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**NOVEL MULTIFUNCTIONAL NANOCOMPOSITE
PHOTOCATALYSTS FOR WATER REMEDIATION
APPLICATIONS**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
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PHOTOCATALYSTS FOR WATER REMEDIATION
APPLICATIONS**

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ABSTRACT

Recently, semiconductor-mediated heterogeneous photocatalysis has gained recognition as an effective treatment method for the removal of emerging organic contaminants (EOCs). Here, this study synthesized some hybrid multifunctional nanocomposites, such as $\text{TiO}_2\text{-CuS}$, GO-COOH-CuS , $\text{g-C}_3\text{N}_4\text{-CuS}$, GO-COOH-CuS-Ag and $\text{mpg-C}_3\text{N}_4/\text{TiO}_2$, with the aim to explore their water remediation applications, which can reach synergistic effect to show better photodegradation performance than pure semiconductor. In addition, in order to overcome the aggregation and agglomeration of powdered nanoparticle in aqueous solution, GO-COOH-CuS-Ag was coated onto the glass and $\text{mpg-C}_3\text{N}_4/\text{TiO}_2$ was immobilized into a PSf membrane to explore their water remediation applications. They all showed excellent photodegradation abilities.

First of all, TiO_2 nanospheres were synthesized and then modified with copper (II) sulfide (CuS) to form $\text{TiO}_2\text{-CuS-a}$ and $\text{TiO}_2\text{-CuS-b}$ respectively by two different loading methods (direct deposition vs. bifunctional linker coupling). The structural, morphological and optical properties of the two different composites $\text{TiO}_2\text{-CuS-a}$ and $\text{TiO}_2\text{-CuS-b}$ were characterized and compared using FESEM, HRTEM, XRD, XPS, BET and DRS techniques. The $\text{TiO}_2\text{-CuS-b}$ with a regular “spiky ball - like” structure exhibited enhanced disinfection ability, improved photodegradation performance of organic pollutants and hydrogen evolution efficiency under solar and UV light as compared to $\text{TiO}_2\text{-CuS-a}$ (direct deposition method) due to its higher effective combination with CuS through the bifunctional linking molecule - L-cysteine. The influence of CuS content, the structure and the charge-transfer mechanism were systematically investigated by PL, CV, EIS and EPR techniques.

Because TiO_2 only can use the UV light, which accounts to 5% of solar light, so in order to harvest the visible light more efficiently, carboxylic acid functionalized graphene oxide-copper (II) sulfide nanoparticle composite (GO-COOH-CuS) was prepared from carboxylated graphene oxide and copper precursor in dimethyl sulfoxide (DMSO) by a facile synthesis process at room temperature. The high-effective combination, the interaction between GO-COOH sheets and CuS

nanoparticles, and the enhanced visible light absorption were confirmed by various characterization techniques. The as-synthesized GO-COOH-CuS nanocomposite exhibited excellent photocatalytic degradation performance of phenol and rhodamine B, high antibacterial activity toward *E. coli* and *B. subtilis*, and good recovery and reusability. The influence of CuS content, the synergistic reaction between CuS and GO-COOH, and the charge-transfer mechanism were systematically investigated. The facile and low-energy synthesis process combined with the excellent degradation and antibacterial performance signify that the GO-COOH-CuS has a great potential for water treatment application.

In addition, using photocatalyst and solar energy to split water into hydrogen is an ideal energy source, and as reported, g-C₃N₄ showed better hydrogen generation ability than GO. Hereto, a novel hybrid multifunctional g-C₃N₄-CuS nanocomposite photocatalyst was synthesized for H₂ evolution by integrating a g-C₃N₄ nanosheet with hexagonal CuS nanoplates via a facile hydrothermal method at room temperature. The ultrathin large surface area g-C₃N₄ nanosheets were prepared by a “green” liquid exfoliation route from bulk g-C₃N₄ in isopropanol. Different nanostructural g-C₃N₄ materials were compared and the results confirmed that the g-C₃N₄ nanosheet had better hydrogen evolution than the bulk material under solar irradiation owing to its larger surface area and higher light absorption efficiency. Furthermore, given the improved charge separation efficiency, the novel nanocomposite g-C₃N₄-CuS-1 demonstrated much better hydrogen evolution rate (126.5 $\mu\text{mol h}^{-1}$) than the pure g-C₃N₄ nanosheet under solar light. Its performance is also superior than of other semiconductor modified g-C₃N₄ materials, and making it a promising photocatalyst for future hydrogen generation application. The optical properties, crystal phase and morphology of the obtained composites were characterized systematically using various analytical methods. It was concluded that O^{2•-} was the dominant radical for hydrogen evolution through photoluminescence (PL) and electron paramagnetic resonance (EPR) analysis.

