, current wastewater treatment plants (WWTPs) present very limited removal efficiency towards SMX as well as other recalcitrant compounds (Hu, Flanders et al. 2007, Kosma, Lambropoulou et al. 2014, Wang, Wu et al. 2015), While here, we synthesized different WO_3 -g- C_3N_4 composites with well controlled morphology and good crystallinity as direct solid-state Z-scheme photocatalysts to explore their capability to degrade SMX.

5.2 Experimental Part

5.2.1 Materials

Melamine, hydrochloric acid (HCl, 35%), ethanol, sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), *iso*-propanol (IPA), benzoquinone (BQ) and sodium oxalate (SO) and sulfamethoxazole (SMX) were purchased from Sigma-Aldrich. All chemicals were used as received and no further purification was needed.

5.2.2 Preparation of g- C_3N_4

Pristine g- C_3N_4 was prepared by heating melamine in a tube furnace. A certain amount of melamine was put into an alumina crucible which was firstly heated at 500 °C for 2h and was further heated at 520 °C for 2 h with a temperature rise rate of 10 °C/min. After reaction, the alumina crucible was cooled down naturally to room temperature. The as-prepared g- C_3N_4 was collected and ground into powder.

5.2.3 Synthesis of WO_3 -g- C_3N_4 composites

One step hydrothermal method was applied to prepare WO_3 -g- C_3N_4 heterogeneous composites. First, g- C_3N_4 was dispersed in DI water with the assistance of ultrasonicator to form a stable suspension with a concentration of 2.0 g L^{-1} . Then 100 mg of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in certain volume (4 ml, 6 ml and 8 ml) of above g- C_3N_4 suspension. The total volume was set to 10 mL and

certain amount of water was added accordingly. After that, 5 mL 35% HCl was slowly and carefully added under continuous stirring. The suspension was then transferred to a 45 mL Teflon-lined stainless steel autoclave to undergo a heating process for 6 h at 150 °C. After cooling down naturally, the sample was collected and washed with ethanol and DI water for several times before being dried by vacuum freeze drier. With different g-C₃N₄ amounts, these three samples were named WCN-4, WCN-6 and WCN-8, respectively. The pure WO₃ samples prepared without g-C₃N₄ was used as control.

5.2.4 Materials Characterization

The SEM, TEM, XRD, UV-Vis, PL, Raman and XPS analysis was same as that of Chapter 4.

5.2.5 Photocatalytic activity test for SMX degradation

Photocatalytic activity of pure WO₃ nanoplates and its various WCN composites was evaluated by degradation of SMX (10 mg L⁻¹) using a 1.5 AM solar simulator (NEWPORT, USA) with a 300 W Xe arc lamp. To control wavebands in specific ranges 420-630 nm (visible light), dichroic mirrors were utilized. To remove the UV residual, a polycarbonate filter was utilized. In a typical experimental procedure, 20 mg sample was firstly dispersed into 20 mL of DI water in the reaction vessel of 250 mL, and then mixed with 20 mL of 20 mg L⁻¹ SMX solution and the final SMX concentration was 10 mg L⁻¹. After that, the mixture was continuously stirred for 1 h in the dark to reach the adsorption equilibrium. The photocatalytic test started when the solar simulator was turned on and samples was taken at various time intervals by drawing 3.0 mL reaction mixture. The samples were immediately centrifuged and filtered with 0.45 µm cellulose acetate syringe membrane filters. The SMX concentration was analyzed by high performance liquid chromatography (HPLC) and the Operating conditions of HPLC can be found in APPENDIX A5.1.

The total organic carbon (TOC) remaining in the solution was determined with a TOC analyzer (Analytikjena multi N/C 2100). The effect of initial pH (3.0, 5.0, 7.0 and 9.0) was studied and the pH was carefully adjusted with 0.1 M HCl and 0.2 M NaOH. Different radical scavengers including SO, BQ and IPA (0.5 mM) was applied to investigate the formation of possible radicals in the photocatalytic process.

5.3 Results and discussion

5.3.1 Crystal structure and morphology characterization

The phase and composition of the as-prepared g-C₃N₄, pure WO₃ and various WCN composites were investigated by XRD as presented in **Fig. 5.2 (a)**. The XRD pattern of bare WO₃ was in good agreement with the standard XRD pattern of m-WO₃ (PDF NO; 01-083-0951). In the XRD pattern of g-C₃N₄, mainly an intensive diffraction peak at 27.2° can be observed corresponding to the (002) plane which is the characteristic interplanar stacking structures of graphic materials (Dong, Wu et al. 2011, Xu, Wu et al. 2013, Yang, Kuznietsov et al. 2013, Li, Dong et al. 2016). All WCN composites presented similar XRD pattern to WO₃ and the peaks detected are sharp and strong, implying that high crystallinity of WO₃ on g-C₃N₄ sheets. With the increase amount of g-C₃N₄, the (002) plane can be observed in WCN-6 and WCN-8, where slightly increased peak intensity can be found with increased amount of g-C₃N₄, which indicates the coexistence of WO₃ and g-C₃N₄.

The morphology of WCN composites was observed by SEM as shown in **Fig. 5.3**. The particle size of WO₃ covered on g-C₃N₄ was around 150-250 nm. Aggregation of WO₃ nanoparticles could be clearly spotted on WCN-4 and WCN-6 (**Fig. 5.3 (a)** and **(b)**) while uncovered g-C₃N₄ surface can be seen on WCN-8. **Fig. 5.3 (d)** presents the TEM image of WCN-8, which is in consistent with the SEM

observation where bare g-C₃N₄ could be observed. Moreover, the lattice fringes of WO₃ on g-C₃N₄ was found to be 0.376 nm which is in good agreement with the (020) planes of m-WO₃ (**Fig. A5.1**). Hence, it is clear that coupling with g-C₃N₄ would not affect the nucleation and growth of WO₃ since no significant lattice distortion can be found.

Fig. 5.2 Comparison of XRD patterns of WO₃, g-C₃N₄, WCN-4, WCN-6 and WCN-8 (a); Raman spectra of WO₃, g-C₃N₄, WCN-4, WCN-6 and WCN-8 (b).

The chemical composition of the as-prepared WCN-composites was studied by XPS spectra together with pure g-C₃N₄ and WO₃. As displayed in **Fig. 5.4 (a)**, the XPS survey of g-C₃N₄ contained element C, N and O, while from the XPS survey of pure WO₃, the elements found were W, O and C. It is worth noting that, in addition to W, O, C, the appearance of element N at around 400 eV can also be observed in the survey spectra of all three WCN composites indicating the combination of WO₃ and g-C₃N₄.

Fig. 5.3 SEM images of WCN-4 (a), WCN-6 (b), WCN-8 (c) and TEM of WCN-8 (d).

To study the possible influence caused by $g\text{-C}_3\text{N}_4$ introduction, the high resolution spectra of C, N and W were conducted using WCN-8 as an example. As illustrated in **Fig. 5.4 (b)**, C 1s spectra mainly showed two peaks locating at 284.8 and 288.2 eV which can be assigned to sp^2 C-C bonds and sp^2 -bonded carbon in N-containing aromatic rings (N-C=N) (Jiang, Zhu et al. 2016), respectively. In the N 1s spectra (**Fig. 5.4 (c)**), the main peak centered at 398.3 eV can be ascribed to sp^2 -bonded N in the triazine ring (C-N=C) of $g\text{-C}_3\text{N}_4$, while another two smaller peaks at 399.7 eV and 401.1 eV are in corresponding to the tertiary N in $\text{N}(\text{C})_3$ units and amino groups with a hydrogen atom (C-N-H), respectively (Huang, Xu et al. 2013, Lu, Pei et al. 2014, Li, Wei et al. 2016). In the case of W 4f, as displayed in **Fig. 5.4**, the typical binding energy values of W^{6+} were observed at 35.9 eV and 38.0 eV presenting W 4 $f_{7/2}$ and W 4 $f_{5/2}$ from bare WO_3 . However, compared to the pure WO_3 , the binding energy values of WCN-8 shift slightly to the lower energy

region (35.6 eV and 37.6 eV), which may originate from the interaction between WO_3 and $\text{g-C}_3\text{N}_4$.

Fig. 5.4 Comparison of XPS survey of WO_3 , $\text{g-C}_3\text{N}_4$, WCN-4, WCN-6, and WCN-8 (a); C 1s spectra of WO_3 , $\text{g-C}_3\text{N}_4$ and WCN-8 (b); N 1s spectra of $\text{g-C}_3\text{N}_4$ and WCN-8 (c) and W 4f spectra of WO_3 and WCN-8 (d).

The chemical composition of the as-prepared WCN-composites was studied by XPS spectra together with pure $\text{g-C}_3\text{N}_4$ and WO_3 . As displayed in **Fig. 5.4 (a)**, the XPS survey of $\text{g-C}_3\text{N}_4$ contained element C, N and O, while from the XPS survey of pure WO_3 , the elements found were W, O and C. It is worth noting that, in addition to W, O, C, the appearance of element N at around 400 eV can also be observed in the survey spectra of all three WCN composites indicating the combination of WO_3 and $\text{g-C}_3\text{N}_4$. To study the possible influence caused by $\text{g-C}_3\text{N}_4$ introduction, the high resolution spectra of C, N and W were conducted using

WCN-8 as an example. As illustrated in **Fig. 5.4 (b)**, C 1s spectra mainly showed two peaks locating at 284.8 and 288.2 eV which can be assigned to sp^2 C-C bonds and sp^2 -bonded carbon in N-containing aromatic rings (N-C=N) (Jiang, Zhu et al. 2016), respectively. In the N 1s spectra (**Fig. 5.4 (c)**), the main peak centered at 398.3 eV can be ascribed to sp^2 -bonded N in the triazine ring (C-N=C) of g-C₃N₄, while another two smaller peaks at 399.7 eV and 401.1 eV are in corresponding to the tertiary N in N-(C)₃ units and amino groups with a hydrogen atom (C-N-H), respectively (Huang, Xu et al. 2013, Lu, Pei et al. 2014, Li, Wei et al. 2016). In the case of W 4f, as displayed in **Fig. 5.4**, the typical binding energy values of W⁶⁺ were observed at 35.9 eV and 38.0 eV presenting W 4 f_{7/2} and W 4f_{5/2} from bare WO₃. However, compared to the pure WO₃, the binding energy values of WCN-8 shift slightly to the lower energy region (35.6 eV and 37.6 eV), which may originate from the interaction between WO₃ and g-C₃N₄.

To investigate the interaction between WO₃ and g-C₃N₄ in the WCN composites, Raman spectra and FTIR spectra were conducted. **Fig. 5.5 (a)** presented the Raman spectra of pure WO₃, g-C₃N₄ and three WCN composites to investigate their phase structures. In the case of pure WO₃, five typical peaks can be observed including peak at 132 cm⁻¹ assigning to the lattice vibration, 272 cm⁻¹ and 326 cm⁻¹ attributing to δ (OW-O) bending mode (Bai, Zhang et al. 2014), 717 cm⁻¹ and 805 cm⁻¹ originating from the ν (O-W-O) vibrational stretching mode of the W-O-W bridging oxygen in the WO₆ octahedral units (Daniel, Desbat et al. 1987, Santato, Odziemkowski et al. 2001, Su, Lin et al. 2009, White, Jang et al. 2010, Xu, Yin et al. 2014).