In addition, in order to overcome the problem from the agglomeration of powdered particles in water, this study explored the photodegradation performance of glass

coating and membrane methods for the photodegradation. For glass coating immobilization method, a hybrid multifunctional nanocomposite (GO-COOH-CuS-Ag) was synthesized via a facile method by integrating copper sulfide (CuS) nanoflakes, carboxylic acid functionalised graphene oxide (GO-COOH) sheets, and silver (Ag) nanoparticles, with the aim to enhance their EOCs photodegradation and antibacterial applications under solar light irradiation. The crystal phase, optical properties and morphology of obtained composite were characterized using various characterization methods. The as-synthesized GO-COOH-CuS-Ag nanocomposites were transformed and applied on glass via a glass coating method aimed at facilitating their practical applications in photodegradation of emerging organic contaminants (EOCs) and disinfection for water treatment under solar light irradiation. The glass coatings had excellent photodegradation and antibacterial performance with good stability and repeatability. It was also found that synergistic reactions existed among CuS, Ag and GO-COOH, and the mechanisms of charge transfer and photo-disinfection were systematically investigated. The results clearly demonstrate its high performance potential in photodegradation and photo-disinfection processes with the advantage of simplifying the recovery and reuse in comparison to powdered forms, and reducing problems including the agglomeration of powdered particles that may cause blockages.

For membrane immobilization method, a novel mesoporous graphitic carbon nitride/titanium dioxide (mpg-C₃N₄/TiO₂) nanocomposite was successfully synthesized and incorporated into polysulfone (PSf) matrix to fabricate photocatalytic membranes. This study aimed to explore the photocatalytic ability of the novel nanomaterial membrane in degrading the antibiotic sulfamethoxazole (SMX) under solar light. The structural and morphological properties of the mpg-C₃N₄/TiO₂ nanocomposite and membrane were characterized using various techniques. The SMX photocatalytic degradation performance, pathway and mechanism by mpg-C₃N₄/TiO₂ photocatalytic membrane reactor (PMR) were systematically investigated using HPLC and LC-MS/MS. As a pharmaceutically active compound, SMX was transformed into 7 kinds of non-toxic and pharmaceutically inactive byproducts by the innovative PMR technology. SMX

removal efficiency of the membrane PSf-3 (with 1% mpg-C₃N₄/TiO₂ loading) was the highest over the 30 h consecutive irradiation. Meantime, the membrane didn't affect the SMX photodegradation, and the structure was able to provide stable support with high integrity and flexibility after solar irradiation. The developed membrane has a great potential to be applied in water treatment industry.

LIST OF PUBLICATIONS

Journals

- **Shuyan Yu**¹, Jincheng Liu^{1,2*}, Wenyu Zhu¹, Zhong-Ting Hu¹, Teik-Thye Lim^{1,3}, Xiaoli Yan^{1,3*} Title: “Facile room-temperature synthesis of carboxylated graphene oxide – copper sulfide nanocomposite with high photodegradation and disinfection activities under solar light irradiation” *Scientific Reports-Nature*, 2015, 5, 16369
- **Shuyan Yu**^{1,2}, Jincheng Liu^{1,3}, Yan Zhou^{1,2}, Richard D. Webster^{2,4}, Xiaoli Yan^{1,5*} Title: “Effect of synthesis method on nanostructure and solar-driven photocatalytic properties of TiO₂-CuS composites” *ACS Sustainable Chemistry & Engineering*, 2017, 5, 1347–1357
- **Shuyan Yu**^{1,2}, Richard D. Webster^{2,3}, Yan Zhou^{1,2*}, Xiaoli Yan^{1,4*} Title: “Novel carboxylated graphene oxide-CuS-Ag nanocomposite glass coating for organic degradation under solar light” *Journal of Chemical Technology and Biotechnology*, 2017, 10, 1002
- **Shuyan Yu**^{1,2}, Richard D. Webster^{2,3}, Yan Zhou^{1,2*}, Xiaoli Yan^{1,4*} Title: “Ultrathin g-C₃N₄ nanosheet with hexagonal CuS nanoplates as a novel composite under solar light irradiation for H₂ production” *Catalysis Science & Technology*, 2017, 7, 2050-2056
- **Shuyan Yu**^{1,2}, Yining Wang², Rong Wang^{1,2}, Yan Zhou^{1,2*} Title: “Novel mpg-C₃N₄/TiO₂ nanocomposite photocatalytic membrane reactor for sulfamethoxazole degradation” *Chemical Engineering Journal* (Accepted)
- Jincheng Liu^{1,2}; **Yu, Shuyan**¹; Wenyu Zhu¹; Xiaoli Yan²; Title: “Oxygen Vacancy- Enhanced Visible Light-driven Photocatalytic Activity of TiO₂ Sphere-W18O49 Nanowire Bundle Heterojunction” *Applied Catalysis A General*, 2015, 500, 30-39
- Wenyu Zhu^a, Jincheng Liu^{a,b*}, **Shuyan Yu**^a, Yan Zhou^{a,c}, Xiaoli Yan^{a,d*} Title: “Ag loaded WO₃ nanoplates for efficient photocatalytic degradation of sulfanilamide and their bactericidal effect under visible light irradiation” *Journal of Hazardous Materials*, 2016, 318, 407-416

- Liu, Jincheng; Zhu, Wenyu; **Yu, Shuyan**, Xiaoli Yan. Title: “Three dimensional carbogenic dots/TiO₂ nanoheterojunctions with enhanced visible light-driven photocatalytic activity” *Carbon*, 2014, 79(1), 369-379

Conferences (Oral presentations)

- **Shuyan Yu**¹, Xiaoli Yan^{1*} Title: “Multifunctional GO-COOH-CuS Nanocomposite with Photocatalytic Activity Under Solar light irradiation” 2015 AIChE Annual Meeting
- **Shuyan Yu**¹, Yan Zhou^{*} Title: “Novel Graphene Oxide Based Photocatalyst Glass Coating for Organic Removal Under Solar light” 2016 13th IWA Specialized Conference on Small Water and Wastewater Systems Meeting
- **Shuyan Yu**¹, Yan Zhou^{*} Title: “Novel mpg-C₃N₄/TiO₂ nanocomposite photocatalytic membrane reactor for sulfamethoxazole photodegradation” 2017 9th International Conference on Materials for Advanced Technologies

Summer School

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German DAAD academic exchange project (Summer School, workshop) with China, Singapore and Vietnam Theme: Low-cost and sustainable sanitation solutions for developing countries NTU Delegate: Oral Presentations

Awards

Nanyang Technological University Research Scholarship	2013.7~present
2015 German DAAD academic exchange project scholarship	2015.09
NTU CEE Memorabilia-photographic competition 3 rd place	2015.10
NTU CEE Campus Run 2014 Girls Category 1 st	2014.02

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviations	Meaning
Ag ₂ S	Silver (I) Sulfide
AOT	Advanced oxidation technologies
CB	Conduction band
C ₃ N ₄	Carbon Nitride
TiO ₂	Titanium Dioxide
CuS	Copper (II) Sulfide
DI water	Deionized water
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
EDCs	Endocrine disrupting chemicals
EDS	Energy-dispersive X-ray spectroscopy
EOCs	Emerging Organic Contaminants
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HAc	Acetic acid
MC	Mesocrystal