Fig. 5.5 Comparison of Raman spectra (a) and FTIR spectra (b) of pure $\text{g-C}_3\text{N}_4$, WO_3 and WCN-4, WCN-6 and WCN-8.

On the other hand, the Raman spectrum of pure $\text{g-C}_3\text{N}_4$ presented a series of characteristic peaks in the range from 400 to 2000 cm^{-1} attributing to the C-N stretching (Martin, Qiu et al. 2014). With regard to the three WCN composites, both characteristic peaks of WO_3 and $\text{g-C}_3\text{N}_4$ were clearly observed. With the increase of $\text{g-C}_3\text{N}_4$ amount in the WCN composites, the intensity of peaks originated from $\text{g-C}_3\text{N}_4$ increased consequently. At the same time, the band at 717 cm^{-1} was obviously broadened in the three WCN composites, while slight peak shift can be found. In particular, the peak at 717 cm^{-1} shifts to 711 cm^{-1} in WCN-8. Such changes may be caused by the formation of chemical bonds between $\text{g-C}_3\text{N}_4$ and WO_3 suggesting that WO_3 are chemically grafted onto the $\text{g-C}_3\text{N}_4$ rather than physical adsorption (Guo, Li et al. 2012, Esfandiar, Irajizad et al. 2014). Such association between $\text{g-C}_3\text{N}_4$ and WO_3 would benefit the charge transfer and therefore enhance the charge separation upon photocatalytic reactions (Guo, Li et al. 2012, Jiang, Zhu et al. 2016).

Fig. 5.5 (b) illustrates the FTIR spectra of the samples. For pure WO_3 , typical peaks at 819 and 770 cm^{-1} were attributed to O-W-O stretching vibration (An, Yu et al. 2012, Bai, Zhang et al. 2012, Zhu, Sun et al. 2017). On the other hand, a series of absorption peaks appeared in the fingerprint range of 1200 to 1700 cm^{-1}

including peaks centered at 1243, 1324, 1412, 1460, 1575, and 1634 cm^{-1} , stemming from typical stretching modes of C-N heterocycles (Huang, Xu et al. 2013, Zang, Li et al. 2013, Ding, Liu et al. 2015, Li, Wei et al. 2016, Liu, Wang et al. 2017). Moreover, peak located at 807 cm^{-1} is originated from the breathing mode of triazine units (Huang, Xu et al. 2013, Lu, Pei et al. 2014, Ding, Liu et al. 2015). The broad band in the range of 2800 to 3600 cm^{-1} may come from the coupling of N-H stretching vibration and catechol O-H stretching vibration. Particularly, from the FTIR spectra of WCN composites the characteristic peaks of both WO_3 and g- C_3N_4 can be noticed. More importantly, with the increase of g- C_3N_4 amount in the composites, strong peak intensities were spotted. Nevertheless, the peak at 807 cm^{-1} cannot be observed in all three WCN composites which may be caused by the overlap of bands of WO_3 in this region. In addition, red shift of peak centered at 1243 cm^{-1} can be found in the WCN composites where the location was at 1261 cm^{-1} in WCN-8. Such phenomenon indicates the existence of interaction between g- C_3N_4 and WO_3 , which weakens the force between C and N atoms as reported in the g- C_3N_4 -CdS composites (Lu, Pei et al. 2014, Ding, Liu et al. 2015). In agreement with the XPS and Raman results, the interaction between g- C_3N_4 and WO_3 would benefit the migration of photogenerated charger carriers and subsequently improve the photocatalytic performance of WCN composites (Shang, Chen et al. 2017).

5.3.2 Optical properties

The optical properties of the as-synthesized samples were characterized by UV-vis DRS spectra and PL spectra as illustrated in **Fig. 5.6 (a)**. Pure WO_3 mainly exhibited absorption in the UV light range and its distinct absorption edge is at around 470 nm. On the other hand, the absorption edge of g- C_3N_4 was at around 440 nm. For WCN composites, they presented significantly broader absorption edges which shift to the longer wavelength into visible light range. Moreover, the

absorption intensities in the visible light range remarkably increased with increased amount of g-C₃N₄. These results indicate the effective formation of tight chemical bonded surfaces between WO₃ and g-C₃N₄ which leads to shift to the lower energy region (Yan and Yang 2011, Sun, Yuan et al. 2012). The band gaps of the samples were calculated using modified Kubelka-Munk function, and g-C₃N₄ had a band gap of 2.63 eV, and the values were 2.41, 2.21, 2.00 and 1.91 eV for WO₃, WCN-4, WCN-6 and WCN-8, respectively. Thus, the introduction of g-C₃N₄ shows the ability to effectively narrow the band gaps of WCN composites, which may result from the interaction and synergism between g-C₃N₄ and WO₃. It is worth noting that such significantly improved light absorption spectra in the visible light range and lower band gaps would be favourable for improving the photocatalytic performance (Di, Xia et al. 2014, Di, Xia et al. 2015).

Fig. 5.6 UV-Vis DRS of WO₃, g-C₃N₄, WCN-4, WCN-6 and WCN-8 (a); PL spectra of WO₃, g-C₃N₄, WCN-4, WCN-6 and WCN-8 with the excitation wavelength at 332 nm (b).

Fig. 5.6 (b) depicts the PL spectra of g-C₃N₄, WO₃ and various WCN samples to investigate the effect of the migration and recombination of the photo-excited charges. Pure WO₃ existed emission profile in the range from 400 to 550 nm, where two peaks at around 461 and 480 nm were observed. While the main emission peak of pure g-C₃N₄ was centered at around 440-460 nm which is in agreement with previous

studies (Huang, Xu et al. 2013, Chai, Liao et al. 2014, Jiang, Zhu et al. 2016). This could be assigned to the band-band PL phenomenon with the energy of light approximately equal to the band gap energy of g-C₃N₄ (Huang, Xu et al. 2013, Chai, Liao et al. 2014, Jiang, Zhu et al. 2016). It is worth noting that WCN hybrids generally presented similar PL profile to WO₃, nevertheless, the emission peak intensity was drastically lower indicating reduced recombination rate of the photogenerated electron-hole pairs. Accordingly, the electron-hole pairs generated from light illumination can be more effectively separated and transferred, which would contribute to improved photocatalytic performance.

5.3.3 Photocatalytic activity towards SMX under visible light irradiation

Fig. 5.7 Degradation of SMX by various catalysts (WO₃, g-C₃N₄, WCN-4, WCN-6 and WCN-8) under visible light irradiation and SMX photolysis without addition of catalyst as control (a); TOC removal efficiency of SMX after 4 h reaction by WO₃, WCN-4, WCN-6 and WCN-8 after 4 h visible light irradiation (b). Conditions: catalyst = 0.5 g L⁻¹, SMX = 10 mg L⁻¹, no pH adjustment.

One of the most commonly used antibiotic SMX was used as target pollutant to evaluate the photocatalytic performance of as-synthesized WCN composites under visible light irradiation. Preliminary study illustrated that without addition of any photocatalyst, no noticeable change of SMX concentration was observed in dark even after 4 h, verifying that the hydrolysis of SMX is negligible. The adsorption of

SMX on WCN composites was also investigated, and results showed that the adsorption of SMX played a minor role ($< 10\%$) in the SMX removal for all samples (**Fig. A5.2**). **Fig. 5.7 (a)** presented the degradation result of SMX under visible light by three WCN composites as well as pure WO_3 . After 4 h visible light irradiation, the concentration of SMX slightly decreased when no catalyst was applied. It is worth noting that the SMX removal efficiency was increased to 34.5% when bare WO_3 was utilized. More importantly, the degradation performance was further enhanced with the use of WCN composites. In particular, the highest degradation efficiency was raised to 76.7% by WCN-8. Moreover, to analyze the mineralization degree of SMX, TOC test was conducted as illustrated in **Fig. 5.7 (b)**, and the TOC removal efficiency was consistent with the degradation efficiency where WCN composites achieved remarkably higher mineralization degree than WO_3 . Since WCN-8 showed the best performance among three WCN composites, it was utilized in the following studies.

Fig. 5.8 Degradation of SMX by WCN-8 at various pH under visible light (a). Conditions: catalyst = 0.5 g L^{-1} , SMX = 10 mg L^{-1} . Degradation of SMX by WCN-8 at different catalyst dosages under visible light (b). Conditions: SMX = 10 mg L^{-1} , no pH adjustment.

Fig. 5.8 presents the effect of pH and catalyst dosage on the photocatalytic activity of WCN-8. Without pH adjustment, the pH of the reaction solution was about 5.4,

and the photocatalytic efficiency reached to 76.7% as shown in **Fig. 5.8 (a)**. As can be seen from **Fig. 5.8 (a)**, SMX degradation could be strongly inhibited at pH 3.0, while at pH 7.0 and 9.0 decrease of photocatalytic activity was also observed. Such changes reveal that pH can be regarded as a critical parameter influencing the photocatalytic performance. Specifically, pH can alter the surface-charge properties of the photocatalysts and subsequently influence the dispersion of the photocatalysts. The pH_{pzc} of WCN-8 was tested to be around 2.57. Therefore, when pH is declined to around pH_{pzc} , agglomeration and sedimentation will occur which detracts the dispersion of particles. In addition, pH can affect the electrostatic interaction between the photocatalysts and SMX. When pH is raised to 7 and 9, the proportion of deprotonated form SMX increase consequently. Therefore, stronger repulsive force between negatively charged WCN-8 and deprotonated SMX will hinder the adsorption process and thereafter decrease the removal efficiency. According to the above result, SMX degradation over WCN-8 favors slight acidic conditions.

Fig. 5.9 Repeated photodegradation of SMX over WCN-8 under visible light irradiation (a); Influence of various scavengers on the photodegradation of SMX over WCN-9 under visible light irradiation (b). Conditions: catalyst = 1.0 g L^{-1} , SMX = 10 mg L^{-1} , no pH adjustment.

Catalyst dosage is another factor influencing photocatalytic performance. As depicted in **Fig. 5.8 (b)**, it is clear that the increase of WCN-8 dosage from 0.2 g L^{-1} to

1.0 g L⁻¹, the SMX removal efficiency was largely improved from 44.8% to 91.7%. Nevertheless, slight decline was observed when dosage reached to 2.0 g L⁻¹. Enhanced efficiency originated from increased catalytic loading may be the result of higher amount of active sites and the larger adsorption capability afforded by the catalysts (Oh, Lua et al. 2014). However, dosing too much catalyst would prevent the light penetration in the reaction suspension which would detriment the reaction efficiency.

In addition to pH and catalyst dosage, stability and reusability are also vital factors affecting the practical application of a photocatalyst. Therefore, the stability and reusability of the WCN-8 were evaluated by four cycles reactions. As revealed in **Fig. 5.9 (a)**, WCN-8 showed vigorous photocatalytic activity even after four cycles. Though slight decline can be observed, this may be caused by the unavoidable catalyst loss during the recycle process. After four cycles, XRD was applied to characterize the possible phase and structure changes of the catalyst (**Fig. A5.3**). No clear change can be found compared to the XRD pattern of fresh WCN-8, indicating WCN-8 had good stability.