PAHs	Polycyclic aromatic hydrocarbons
PhACs	Pharmaceutically active compounds
PPCPs	Personal care products
RhB	Rhodamine B
SEM	Scanning electron microscope
TBT	Tetrabutyl titanate
TEM	Transmission electron microscopy
TiO ₂	Titanium Dioxide
TNT	TiO ₂ nanotubes
VB	Valence band
XRD	X-ray diffraction

CHAPTER 1. INTRODUCTION

1.1 Research background and gaps

Fresh drinking water is a basic necessity to life and good health but its scarcity remains a grand challenge. As such, it is paramount for a water scarce island-country like Singapore to be self sufficient in its water supply, through the promotion of water reuse, to cater to the country's continued growth. Unfortunately, current water treatment technologies and infrastructures are reaching their limits to meet such needs(Shannon et al. 2008). This has led to increased interest in nanotechnology for water purification applications.

The newly available nanotechnology and nanomaterials tools enable the synthesis of novel hybrid materials, which include nano-adsorbents, nanophotocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, and nanoparticle enhanced filtration(Savage and Diallo 2005). Among those, nanonphotocatalyst has been reported as one of the most facile and important water treatment materials, such as TiO_2 , GO and C_3N_4 , which are some of the most effective nanophotocatalyst. These nanophotocatalysts possess many novel scalable size-dependent properties, which are attractive for applications in photodegradation water treatment. Its activated functionalized sites and high specific surface area allow for fast dissolution, strong sorption, and high reactivity. Those properties not only contribute to excellent photocatalytic ability, but also make them to be suitable support for other smaller size photocatalysts to make nanocomposite so that it can have a synergistic effect (Dikin et al. 2007). However, the aggregation and restacking of these nanomaterials greatly impede their application. Along with a large number of different approaches that have been developed to address this obstacle, the most reliable and facile technique is the fabrication with a narrow bandgap semiconductor. The choice of semiconductor is essential in the photocatalytic degradation of the organic contaminants, taking into account its photocatalytic efficiency, cost and ease of production. A great number of materials have been developed and involved, including CuS, CdS and ZnO etc. Among those,

copper sulfide (CuS), a p-type semiconductor, has been reported as one of the most important semiconductors due to its excellent chemical and physical properties at room temperature (Basu et al. 2010). It can also be transformed into a superconductor at low temperatures (1.6 K), exhibiting excellent chemical and physical properties (Basu et al. 2010). By combined with CuS, the photocatalytic activity of nanocomposites TiO₂-CuS, GO-CuS, C₃N₄-CuS can be significantly improved and their application range can be expanded

In recent years, semiconductor-mediated heterogeneous photocatalysis has become ubiquitous in water treatment for the removal of Emerging Organic Contaminants (EOCs) such as pathogens and organic pollutants (Serpone 1995, Carmen and Daniela 2012). Recent studies have also verified that the higher specific surface area of Ag nanoparticles (<10 nm) results in a better disinfection performance (Liu et al. 2013). However, photocatalysts are commonly applied in fine-powder form in water treatment. Aggregation and agglomeration of powdered nanoparticle in aqueous solution is usually a big issue associated with such applications. Immobilizing photocatalyst into a supporting media, e.g. membrane or glass, which may reduce the difficulty in recovery, recycling and isolating these nanoparticles.

1.2 Research objectives and significance

The overall objective of this thesis was to synthesize highly solar-light responsive CuS-based or TiO₂-based multifunctional nanocomposite photocatalysts to explore their water remediation applications under solar-light irradiation. Furthermore, this research also aimed to develop effective separation systems for recovery and reuse of the photocatalysts, such as glass coating method or photocatalytic membrane reactor. The scope of the research is described below:

- (1) Both direct deposition and bifunctional linker coupling methods were employed for CuS coupling onto TiO₂ nanospheres. The effects of the different loading methods on the structure of TiO₂-CuS composites and the influence of CuS content were further investigated. The performances of TiO₂-CuS composites in the applications of RhB and phenol

photodegradation, *E.coli* inactivation and the hydrogen generation under solar and UV light were also evaluated.