To explore the possible radicals involved in the photocatalytic process, IPA, BQ and SO were applied as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and hole scavengers. As illustrated in **Fig. 5.9 (b)**, decline of photocatalytic activity to various degrees was spotted upon the addition of scavengers. In particular, IPA and SO showed stronger inhibition than BQ, suggesting that $\cdot\text{OH}$ and holes are the two main contributors in the photocatalytic process and $\text{O}_2^{\cdot-}$ is relatively less active.

According to above results, the possible photocatalytic mechanism of WCN-8 is proposed in **Fig. 5.10**. The significantly improved photocatalytic performance of WCN obtained may come from the synergistic effect of WO_3 and $\text{g-C}_3\text{N}_4$. As revealed by the UV-Vis DRS spectra (**Fig. 5.6 (a)**), as-prepared WCN composites present remarkably enhanced light absorption compared to both bare WO_3 and

g-C₃N₄, illustrating that WCN composites have better capability to harvest and utilize light. Moreover, as revealed in **Fig. 5.6 (b)**, WCN composites show strongly quenched PL spectra, which indicates that WCN composites show remarkably improved electron-hole separation efficiency.

According to previous studies, if the electrons in the CB of g-C₃N₄ (-1.15 eV *vs.* NHE) transfer to the CB of WO₃ (+0.81 eV *vs.* NHE) and the holes in the VB of WO₃ (+3.19 eV *vs.* NHE) will migrate to that of g-C₃N₄ (+1.49 eV), this process follows the common separation process which would result in decreased reduction capability of the electrons and the weakened oxidation capability of the holes (Ye, Fang et al. 2016, Zhu, Xia et al. 2017). In this case, the electrons accumulated in the CB of WO₃ cannot reduce O₂ to form O₂^{•-} since the CB of WO₃ is more positive than the standard redox potential of O₂/O₂^{•-} (-0.33 eV *vs.* NHE). Similarly, the holes stored in the VB of g-C₃N₄ cannot oxidize OH⁻ or H₂O to form [•]OH since the VB of g-C₃N₄ is less positive than the standard redox potential of [•]OH/OH⁻ (+2.4 eV *vs.* NHE) (Zhu, Xia et al. 2017). Hence, such mechanism is not effective at formation of active species which involved in the photodegradation process. Nevertheless, another possible mechanism, that is Z-Scheme system can be applied to explain the enhanced photocatalytic activity of binary composites (Zhu, Xia et al. 2017).

Particularly, here we propose that the effective electron-hole separation of WCN composites should be originate from WO₃ and g-C₃N₄ prefer to form a direct solid-state Z-scheme photocatalytic system since g-C₃N₄ has suitable band edges that well matched with WO₃. Under visible light irradiation, both g-C₃N₄ and WO₃ can be excited and produce photogenerated electron-hole pairs. The gap between the CB of g-C₃N₄ and the CB of WO₃ is about 1.96 eV, and this value is significantly larger than the gap between the VB of g-C₃N₄ and the CB of WO₃ (0.68 eV), therefore, due to the strong electrostatic attraction, the electrons on the

CB of WO_3 would quickly transfer to the VB of $\text{g-C}_3\text{N}_4$ and recombine with the photoexcited holes on the VB of $\text{g-C}_3\text{N}_4$. Hence, electrons will accumulate in the CB of $\text{g-C}_3\text{N}_4$ while holes will accumulate in the VB of WO_3 , leading to enhancement electron-hole separation efficiency and prolongation of the charge carrier lifetime (Li, Zhou et al. 2015, Jiang, Zhu et al. 2016). Consequently, the photoexcited electrons on the CB of $\text{g-C}_3\text{N}_4$ will present strong reducibility by reducing the adsorbed O_2 to $\text{O}_2^{\cdot-}$ as CB of $\text{g-C}_3\text{N}_4$ is more negative than the standard redox potential of $\text{O}_2/\text{O}_2^{\cdot-}$.

Fig. 5.10 Schematic illustration of SMX photodegradation process over WCN composites under visible light irradiation.

At the same time, the photoexcited holes on the VB of WO_3 will exhibit strong oxidizability (Hong, Jiang et al. 2016). On the VB of WO_3 , the holes can directly oxidize SMX adsorbed on the surface. More importantly, since the VB of WO_3 is more positive than the standard redox potential of $\cdot\text{OH}/\text{OH}^-$ they can react with water and/or surface hydroxyl (OH^-) to produce $\cdot\text{OH}$ to attack SMX as well. As a result, SMX can be effectively degraded due to radical attack under visible light illumination.

The possible intermediates generated during the photocatalytic process were studied by LC/MS/MS to investigate the photodegradation pathway of SMX. From

the result obtained in the ES (-) mode (**Fig. A5.4**), six peaks locating at m/z 286.1, 269.1, 268.2, 252.1, 172.2, and 156.1 were observed. Specifically, peak at m/z 252.2 represented the deprotonated ion of SMX (Mw 253). The peak at m/z 268.2 could be assigned to mono-hydroxylated derivatives (C1 and/or C2, Mw 269) which might be caused by the addition of an $\cdot\text{OH}$ radical to different positions of SMX. Meanwhile, the appearance of m/z 269.1 peak (C3 and/or C4, Mw 270) might originate from the further oxidization of the above mono-hydroxylated compounds by replacing $-\text{NH}_2$ with $-\text{OH}$. The peak sitting at m/z 286.1 might be di-hydroxylated compound (C5, Mw 287) due to $\cdot\text{OH}$ attack on the double bond of the isoxazole ring. C6 is the tautomeric form of C5, which could be generated when the radical attack opened the isoxazole ring (Abellán, Bayarri et al. 2007). The appearance of peak at m/z 156.1 (C7, Mw 157) confirmed the occurrence of S-N bond cleavage (Hu, Flanders et al. 2007, Trovo, Nogueira et al. 2009, Qi, Liu et al. 2014, Liu, Zhang et al. 2016), while peak at m/z 172.2 (Mw 173) indicates the generation of sulfanilic acid (C9) and/or hydroxyl substituted sulfanilic acid (C10). The radical attack would result in the aniline and isoxazole rings opened and these the organic intermediates would be finally mineralized to CO_2 and H_2O .

Consequently, a possible SMX degradation pathway can be accordingly proposed as shown in **Fig. 6.11**. First, $\cdot\text{OH}$ attack (hydroxylation) on the benzene ring or isoxazole ring can produce mono- or di- hydroxyl derivatives of SMX, and then the S-N bond would be broken under radical attack. The benzene ring and isoxazole ring would be opened, and finally these organic products would be oxidized and mineralized eventually.

Fig. 5.11 Proposed pathway for SMX photocatalytic degradation by WCN-8 composites.

5.4 Conclusions

In this work, $\text{WO}_3\text{-g-C}_3\text{N}_4$ composites with remarkably improved photocatalytic activity were successfully synthesized via a facile hydrothermal method. Improved photocatalytic performance upon SMX degradation was achieved by these $\text{WO}_3\text{-g-C}_3\text{N}_4$ hybrids under visible light illumination. The amount of $\text{g-C}_3\text{N}_4$ in the composites could affect the photocatalytic efficiency, and WCN-8 presented best

SMX photodegradation efficiently. In addition, the optimized reaction condition was explored and it showed that when catalyst dosage was 1.0 g L^{-1} , the best efficiency can be obtained without no adjustment of pH. Such enhanced performance could be assigned to the Z-scheme mechanism, where the well-matched band gap structure between $\text{g-C}_3\text{N}_4$ and WO_3 could form a direct solid-state Z-scheme heterojunction. Therefore, the accumulated electrons in the CB of $\text{g-C}_3\text{N}_4$ show high reducibility and the holes in the VB of WO_3 possess high oxidizability. These results illustrate that $\text{WO}_3\text{-g-C}_3\text{N}_4$ composites with proper amount of $\text{g-C}_3\text{N}_4$ has potential to be utilized as effective photocatalysts driven by visible light to remove SMX and other kinds of sulfonamide class antibiotics driven by visible light.

CHAPTER 6 EFFICIENT PHOTOCATALYTIC DEGRADATION AND REACTION PATHWAY OF SULFAMETHOXAZOLE OVER WO₃-RGO COMPOSITES

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6.1 Introduction

In **chapter 4**, Ag NPs were employed to construct S-M heterojunctions of WO₃, while g-C₃N₄ was adopted to modify WO₃ forming S-S heterojunctions (a direct solid-state Z-scheme heterojunction) in **chapter 5**. Such WO₃ heterogeneous were proved to be much more efficient than bare WO₃, indicating that they show the potential to be applied as effective photocatalysts in degrading organic compounds. As pointed out in **Chapter 5**, g-C₃N₄ with 2D nanosheets structure is able to provide larger surface area for pollutants adsorption as well as more active sites for redox reactions which would contribute to the photocatalytic process. However, it is suggested that the surface area of g-C₃N₄ is still low compared to those of carbon materials which possess much larger surface areas. More importantly, carbon materials, especially graphene and RGO, are recommended as excellent co-catalysts in fabrication of efficient S-C heterogeneous photocatalysts (Kamat 2010, Xiang, Yu

et al. 2012, Zhang, Yang et al. 2013). Specifically, in this chapter, RGO was selected because of its excellent properties.

As a new carbon material firstly experimentally discovered in 2004, graphene has unique 2D structure, large surface area, excellent electronic and physicochemical properties (Schedin, Geim et al. 2007, Dato, Radmilovic et al. 2008, Xiang, Yu et al. 2012, Fu, Xia et al. 2015, Hajishafiee, Sangpour et al. 2015). When being employed in a photocatalytic system, graphene and/or RGO can work not only as superior supporting matrixes for bonding functional components but also excellent electron mediators to adjust electron transfer, and thus restrain the recombination of photogenerated charges and subsequently improve the electron-hole separation (Xiang, Yu et al. 2012, Huang, Yue et al. 2013, Yang and Xu 2013). Together with the increased adsorption capacity for reactants, extended photoresponding range and enhanced visible light absorption intensity, graphene-based heterogeneous photocatalysts have shown improved photocatalytic activity.

To date, several researchers have reported the synthesis of WO_3 -RGO composites as gas sensor (An, Yu et al. 2012, Srivastava, Jain et al. 2012, Esfandiar, Irajizad et al. 2014, Su and Peng 2015), UV photodetector (Shao, Yu et al. 2013), photocatalysts (An, Yu et al. 2012, Thangavel, Elayaperumal et al. 2012, Wang, Bai et al. 2013, Chai, Li et al. 2014, Fu, Xia et al. 2015), and oxygen evolution catalysts in PEC system (Qin, Cao et al. 2011, Huang, Yue et al. 2013, Lin, Hu et al. 2013, Wu, Xu et al. 2013, Weng, Wu et al. 2014). However, it is essential to note that the synthesis of uniform scattered WO_3 with good crystallinity, controlled morphology and particle sizes on RGO sheets is still a challenge now (Guo, Li et al. 2012). Moreover, there has been no attempt to apply RGO- WO_3 composites to remove emerging pollutants. Though several studies reported the use WO_3 as photocatalyst to degrade antibiotics, the addition of inorganic oxidants was usually required.

Thus, in this study, the main objective was to explore a simple way to construct RGO-WO₃ composites with good crystallinity and small size WO₃. More importantly, the possible employment of such composites as photocatalysts to degrade SMX under visible light illumination towards SMX degradation without other additives.

6.2 Experimental Part

6.2.1 Materials

Natural graphite powder (LBG8010) was purchased from Superior Graphite (USA). Sulfuric acid (H₂SO₄, 95-98%), hydrochloric acid (HCl, 35%), potassium permanganate (KMnO₄), ethanol, Na₂WO₄·2H₂O, sodium nitrate (NaNO₃), IPA, BQ, SO and SMX were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30%) was supplied by VWR. All chemicals were used as received and no further purification was needed.

6.2.2 Preparation of Graphene oxide (GO)

GO was synthesized based on the modified Hummer's method (Hummers Jr and Offeman 1958, Tang, Mu et al. 2016). In brief, 2.5 g natural graphite powders and 2.5 g NaNO₃ were firstly mixed by 120 mL concentrated H₂SO₄ in an ice bath. Then, 15 g KMnO₄ was divided into five equal parts and was slowly added into above slurry under continuous stirring. The mixture was then allowed to react at 35 °C for 6 h and after that 150 mL DI water was carefully added to avoid boiling. The diluted solution was then kept at around 95 °C for 15 min and subsequently the suspension was poured into a beaker with 700 mL DI water. To purify the product, 60 mL H₂O₂ (30%) was added, and the obtained yellow solution was then washed by diluted HCl (10 wt%), dialyzed for one week and centrifuged with DI water until

the pH of the supernatant is close to 7. Finally, the obtained GO was dried at 80 °C and grinded into powders for further usage.

6.2.3 Synthesis of RGO-WO₃ composites

For the preparation of RGO-WO₃ composites, still one-step hydrothermal method was employed. First, GO was dispersed in DI water with the assistance of ultrasonicator forming a stable suspension with a concentration of 0.5 mg mL⁻¹. Then preset amount of Na₂WO₄·2H₂O (100 mg, 200 mg and 400 mg, respectively) were dissolved in 10 mL above GO suspension. 5 mL 35% HCl was then slowly added in the 10 mL mixture with continuous stirring. The suspension was transferred to a 45 mL Teflon-lined stainless steel autoclave to undergo a heating process for 8 h at 140 °C. After cooling down naturally, the sample was collected and washed with ethanol and DI water for several times before being dried by vacuum freeze drier. The samples obtained were annealed at 300 °C for 30 min to further reduce the GO sheets. With different Na₂WO₄·2H₂O dosages, the three samples were named RW-100, RW-200, and RW-400 respectively. The same method was used to prepare bare WO₃ without addition of GO.

The characterization and performance evaluation of catalysts was similar to those of **Chapter 5**. Particularly, the effect of initial pH (3.0, 5.2, 7.0 and 10.0) was studied and the pH was carefully adjusted with 0.1 M HCl and 0.2 M NaOH. RW-200 was chosen for the recyclability test, and the catalysts were collected, centrifuged and washed by water for three times before they were used for the next cycle. The degradation intermediates were detected by LC/MS/MS and the analysis method is illustrated in the APPENDIX A5.2.

6.3 Results and discussion

6.3.1 Morphology and crystal structure characterization

Fig. 6.1 Reaction Scheme of synthesizing RGO-WO₃ composites (a); Photos of different RGO-WO₃ composites and bare WO₃: WO₃ (b), RW-400 (c); RW-200 (d) and RW-100 (e).

The schematic illustration of various synthesis conditions is presented in **Fig.6.1**. Compared to the light yellow WO₃, the RGO-WO₃ composites had a gray color due to the introduction of RGO sheets and the samples color became darker with the increase of RGO amount. The morphology of as-synthesized RGO-WO₃ was observed by FESEM and TEM (**Fig. 6.2**). The WO₃ nanoplates formed on the RGO sheets had an average length of 150-200 nm. Due to the larger amount of WO₃ on the

RGO sheets, aggregation could be found in RW-400 (**Fig. 6.2 (a) and (b)**). By contrast, no obvious WO_3 aggregation was spotted from the TEM images of RW-200 and RW-100 (**Fig. 6.2 (d) and (f)**), and the WO_3 nanoplates scattered uniformly on the RGO sheets. The lattice fringes of WO_3 on RGO was 0.376 nm (**Fig. A6.1 (e)**) and was in consistent with the (020) planes of m- WO_3 . The TEM observation suggested that no significant lattice distortion occurred during the nucleation and growth of WO_3 on the RGO sheets.

Fig. 6.2 FESEM and TEM images of RW-400 (a and b), RW-200 (c and d), and RW-100 (e and f).

The composition and crystallinity of the as-prepared samples were firstly characterized with XRD (**Fig. 6.3**). The XRD pattern of pure WO_3 well followed the standard XRD pattern of m- WO_3 (PDF NO: 01-083-0951) (Xiao, Wang et al. 2014, Zhu, Liu et al. 2016). The sharp peaks indicate the good crystallinity and no other peak was found revealing the high purity of WO_3 obtained. For RGO- WO_3 composites, the XRD patterns were quite similar to that of WO_3 except that a broad peak locating at around $25\text{-}30^\circ$ were observed in the XRD pattern of RW-100. This broad peak was in agreement with the (002) planes originating from the graphitic

layered structure (Wang, Chou et al. 2013). More importantly, the distinguishing peak of GO at around 10° was not observed in the three RGO-WO₃ composites compared with the XRD pattern of GO (**Fig. A6.2 (a)**), verifying that GO had been successfully reduced to RGO. The XRD results confirm that the introduction of RGO would not affect the growth of new crystal orientations of WO₃ where RGO sheets can work as a platform for WO₃ to nucleate and grow.

Fig. 6.3 Comparison of XRD patterns of WO₃, RW-100, RW-200 and RW 400.

The phase structures of the obtained RGO-WO₃ composites were further explored by Raman spectra using WO₃ as control (**Fig. 6.4 (a)**). Five typical peaks situating at 132, 268, 326, 714 and 808 cm⁻¹ were detected in bare WO₃ belonging to the wavenumbers of m-WO₃. Particularly, the peak at 132 cm⁻¹ is assigned to the lattice vibration of crystalline WO₃, while the peaks at around 268 cm⁻¹ and 326 cm⁻¹ are attributed to $\delta(\text{O-W-O})$ bending mode (Bai, Zhang et al. 2014). The rest two peaks at 714 and 808 cm⁻¹ are originated from the $\nu(\text{O-W-O})$ vibrational stretching mode of the W-O-W bridging oxygen in the WO₆ octahedral units (Daniel, Desbat et al. 1987, Santato, Odziemkowski et al. 2001, Su, Lin et al. 2009, White, Jang et al. 2010, Xu, Yin et al. 2014).

Fig. 6.4 Raman spectra of WO_3 , RW-100, RW-200 and RW-400 (a); FTIR spectra of GO, WO_3 , RW-100, RW-200 and RW-400 (b).

The Raman spectra of the three RGO- WO_3 composites were quite similar to that of WO_3 in the 100-850 cm^{-1} region. Slight shift could be observed in the RGO- WO_3 Raman spectra compared to that of bare WO_3 . In particular, the vibrational stretching mode of $\nu(\text{O-W-O})$ at 808 cm^{-1} shifted to 805, 803 and 800 cm^{-1} for RW-400, RW-200 and RW-100, respectively. Similar phenomena have been observed in previous studies as well (Guo, Li et al. 2012, Weng, Wu et al. 2014, Fu, Xia et al. 2015), which may result from the strong interaction between RGO and WO_3 which implies that WO_3 are bonded to rather than physically adsorbed on RGO sheets. Moreover, two characteristic D (disorder carbon) and G (graphitic carbon) bands were detected in all three RGO- WO_3 composites, demonstrating the existence of RGO in the composites. The position of G band of RGO- WO_3 composites shifted up compared with that of GO (**Fig. A6.2 (b)**) which could be ascribed to the superior interactions between WO_3 and RGO sheets (Huang, Yue et al. 2013). The band intensity ratio (I_D/I_G) can be used to describe the degree of structural defects and a higher I_D/I_G is proposed to indicate a higher degree of structural defects (Luo, Zhang et al. 2011, Yu, Tian et al. 2015). Among three RGO- WO_3 composites, RW-200 had the highest I_D/I_G value (0.991) implying that RGO sheets in RW-200 contained more defects originated from incorporation such as formation of stronger or more

interfacial interaction like W-O-C band between WO_3 and RGO sheets (Yu, Tian et al. 2015). This further confirms the removal of oxygen containing groups (Benjwal, Kumar et al. 2015). Moreover, such strong interaction will benefit the charge transfer between WO_3 and RGO once being irradiated (Guo, Li et al. 2012, Weng, Wu et al. 2014).

The FTIR results are depicted in **Fig. 6.4 (b)**. The band at around 3431 cm^{-1} was found in all five spectra which match well with the stretching vibration mode of -OH and the physically adsorbed H_2O . In the FTIR spectrum of GO, characteristic absorption bands were observed at 1051 cm^{-1} (C-O), 1225 cm^{-1} (C-O-C), 1384 cm^{-1} (C-OH), 1630 cm^{-1} (C=C), and 1731 cm^{-1} (C=O), respectively (Huang, Yue et al. 2013, Chai, Li et al. 2014). For bare WO_3 , the broad absorption in the range of $500\text{-}1000\text{ cm}^{-1}$ were characteristic peaks of different O-W-O stretching vibrations in WO_3 crystal lattice (An, Yu et al. 2012, Bai, Zhang et al. 2012). In the FTIR spectra of three RGO- WO_3 composites, the characteristic bands of WO_3 still remained, at the same time bands originated from RGO can be found as well. In particular, the peak at 1225 cm^{-1} (C-O-C) could be spotted in all three RGO- WO_3 composites, and the band at 1731 cm^{-1} (C=O) was clearly detected in the spectrum of RW-100 though it was not significant enough to be observed in the RW-200 and RW-400 FTIR spectra due to the low RGO content. Moreover, a new peak at 1581 cm^{-1} corresponding to the aromatic skeletal C=C stretching vibration appeared, further proved the reduction of GO (Chen, Huang et al. 2014, Liu, Li et al. 2015).

XPS was applied to study the element composition and valence state of the as-prepared samples (**Fig. 6.5**). The overall XPS survey spectra of bare WO_3 and RGO- WO_3 composites confirmed the existence of element C, O and W (**Fig. 6.5 (a)**) and no other impurity element was discovered implying the high purity of the samples. From the high resolution spectra of W of WO_3 , two peaks located at 38.1 and 35.9 eV representing the two characteristic W $4f_{7/2}$ and W $4f_{5/2}$ peaks of W^{6+} in

WO₃, were found (**Fig. 6.5 (b)**) (Esfandiar, Irajizad et al. 2014, Weng, Wu et al. 2014, Zhang, Zhu et al. 2015).

Fig. 6.5 XPS survey of WO₃, RW-100, RW-200 and RW-400 (a); High resolution XPS spectra of C 1s for WO₃ and RW-200 (b), High resolution XPS spectra of O 1s from RW-200 (c), and high resolution XPS spectra of O 1s from RW-200.

Slight shift towards the higher binding energy of W 4f_{7/2} and W 4f_{5/2} doublets in the RGO-WO₃ composites was observed which may be caused by the interaction between WO₃ and RGO sheets. For example, the peaks moved 0.2 eV to the higher binding energy for RW-200 compared to those of WO₃. Similar O 1s spectra were observed among three RGO-WO₃ samples (**Fig. A6.4 (a-c)**), which could be de-convoluted to mainly three peaks. In the case of RW-200 (**Fig. 6.5 (d)**), the de-convoluted O 1s spectra consisted three peaks that could be assigned to W-O (530.6 eV), C-O-C (532.3 eV) and O=C-O (533.6 eV). By contrast, the O 1s

spectrum of WO_3 (**Fig. A6.3 (d)**) could be only divided into two peaks, W-O peak at 530.1 eV and another peak at 531.9 eV due to the surface hydroxide (OH^-) (Zhang, Li et al. 2013, Park, Lee et al. 2015). Thus, it is clear that the appearance of later two peaks in O 1s spectra of RGO- WO_3 composites was caused by RGO introduction.

The C 1s spectrum of pristine GO (**Fig. A6.3 (c)**) contained mainly four carbon bonds, including C-C/C=C (284.8 eV) originated from the graphitic sp^2 carbons; C-O-C (286.6 eV), C=O (287.1 eV), and O-C=O (288.8 eV) stemmed from oxygenate groups attached to the carbon atom (Yang, Zhai et al. 2010, Zhang, Xiong et al. 2011). According to the C 1s spectra, the C/O ratio of GO was calculated to be 0.884. The RGO- WO_3 samples showed similar C 1s spectra as shown in **Fig. A6.4 (d-f)**.

Take RW-200 as an example (**Fig. 6.5 (c)**), the main peak of C 1s could be dissociated into three peaks: C-C/C=C at 284.8 eV, C-O-C at 286.5 eV and O-C=O at 288.7 eV, respectively. It is worth noting that the dominant peak found in RGO- WO_3 samples was C-C/C=C while the intensity of the peaks related to oxygenate functionalities (such as C-O-C and C=O) was much weaker than those of the GO. In addition, the C/O ratio obtained from the C 1s spectra of three RGO- WO_3 samples were 2.86, 3.03 and 2.97 for RW-100, RW-200 and RW-400, respectively. The weaker peaks originated from oxygenate groups and the higher C/O ratios indicate that a large number of oxygen containing groups were successfully removed.

6.3.2 Optical properties

Fig. 6.6 (a) displays the UV-vis DRS spectra of WO_3 and three RGO- WO_3 composites. Bare WO_3 mainly presented light absorption in the UV range with the absorption on-set at 450 nm. By comparison, the RGO- WO_3 composites showed largely enhanced absorption in the visible light range (450-800 nm) resulted from RGO introduction as previously reported in other graphene-based composites (Sher

Shah, Park et al. 2012, Ning, Shao et al. 2016). Furthermore, the larger amount of RGO presented in the composites, the higher intensity could be achieved (RW-100 > RW-200 > RW-400). This enhanced visible light response could be ascribed to two possible reasons: (1) the background light absorption of RGO in the visible light region, and (2) the enhanced surface electric charge of WO₃ due to the possible electronic transition of $\pi \rightarrow \pi^*$ of RGO and $n \rightarrow \pi^*$ between the n orbit of the oxygen species of WO₃ and RGO (Ou, Lin et al. 2006, Peng, Zeng et al. 2011, Weng, Wu et al. 2014). The band gaps were calculated by using modified Kubelka-Munk function as plot in the inset of **Fig. 6.6 (a)**. RW-100 had a band gap of 2.15 eV, while band gap of RW-200 and RW400 was 2.65 and 2.70 eV, respectively. Compared with bare WO₃ (2.75 eV), the band gaps of RGO-WO₃ composites are remarkably narrowed which may come from the direct interaction between WO₃ and RGO sheets.

Fig. 6.6 UV-Vis DRS of WO₃, RW-100, RW-200 and RW-400 (a), inset of (a) is the plots of $(\alpha h\nu)^2$ vs. energy $h\nu$ of WO₃ and three RGO-WO₃ composites; PL spectra of WO₃, RW-100, RW-200 and RW-400 with the excitation wavelength at 325 nm (b).

Fig. 6.6 (b) illustrates the PL spectra of WO₃ and RGO-WO₃ samples. All four samples presented similar emission profile where mainly two peaks at around 461 nm and 480 nm could be observed. The stronger peak at 461 nm could be assigned to localized state in the band gap while the weaker one centered at 484 nm was attributed to the presence of oxygen vacancies or defects (Chang, Chou et al. 2007,

Su and Lin 2009, Tian, Ye et al. 2012, Katsumata, Oda et al. 2013, Zhang, Li et al. 2013, Jia, Ji et al. 2015). As revealed in **Fig. 6.6 (b)**, WO_3 displayed the highest PL intensity, while the peak intensities of three RGO- WO_3 were considerably diminished. Such quenched peak intensity indicates notably lower photogenerated electron-hole recombination rate in RGO- WO_3 composites. Accordingly, the electrons generated from light illumination can be more effectively separated and transferred where RGO sheets can act as an electron reservoir to accept and transfer electrons due to its better electron conductivity.

6.3.3 Photocatalytic activity towards SMX

6.3.3.1 SMX degradation by various photocatalysts

The photocatalytic activity of the as-prepared RGO- WO_3 composites was evaluated by the degradation of SMX under visible light illumination at room temperature and ambient pressure. Before applying visible light, SMX solution was continuously stirred for 3 h in dark without adding of any photocatalyst. No noticeable change of concentration was observed, demonstrating that the hydrolysis of SMX was negligible. Preliminary study found that the adsorption of SMX on all three RGO- WO_3 composites in dark was less than 8% indicating that the adsorption is not the main contributor to SMX removal (**Fig. A6.5**). The photodegradation of SMX without pH adjustment (about 5.2) over various catalysts is illustrated in **Fig. 6 (a)**. After 3 h visible light illumination without any catalyst, the concentration of SMX showed a very slight decrease (4.3%) while the degradation efficiency increased to 46.2% with the presence of WO_3 . Better degradation efficiency was found by all RGO- WO_3 catalysts. Particularly, almost complete removal (> 98%) of SMX was observed within 3 h when RW-200 and RW-100 were utilized. Meanwhile, as displayed in **Fig. 6.7 (a) inset**, RGO- WO_3 composites showed higher TOC removal efficiency than that of WO_3 . Generally, the TOC result was consistent with

the degradation efficiency indicating the degree of mineralization towards SMX. In the case of SMX solution without adding catalyst, the TOC change was not clearly observed.

Fig. 6.7 Degradation of SMX under visible light over WO_3 , RW-400, RW-200, RW-100 (a). Inset in (a) shows TOC removal efficiency of SMX with WO_3 , RW-400, RW-200, RW-100 after 3 h reaction. Photocatalytic degradation performance of RW-200 in SMX removal with the presence of various scavengers after 3 h (b). Conditions: catalyst = 1.0 g L^{-1} , SMX = 10 mg L^{-1} , no pH adjustment.

Fig. 6.8 Five cycles of SMX degradation with RW-200 as photocatalysts under visible light for 3 h. Condition: SMX = 10 mg L^{-1} , catalyst dosage = 1.0 g L^{-1} , no pH adjustment.

Though RW-100 showed slightly higher (0.4%) SMX removal efficiency than

RW-200, its poor recyclability due to low density and poorer dispersion in the reaction system hinder its application in real situation. By contrast, RW-200 displayed not only comparable photocatalytic activity to RW-100 but also good recyclability, and RW-200 remained vigorous photocatalytic performance even after five cycles (**Fig. 6.8**). Hence, RW-200 is a better candidate in practical application. Though slight loss of efficiency was found, this could be assigned to the unavoidable catalyst loss during the recovery process after each reaction cycle. Subsequently, RW-200 was applied in the following studies.

6.3.3.2 Mechanism for SMX photodegradation

Fig. 7.9 Schematic illustration of the proposed mechanism for the enhanced degradation of SMX by RGO-WO₃ composites under visible light irradiation.

According to the above results, RGO-WO₃ composites possessed significantly enhanced photocatalytic performance in degrading SMX under visible light irradiation. Such improvement could be assigned to three possible reasons. Firstly, the UV-Vis DRS spectra confirmed that the introduction of RGO had the ability to effectually narrow the band gap of WO₃ and subsequently extend its light response range to visible light range (Chen, Cai et al. 2010). Meanwhile, RGO could act as

electron trap and hence the photogenerated electrons could be transferred to the RGO sheets leading to the efficient electron-hole separation as verified by the suppressed PL spectra (Kamat 2011). Additionally, RGO sheets with a large surface area could work as a supporter to provide adequate adsorption sites as well as catalytic sites during the photocatalytic reaction (Xiang, Yu et al. 2012, Xiang and Yu 2013).

The possible mechanism of SMX degradation by RGO-WO₃ composites is portrayed in **Fig. 6.9**. When irradiated by visible light, WO₃ will absorb the incident photons generating electrons and holes. The excited electrons can transfer from CB of WO₃ to RGO sheets which owns a lower Fermi level ($E_F = -4.26$ eV) (Kamat 2011, Sher Shah, Park et al. 2012) and a better electrical conductivity (**Eqs (6.1-6.2)**). After that, the photogenerated electrons will be scavenged by dissolved oxygen (DO) in water resulting in effective electron-hole separation (**Eq (6.3)**) producing O₂^{·-} (Teoh, Scott et al. 2012). These O₂^{·-} will then turn to ·OOH which will combine with the trapped electrons to generate H₂O₂, and finally to produce ·OH radicals (**Eqs (6.4-6.7)**) (Wu, Liu et al. 1998). Simultaneously, the holes left on VB of WO₃ can react with water and/or surface hydroxyl (-OH) to form ·OH (**Eqs (6.7-6.8)**). After a series of reactions, the radicals generated attack SMX in the close vicinity resulting in the degradation and mineralization of SMX (**Eq (6.9)**).

To study the role of various radicals during the photocatalytic process, SO, IPA and BQ acting as h^+ , $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ scavengers were added as depicted in **Fig. 6.7 (b)**. Generally, the presence of BQ and IPA remarkably inhibited the degradation of SMX under visible light while the inhibition effect caused by SO was less significant. Such results illustrate that $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ were the two primary radicals generated by RW-200 that involved in the photocatalytic degradation of SMX under visible light irradiation while h^+ played a minor role.

6.3.3.3 Parametric optimization study: effect of pH and catalyst dosage

To optimize the photocatalytic performance, the effect of two most important parameters affecting SMX photodegradation, namely pH and catalyst dosage were investigated (**Fig. 6.10 (a) and (b)**) using RW-200 as photocatalyst. The reaction kinetics were estimated by fitting the data into the pseudo-first-order rate constant (See in the APPENDIX A6.2).

Fig. 6.10 Degradation of SMX under visible light by RW-200 at various pH (a). Condition: catalyst = 1.0 g L⁻¹, SMX = 10 mg L⁻¹. Degradation of SMX under visible light by RW-200 at different catalyst dosages (b). Conditions: SMX = 10 mg L⁻¹, no adjustment of pH.

At initial pH 7.0, the removal rate of SMX was comparable to the efficiency achieved without pH adjustment. However, the degradation efficiency of SMX declined remarkably when initial pH was 3 and 10. As revealed by the strongly

suppressed k values (**Fig. 6.10 (a)** inset), pH can be considered as one of the most important factors affecting the photocatalytic process of RGO-WO₃ composites since it may influence (1) the electrostatic interaction between the photocatalysts and targeted organic pollutants; (2) the dispersion of photocatalysts in the reaction system.

The pH_{pzc} , which means that net zero charge, of RW-200 was estimated to be 2.46 (**Fig. A6.7**). The surface activity of RW-200 can be affected by pH as verified in the preliminary study where particle agglomerations and quick precipitation occurred when pH was decreased to 2.46. Therefore, when pH was 3, which was close to pH_{pzc} , the poor dispersion and formation of particle agglomeration would strongly hinder the photocatalytic process. When pH was risen to a higher value, the proportion of negatively charged RW-200 increased. At pH 7.0, most SMX existed in deprotonated form and thereafter the repulsive force between negatively charged surface of RW-200 and the negatively charged SMX would inhibit the adsorption of SMX onto the catalyst surface, leading to a slightly drop of the degradation rate. Similarly, the stronger repulsive force would further hinder the SMX removal efficiently at pH 10.

The effect of catalyst loading was revealed in **Fig. 6.10 (b)** and it shows that increasing of catalyst dosage expedited SMX removal efficiency as confirmed by the k values where the highest value was achieved at dosage 1.0 g L⁻¹. Increase of catalyst loading would supply more available active sites for photocatalytic reactions as well as abundant effective surface area for adsorption process. Nevertheless, when the catalyst dosage was further increased to 2.0 g L⁻¹, slight reduction of SMX degradation rate was found which may be ascribed to the poorer light penetration in to the reaction system.

From the above study, it can be deduced that circumneutral or slight acidic pH would be beneficial to SMX degradation by RGO-WO₃ composites under visible light. Therefore, no further adjustment of pH is required in real application.

6.3.3.4 Proposed degradation pathway

To explore the intermediate products and photodegradation pathway of SMX, LC/MS/MS was utilized and the results were carefully analyzed. In the ES (-) mode (**Fig. A6.8**), peaks at m/z 286.1, 269.1, 268.2, 253.2, 252.2, 212.1, 196.1, 172.2, and 156.1 were detected. In particular, the peak at m/z 252.2 was referred to the deprotonated ion of SMX (Mw 253) and the appearance of peak at m/z 253.2 (C6, Mw 254) could be caused by the substitution of amino group ($-NH_2$) by hydroxyl group ($-OH$) as a result of $\cdot OH$ attack. The peak at m/z 268.2 was in consistent with mono-hydroxylated derivatives (C1 and/or C4, Mw 269) stemming from addition of an $\cdot OH$ radical to the SMX structure at different positions. These mono-hydroxylated compounds could be further oxidized where $-NH_2$ was replaced by $-OH$ as verified by the appearance of peak at m/z 269.1 (C2 and/or C3, Mw 270). Moreover, a di-hydroxylated compound (C5, Mw 287) was found at m/z 286.1 which could be ascribed to the $\cdot OH$ attack on the double bond of the isoxazole ring. Subsequently, radical attack was able to open the isoxazole ring and generate C9 (m/z 196.1, Mw 197) (Trovo, Nogueira et al. 2009) while the observation of m/z 212.1 (C10, Mw 213) could be attributed to the attachment of $\cdot OH$ radical on benzene ring of C5. Another possibility is that the following radical attack to C4 could result in isoxazole ring open which would give rise to the appearance of C7, the other tautomeric form of C5 (Abellán, Bayarri et al. 2007). C7 can be subsequently transformed to C8 (tautomeric of C9) as a result of radical attack on the aniline ring.

The peaks identified at m/z 156.1 (C11, Mw 157) indicates the cleavage of S-N bond as reported previously (Hu, Flanders et al. 2007, Trovo, Nogueira et al. 2009, Qi, Liu et al. 2014, Liu, Zhang et al. 2016), and the rise of peak at m/z 172.2 (Mw 173) implied the appearance of sulfanilic acid (C13) and/or hydroxyl substituted sulfanilic acid (C14). Different from previous reports, C12 with a molecular weight of 98 that originated from the opening of the isoxazole ring was not identified in this study.

However, degradation compound with a molecular weight of 99 (C15) was observed in the ES (+) mode (**Fig. A6.9**) which may result from the substitution of $-\text{NH}_2$ by $-\text{OH}$. Eventually, the aniline and isoxazole rings opened by radical attack and all the organic intermediates would be further mineralized to CO_2 and H_2O under visible light illumination.

On the basis of the detected intermediates, a possible degradation pathway of SMX is subsequently proposed as illustrated in **Fig. 6.11**, and this pathway mainly contains four steps, including: (1) $\cdot\text{OH}$ attack (hydroxylation) on the benzene ring or isoxazole ring with the formation of mono- or di- hydroxyl derivatives of SMX; (2) cleavage of the S-N bond; (3) bond cleavage of the benzene ring and isoxazole ring and (4) oxidation and mineralization of the organic intermediates. In brief, as a result of radical attack, SMX could be degraded and mineralized step by step generating smaller by products and CO_2 and H_2O eventually.

Fig. 6.11 Proposed pathway for SMX photocatalytic degradation by RGO- WO_3 composites.

6.4 Conclusions

To sum up, a facile one step hydrothermal method was developed to synthesize RGO-WO₃ composites with good photostability and recyclability. Compared with pure WO₃, all three RGO-WO₃ composites showed significantly improved photocatalytic activity under visible light irradiation. Among three RGO-WO₃ composites, RW-200 showed excellent photocatalytic activity and good dispersion, making it a more competitive candidate among the three as-prepared RGO-WO₃ composites. At the same time, catalyst dosage is proved to show a significant impact on the photocatalytic activity. In particular, the best SMX removal efficiency was achieved when RW-200 loading was 1.0 g L⁻¹. Additionally, SMX photodegradation over RW-200 can be significantly influenced by pH, where the near-neutral conditions showed the best process. It is important to note that this preference would benefit the practical application since most aquatic systems in reality is at circumneutral range.

Such improvement photocatalytic performance of RGO-WO₃ composites can be attributed to the introduction of RGO, which can effectively enhance the electron-hole separation and transportation as a result of its good electrical conductivity. Meanwhile, the light response of WO₃ was found to extend to the visible light range after combination with RGO, and this suggests that RGO-WO₃ composites are capable to more efficiently utilize visible light during the photocatalytic process. LC/MS/MS was utilized to investigate the intermediates generated during the photocatalytic reactions, and by analyzing the LC/MS/MS results, a possible SMX degradation pathway under visible light was consequently proposed, of which four steps may occur leading to the degradation and eventually mineralization of SMX.

In brief, in this chapter, a low-cost and simpler method to fabricate RGO-WO₃ composites was proposed. Such RGO-WO₃ composites can be regarded as potential

photocatalysts for environmental purification of organic pollutants.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In the first stage, p-type BiOCl nanodiscs was prepared via a simple hydrothermal method while S-M type BiOCl-Ag heterogeneous composites were obtained via a photo-reduction approach. Compared to bare BiOCl, BiOCl-Ag presented significantly enhanced photocatalytic performance (82.4% within 5 h) for the elimination of SAM under visible light irradiation. At the same time, BiOCl-Ag composites showed excellent antimicrobial effect under visible light where nearly 100% inactivation towards *E. coli* and *B. subtilis* in 2 h. Such enhancement can be ascribed to the reduced recombination rate of electron-hole pairs and the improved light absorption in the visible light range due to the SERS effect induced by Ag NPs.

In the second part of this study, n-type WO₃ nanoplates were synthesized by a facile one step hydrothermal method. In particular, WO₃ was chosen due to its narrower band gap and simpler synthesis method compared to those of BiOCl. To further increase its photocatalytic performance, different amounts of Ag NPs were deposited on the surface of WO₃ via a photo-reduction method generating various S-M type WO₃-Ag heterogeneous composites as VLD photocatalysts. Among three WA composites, WA2 was found to possess not only high efficiency (96.7% SAM removal within 5 h and nearly 100% inactivation of *E. coli* and *B. subtilis* within 2 h) but also good stability and reusability (low leaking amount of Ag⁺ within one cycle) making it an outstanding candidate. The amount of Ag NPs can notably affect the photocatalytic performance and by optimizing the main operation

conditions, the favorite reaction condition was found to be at slightly acidic conditions with a WA2 dosage of 1.0 g L^{-1} .

Though the loading of Ag NPs would endow excellent antimicrobial activity, the leaching of Ag^+ from WA composites may still show the potential threat to the environment, thereafter, in the next phase of this study, efforts were devoted to construct effectual WO_3 -based heterogeneous composites without usage of noble metals.

In the subsequent chapter, polymeric material g- C_3N_4 was applied to fabricated S-S heterojunctions together with WO_3 . The WO_3 -g- C_3N_4 composites obtained with different amount of g- C_3N_4 composites displayed remarkably improved photocatalytic activity towards SMX degradation under visible light illumination, and WCN-8 presented best efficiently ($> 90\%$ within 4 h). Such enhanced performance could be assigned to the Z-scheme mechanism, where the well-matched band gap structure between g- C_3N_4 and WO_3 could form a direct solid-state Z-scheme heterojunction. Therefore, the accumulated electrons in the CB of g- C_3N_4 show high reducibility and the holes in the VB of WO_3 possess high oxidizability.

In the last part of this study, RGO, an excellent carbon material was applied to modify WO_3 to form S-C type RGO- WO_3 composites as VLD photocatalysts. Compared with pure WO_3 , all three RGO- WO_3 composites showed significantly improved photocatalytic activity to SMX, and particularly RW-200 presented outstanding photocatalytic activity ($> 98\%$ within 3 h) and good dispersion, making it a more competitive candidate among the three as-prepared RGO- WO_3 composites. RGO could provide abundant surface area with active sites for SMX adsorption as well as photocatalytic reactions. More importantly, the introduction of RGO is able to significantly extend the visible light absorption of the composites and to act as effective electron trap to improve the electron-hole pairs separation rate.

Consequently, increased photocatalytic efficiency can be realized. In addition, the degradation intermediates were determined by LC/MS/MS and accordingly a possible degradation pathway was proposed.

Overall, in this thesis, various strategies were adopted to fabricate different kinds of effectual semiconductor-based heterojunctions as VLD photocatalysts, in which mainly three semiconductors, namely BiOCl, WO₃, and g-C₃N₄ were involved. Specifically, all the obtained heterogeneous catalysts, including BiOCl-Ag, WO₃-Ag, WO₃-g-C₃N₄ as well as RGO-WO₃ presented better photocatalytic ability than their pristine single phase semiconductors. Such heterogeneous has enhanced visible light absorption capability and better electron-hole separation and transportation. Thereafter, they can more efficiently utilize visible light of the solar spectrum, and to more effectively generate various ROS such as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, and $\cdot\text{OOH}$, which will initialize or accelerate the redox reactions and leading to degradation of organic pollutants and inactivation microbial cells. More importantly, WO₃-based composites seem to be better candidates as eco-friendly VLD photocatalysts due to their simple synthesis, narrower band gap as well as good stability. Especially the quick removal for SMX achieved by RGO-WO₃ implies their great potential in practical application.

7.2 Recommendations for future research

In this study, most efforts were made to develop novel and efficient materials as photocatalysts, which tended to benefit the photocatalysis process from a material developing point of view. Nevertheless, as revealed earlier, the practical application of this technology still faces various problems which cannot be neglected from the economic, engineering, and environmental points of view. Consequently, it is still a long way to go to realize the practical, economic and commercial application of photocatalysis process. In the future, there following studies can be recommended.

7.2.1 Evaluation of potential negative impacts of released nanoparticles

As described in **chapter 2**, the application of nanosized catalysts, may result in the release of manufactured nanoparticles to the environment, which would probably pose negative influences to not only the environment but also human health (Dreher 2004, French, Jacobson et al. 2009, Keller and Lazareva 2013, López-Serrano, Olivas et al. 2014). In **Fig. 7.1**, Nowack *et al*, summarized the possible pathways of nanoparticles entering the environment, where no matter how they are released (directly or indirectly), they would end up in soil or water. Though some nanoparticles may aggregate or be adsorbed thus showing less mobility, they can still enter the food chain leading to the risk of biomagnification of nanoparticles (EPA 2007, Nowack and Bucheli 2007, Karn, Kuiken et al. 2009).

Fig. 7.1 Proposed pathways from the anthroposphere into the environment, reactions in the environment and exposure of human (Nowack and Bucheli 2007).

Therefore, systematic study is required, including to investigate the mobility, bioavailability and toxicity of nanoparticles. However, our understanding is currently quite limited and these studies are still in the initial stage due to technique limitation, complexity of environmental conditions, diversity of nanomaterials, and unique physical and chemical properties of nanoparticles. Thus, collaborative among researchers from different disciplines are needed. Especially, a global database can be established to avoid repeated works, and to share latest results. The main issues to be solved can be summarized as below:

- (a) developing effective methods to detect the materials in the environment;
- (b) investigating the mobility and fate of nanoparticles in the environment;
- (c) developing methods to assess the potential hazardous effect of nanomaterials to human and other organisms as well as the environment;
- (d) establishing relevant rules and regulations to guide the progress of manufactured nanomaterials.

7.2.2 Configuration of photocatalytic membranes

Generally, the most common way to apply photocatalysts is to disperse them into water forming suspensions. However, this means that it is also very difficult to separate these catalysts from water since most of them have very small sizes (Gao, Hu et al. 2014, Leong, Razmjou et al. 2014). The poor separation may cause unavoidable loss of catalysts which then will increase the operation cost. While such release of nanomaterials would cause reverse impact to human health and environment, and the fixation of these nanoparticles, such as to construct photocatalytic membrane system, may be an effective way to avoid or reduce the leaching.

As shown in **Fig. 7.2**, Leong *et al.* proposed four ways to configure a photocatalytic membrane reactors where type (d) used TiO₂ to manufacture the

membrane was suggested to be the most promising one. This is because, such set up are capable to achieve the photodegradation of organic contaminants and the physical separation as a result of the membrane filtration occurs at the same time (Leong, Razmjou et al. 2014). Moreover, such combination would be helpful to prevent the fouling on the membrane surface which is believed to be one of the most challenging issues in the application of membrane technology.

Fig. 7.2 Different types of TiO_2 photocatalytic membrane reactors: Slurry reactor followed by a membrane filtration (a); submerged membrane in a slurry reactor (b); submerged membrane TiO_2 coated reactor (c); and photocatalytic membrane (d) (Leong, Razmjou et al. 2014).

Currently, there have been attempts to prepared different types of TiO_2 -based photocatalytic membranes, using organic, inorganic and metallic materials as supports/substrates, such as Al_2O_3 , PVDF (polyvinylidene fluoride), PSF (polysulfone), ceramic, and γ -alumina UF tubular membranes (Choi, Sofranko et al. 2006, Gao, Hu et al. 2014, Goei and Lim 2014, Moustakas, Katsaros et al. 2014, Athanasekou, Moustakas et al. 2015). For instance, **Fig. 7.3** illustrated one kind of PVDF/ TiO_2 hollow fibre single layer and dual layer membrane which fabricated by Dzinun *et al.* in 2015. Furthermore, they employed the as-prepared membranes to

degrade nonylphenol in an ultraviolet A (UVA) photoreactor system, finding that dual layer membrane could degrade around 85% nonylphenol within 4 h.

It is worth noting that though TiO_2 -based photocatalytic membranes were found to be able to improve the photocatalytic performance towards organic matters such as dyes, phenol and humic acids compared to conventional membranes, the majority of previous studies chose UV light as energy source. This only limited its practical application but also raised the requirement to search for stable substrates that can bare UV irradiation.

Fig. 7.3 SEM and EDX images of PVDF/ TiO_2 hollow fibre membranes of dual layer (a) and single layer (b) (Dzinun, Othman et al. 2015).

When it comes to WO_3 , there is nearly no previous study reporting the usage of WO_3 to construct WO_3 -based membranes. As discussed in the previous chapters, WO_3 and its heterogeneous composites can be effectual photocatalysts, therefore, they also have the potential to be employed to configure photocatalytic membranes. To achieve this objective, studies can focus on the following points:

- a. finding suitable membranes with good photostability as supporters.

- b. searching for simple but effectual method to coat WO_3 -based heterogeneous on/in the membranes.
- c. optimizing the amount of photocatalysts needed.
- d. optimizing the operation parameters to achieve best operation conditions.

7.2.3 Reactor design and process integration

From an engineering point of view, proper reactor design and integration of photocatalysis process in the water treatment system are extremely important in the case of real application. Generally, the photocatalysts can be adopted either in a slurry form or in an immobilized form, and consequently the reactors can be classified as a slurry-type or an immobilized-type (Chong, Jin et al. 2010, Ibadon and Fitzpatrick 2013). McCullagh *et al.* already summarized the variety of reactors, hence, this part will not be further discussed here (McCullagh, Skillen et al. 2011). It is pointed out that one major requirement that no matter what kind of reactors are applied is to possess the capability to efficiently collect light irradiation (Chong, Jin et al. 2010). In addition to light usage, how to effectively fix or recycle the photocatalysts and to collect the products should be considered when design reactors.

Fig. 7.4 Schematic diagram of the combination of photocatalysis and membrane filtration process: Photocatalysis and external membrane filtration (a) and photocatalysis with submerged membrane filtration (b) (Iglesias, Rivero et al. 2016).

well. Particularly, one widely proposed strategy is that photocatalysis process can be located in the system as a pre-treatment or post-treatment process for biological treatment depending on the overall purpose.

In particular, when being used as a pre-treatment step, photocatalysis as well as other AOPs can convert initially biorecalcitrant compounds to more biodegradable intermediates which would facilitate the following biological treatment process. If the water to be treated contains mainly biodegradable contaminants, biological process will be firstly preferred, followed by the photocatalysis as post-treatment stage (Klavarioti, Mantzavinos et al. 2009). For example, Oller *et al.* proposed that when dealing with a specific toxic and/or non-biodegradable industrial wastewater, AOP methods such as photocatalysis can be placed right before or after biological treatment process as depicted in **Fig. 7.5** (Oller, Malato et al. 2011).

However, to decide the necessity and the suitable strategy to integrate photocatalysis into the water treatment system can be a highly complex task, which desires thorough consideration from different aspects, including the quality of original water/wastewater (type and amount of pollutants in the water), treatment flexibility, the capacity of the system, potential use of the treated water, the final water quality, and the overall cost efficiency. Not like conventional treatment technologies of which their possibilities and capabilities are well acknowledged, such information is quite rare for photocatalysis process as well as other AOPs (Oller, Malato et al. 2011).

As a result, further research is urgently required of which the possible combination patterns of photocatalysis process with other technologies should be analyzed and studied on bench-scale and pilot-scale in the first stage. Moreover, most current studies focused mainly on uniform experiment conditions, while the situation in real world would be much more complicated. This means that more importance should be attached to the understanding of the realistic conditions and

searching feasible approaches to tackle the possible difficulties. At the same time, another essential matter that cannot be neglected in the future study is that to make sure the overall cost of the whole water treatment system is economic by placing different techniques, facilities in right order.

7.2.4 Elimination of heavy metals from water by photocatalysis method

The existence of heavy metals in water bodies is another urgent issue we are facing now. In particular, chromium, mercury, lead, copper, nickel, cadmium or arsenic are widely detected species in various water systems. Unlike organic matters, they are non-biodegradable, and more importantly, they can be accumulated in living tissues which can subsequently affect the ecosystems as well as human health (Tang, Zeng et al. 2014, Liu, Sun et al. 2016). In addition to current methods involved in conventional WWTPs, photocatalysis is regarded as an alternative approach to remove heavy metals from water since the electrons and holes generated under light irradiation can trigger the occurrence of redox reactions to either reduce or oxidize the metallic ions. For example, one of widely observed metallic ions Cr (VI) can be efficiently reduced to remarkably less toxic Cr (III) via photocatalysis methods following equations as listed in **Eqs (7.1) - (7.3)**. (Liu, Ni et al. 2014, Wang, Yuan et al. 2015).

Up to date, there is very limited research towards heavy metal elimination by WO_3 -based photocatalysts. Therefore, in the following study, the various WO_3 heterojunctions can be applied to remove toxic metallic ions from water. Moreover, since organic matters are usually co-existence with heavy metals, the adoption of

photocatalysis process can result in the simultaneously removal of both heavy metals and organic contaminants (Liu, Sun et al. 2016).

APPENDIX

Appendix for Chapter 3

A3.1 HPLC operation for SAM

The samples were filtered with 0.45 μm cellulose acetate syringe membrane filter to determine the SAM concentration via high performance liquid chromatography (HPLC) with a Spherisorb ODS-2 column (150 mm $\times$ 4.6 mm I.D., 5 μm) and an SPD-M20A diode array detector (DAD) using a Shimadzu LC system (LC-20AD). The Mobile phase consisting of 40% methanol (HPLC-grade) to 60% MQ water (Millipore Co. MilliQ water with resistivity of 18.2 $\text{M}\Omega\text{ cm}$) at a flow rate of 0.5 mL min^{-1} was used. The oven temperature was maintained at 30 $^{\circ}\text{C}$. The detector wavelength was set at 260 nm and injection volume was 20 μL .

A3.2 LC/MS/MS operation for SAM

After HPLC, intermediates were further analyzed by an Agilent 1290 Infinity HPLC coupled to an Agilent 6460 Triple quadrupole mass spectrometry, which was equipped with an Electrospray ionization (ESI) source using Agilent Jet Stream Technology (Agilent, US). Separations were performed using a 100 mm $\times$ 2.1 mm Kinetex 2.6 μm C18 column. The flow rate was set to 0.2 mL min^{-1} and the injection volume was 5 μL . The mobile phase consisted of water (A) and acetonitrile (B) modified with 0.1% formic acid. The MS system was operated in MS2 scan mode and in both positive and negative ionization modes. The mass range between m/z 30 and m/z 600 was scanned to obtain full scan mass spectra.

Fig. A3.1 EDX patterns of BiOCl and BiOCl-Ag.

As displayed in **Fig. A3.1**, only Bi, O, and Cl were observed from BiOCl sample. By contrast, new peaks at round 3 KeV belong to Ag were found from BiOCl-Ag, indicating Ag deposition on BiOCl.

Fig. A3.2 Ag NPs (nanoparticles) size distribution on BiOCl nanodiscs.

As presented in **Fig. A3.2**, after 2 h irradiation, the size of Ag NPs on the BiOCl nanodiscs was mainly in the range of 15 to 35 nm.

Fig. A3.3 N_2 adsorption-desorption isotherms of BiOCl nanodiscs.

The specific surface area of BiOCl nanodiscs was measured with nitrogen adsorption and desorption isotherms as illustrated in **Fig. A3.3**. The isotherms can be nearly categorized as type III and the BET surface area of BiOCl calculated from the result of N_2 isotherms was $6.54 \text{ m}^2 \text{ g}^{-1}$.

A3.3 SAM adsorption

The adsorption equilibriums of SAM of BiOCl and BiOCl-Ag were tested within 1 h, and results show only around 5% of SAM were adsorbed on the catalysts and the equilibrium could be successfully achieved in 60 min. This relatively low adsorption ability also confirms that the decline of SAM concentration during the light irradiation was the result of photo-degradation rather than simply adsorption on the catalysts.

Fig. A3.4 Adsorption of SAM in 1 h under dark, SAM=10 mg L⁻¹ and catalyst dosage=1.0 g L⁻¹.

Fig. A3.5 Mass spectra in the ES (-) mode for SAM after 5 h photocatalytic degradation over BiOCl-Ag under visible light.

The bacterial colonies formed on the LB agar mediums were observed as presented in **Fig. A3.6**. For both *E. coli* and *B. subtilis*, no colony was spotted after the cells were treated by BiOCl-Ag for 2 h, suggesting that BiOCl-Ag has a strong and efficient inactivation performance under visible light irradiation. By contrast, a number of colonies were found on LB agar mediums incubated by cells treated with

BiOCl. Such huge difference can be explained by the different antibacterial mechanisms. The main contributor to antibacterial activity of BiOCl under visible light are ROS generated during the photocatalytic process. In the case of BiOCl-Ag, the enhanced photocatalytic activity could create more ROS, leading to the improved antibacterial performance. Moreover, the excellent antibacterial effect of Ag would also contribute to the biocidal performance of BiOCl-Ag.

Fig. A3.6 Photographs of colony formation of *E. coli* and *B. subtilis* treated by 1.0 g L⁻¹ BiOCl and BiOCl-Ag for 2h under visible light irradiation. Bacterial colonies formed without adding any catalyst was used as control.

Table A3.1 The products prepared under different conditions at 120°C for 4h

Bi/W ratio	Water (mL)	Urea (mmol)	Chemical Compositions	Shape
1:1	—	6	BiOCl	Nanodiscs (Fig. S1 (a))
2:1	—	6	BiOCl-Bi ₂ WO ₆	Microflowers (Fig. S1 (b))
1:1	1-5	6	Bi ₂ WO ₆	Microflowers (Fig. S1 (c,d))

Fig. A3.7 SEM images of products synthesized under different conditions: BiOCl nanodiscs (a); BiOCl-Bi₂WO₆ microflowers (b) and Bi₂WO₆ nanoflowers with addition of 1 mL water (c) and 5 mL water (d).

Fig. A3.8 XRD patterns of products synthesized under different conditions.

Appendix for Chapter 4

A4.1 Effect of pH on WO₃ synthesis

The pH of precursor solution can affect the crystal phase and morphology of WO₃ nanostructure (Wang, Khoo et al. 2009, Zhang, Liu et al. 2014). According to our results, the uniform WO₃ nanoplates can only be produced at pH<1 (**Fig. A4.1 (b) and (c)**), which can be explained by the well-known theory for crystal nucleation and growth (Gao 2004), as high H⁺ concentration could provide large super-saturation of H₂WO₄ as the driving force for nucleus formation (Wang, Khoo et al. 2009).

Fig. A4.1 Products obtained under different conditions: neither WO₃·H₂O nor WO₃, pH>1 at 180 °C for 8 h (a); WO₃·H₂O, pH<1 at 80 °C for 8 h (b); and WO₃, pH<1 at 180 °C for 8 h (c).

A4.2 SAM adsorption

The adsorption of SAM on materials were also conducted under dark. Results (**Fig. A4.2**) showed that the adsorption of SAM on catalysts was quite low (<6%) due to low surface area and therefore, adsorption was not the main contributor to SAM removal during the reaction time. No significant increase of SAM adsorption was observed for WA composites which could be assigned to the minor increase of the surface areas after Ag loading.

Fig. A4.2 Adsorption-desorption equilibrium rate of SAM under dark with different photocatalysts, Conditions: catalyst = 0.5 g L^{-1} , SAM = 10 mg L^{-1} , pH = 5.0 ± 0.2 (a), pH = 7.0 ± 0.2 (b), pH = 9.0 ± 0.2 (c).

Fig. A4.3 Mass spectra in the ES (-) mode for SAM after 5 h photocatalytic degradation over WA2 under visible light.

At higher pH, slight decrease of SAM adsorption was observed. Since WO_3 is reported to have a low point of zero charge (PZC, 0.4~1.0) (Brunelle 1978, Gazzoli, Valigi et al. 1997, Abdullah and Chong 2010), it would be negatively charged at testing pH. SAM has a pK_a values of 2.40 and 10.43 (Baran, Adamek et al. 2009), and when pH increase, the proportion of negatively charged SAM will increase leading to the electrostatic repulsion between negatively charged WO_3 and negatively charged SAM. As a result, SAM adsorption on the surface of WO_3 and WO_3 -Ag composites decreased. Overall, the changes of adsorption due to pH variation was not significant.

Fig. A4.4 Sorption of nitrogen isotherms for WO, WA1, WA2 and WA3.

Fig. A4.5 Photographs of bacterial colonies formed by *E. coli* treated by WA3 for 30min (a), 1 h (b), 2 h (c); by *B. subtilis* treated by WA3 for 30min (d), 1 h (e), 2 h (f).

Appendix for Chapter 5

A5.1 HPLC operation

The samples were filtered with 0.45 μm cellulose acetate syringe membrane filter to determine the SMX concentration via ultra-fast liquid chromatography (UFLC) with an Agilent Proshell 120 EC-C 18 column (4.1 $\times$ 100 mm, 2.7 μm) and an SPD-M20A diode array detector using a Shimadzu LC system (LC-20AD, Japan). The mobile phases consisted of water (A) and 10 mM ammonium acetate in methanol (B) with 0.1% formic acid. The gradient elution was: 0-0.5 min, 10% B; 0.5-1 min, 10-40% B; 9.0-13 min, 90% A; from 13 to 13.10 to return to the initial conditions and finally from 13.10 to 22 min equilibration of the column. The flow rate and injection volume were 0.8 mL min^{-1} and 5 μL , respectively. The detector wavelength was set at 270 nm. The retention time of SMX was 7.5 min.

A5.2 LC/MS/MS operation

After HPLC, intermediates were further analyzed using an Agilent 1290 Infinity HPLC coupled to an Agilent 6460 Triple quadrupole mass spectrometry, which was equipped with an Electrospray ionization (ESI) source using Agilent Jet Stream Technology (Agilent, US). Separations were performed using a 100 mm $\times$ 2.1 mm Kinetex 2.6 μm C18 column. The flow rate was set to 0.2 mL min^{-1} and the injection volume was 5 μL . The mobile phases consisted of water (A) and 10 mM ammonium acetate in methanol (B) with 0.1% formic acid. The gradient elution was: initial 10% B, 0.5 min, 40% B; 7 min, 85% B; 7.10 min, 90% B, held for 1.9 min, and back to 10% at 9 min, held for 2 min for equilibration of the column. The MS system was operated in MS2 scan mode and in ESI mode using Jetstream positive ionization. The ionization source conditions used were as follows: the nebulizer gas 8 L min^{-1} , and sheath gas 11 L min^{-1} at a temperature of

325 °C; the nebulizer pressure 30 psi and the capillary voltage 3500 V. The mass range between m/z 30 and m/z 600 was scanned to obtain full scan mass spectra.

Fig. A5.1 TEM images of WCN-8 at different magnification: low magnification (a) and high resolution (b)

Fig. A5.2 SMX adsorption on different catalyst within 60 min.

Fig. A5.3 XRD spectra comparison between fresh WCN-8 and used WCN-8.

Fig. A5.4 Mass spectra in the ES (-) mode for SMX after 4 h photocatalytic degradation over WCN-8 under visible light.

Appendix for Chapter 6

A6.1 Photocatalytic degradation kinetics

Application of Langmuir-Hinshelwood Model

$$r = k\theta = k \left(\frac{KC}{1+KC} \right)$$

$$r = -\frac{dC}{dt} = -\frac{kKC}{1+KC}$$

In the above equations:

r is the reaction rate, θ is the substrate coverage, k is the intrinsic reaction rate constant, K is the Langmuir adsorption equilibrium constant, c is the SMX concentration and t is the reaction time.

The Langmuir-Hinshelwood can be simplified into a pseudo-first-order kinetics model

$$r = -\frac{dC}{dt} = -kKC$$

$$\ln\left(\frac{C}{C_0}\right) = -kKt = -k_{app}t$$

where k_{app} is the apparent degradation rate constant and C_0 is the initial concentration of SMX.

Fig. A6.1 SEM images of RW-400 (a), RW-200 (b) and RW-100 (c) at lower magnification; SEM image of WO₃ (d) and TEM images of RW-200 (e) and WO₃ (f) at higher magnification.

Fig. A6.2 XRD pattern of GO (a) and Raman spectra of GO (b).

Fig. A6.3 XPS survey (a), O 1s (b), C 1s (c) of GO, and O 1s of WO_3 (d).

Fig. A6.4 High resolution XPS spectra of O 1s for RW-100 (a), RW-200 (b) and RW-400 (c); C 1s for RW-100 (d), RW-200 (e) and RW-400 (f).

Fig. A6.5 Adsorption of SMX on WO₃ and RGO-WO₃ composites in 60 min.

A6.3 Stability and recyclability of RW-200

The used RW-200 was also characterized by SEM after five cycles (**Fig. A6.6 (a)** and **(b)**). No remarkable morphology or XRD pattern (**Fig. A6.6 (c)**) change was found compared with fresh sample, implying that RW-200 had high photostability and repeatability.

Fig. A6.6 SEM images of RW-200 after five cycles of photodegradation of SMX under visible light (a) and (b); XRD pattern of RW-200 after five cycles of photodegradation of SMX under visible light.

Fig. A6.7 Zeta potential of RW-200. **Fig. A6.8** Mass spectra in the ES (-) mode for SMX after 3 h photocatalytic degradation over RW-200 under visible light.

Fig. A6.9 Mass spectra in the ES (+) mode for SMX after 3 h photocatalytic degradation over RW-200 under visible light.

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