- (2) Put forward a facile yet efficient room-temperature synthesis approach for the fabrication of GO-COOH-CuS nanocomposite and explored its general environmental applications, such as, the photocatalytic degradation of phenol and rhodamine B (RhB), as well as the inactivation of *Escherichia coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*) under solar light irradiation.
- (3) Ultrathin g-C₃N₄ nanosheets were successfully prepared by a “green” liquid exfoliation route from bulk g-C₃N₄ in isopropanol (IPA). And copper sulfide (CuS) as the narrow band gap semiconductor to enhance the photocatalytic properties of g-C₃N₄. The optical properties, crystal phase, morphology of the different nanostructural g-C₃N₄ and g-C₃N₄-CuS composites were analysed. The hydrogen evolution performance of all obtained composites under solar irradiation and the H₂ generation mechanism were systematically investigated.
- (4) Synthesized a hybrid multifunctional nanocomposite (GO-COOH-CuS-Ag) via a facile method by integrating CuS nanoflakes, GO-COOH sheets, and Ag nanoparticles, with the aim to enhance their EOCs photodegradation and antibacterial applications under solar light irradiation. It is proposed that the performance and stability of GO-COOH-CuS-Ag can be enhanced with glass coating technology thus facilitate its practical application in water treatment.
- (5) UF membrane was prepared with polysulfone (PSf), which has high thermal, mechanical and chemical resistances. A typical antibiotic named sulfamethoxazole (SMX) was used as a model pharmaceutical. In specific, the structural, morphological and optical properties of the mpg-C₃N₄/TiO₂ nanocomposite, and the performance of mpg-C₃N₄/TiO₂ membrane in terms of SMX photodegradation were systematically investigated.

In particular, the main innovations and significance of the research include:

- I. The multifunctional GO-COOH-CuS nanocomposite is for the first time rapid synthesized via such facile and scalable room-temperature method and used

for water decontamination and disinfection with excellent performance just during a short operating period under solar irradiation.

- II. Few researchers have compared these two methods (direct deposition vs. bifunctional linker coupling methods) of TiO_2 nanospheres surface modification with CuS for photocatalytic and hydrogen generation performance.
- III. To the best of our knowledge, this is the first study to integrate hexagonal CuS nanoplates with g- C_3N_4 nanosheets to fabricate g- C_3N_4 -CuS nanocomposite and investigate its hydrogen evolution performance.
- IV. The glass coating method via as-synthesized GO-COOH-CuS-Ag nanocomposites were transformed and applied on glass demonstrate its high performance potential in photodegradation and photo-disinfection processes with the advantage of simplifying the recovery and reuse in comparison to powdered forms, and reducing problems including the agglomeration of powdered particles that may cause blockages.
- V. Fast and effective phototransformation of SMX under direct and indirect photocatalysis, heterogeneous photocatalysis and photo-fenton reactions have been reported (Abellán et al. 2007, Trovo et al. 2009, Trovo et al. 2009, Oh et al. 2016). However, employment of photocatalytic membrane to degrade SMX has not been studied. To the best of our knowledge, it is the first time to manufacture a UF membrane with embedded mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ nanocomposite and to explore its photodegradation performance under solar light irradiation.

1.3 Thesis outline

This thesis contains 8 chapters.

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

Chapter 2 presents a comprehensive literature review, which covers traditional water treatment technology, semiconductor-mediated heterogeneous photocatalysis technology, photocatalytic technology, overall introduction of photocatalysts, and

photocatalytic membrane technology

Chapter 3 investigates the effect of synthesis method on the nanostructure and solar-driven photocatalytic properties of TiO₂-CuS composites

Chapter 4 provides the facile room-temperature synthesis of carboxylated graphene oxide-copper sulfide (GO-COOH-CuS) nanocomposite with high photodegradation and disinfection activities under solar light irradiation, further compared to the TiO₂-CuS nanocomposite in **Chapter 3**

Chapter 5 presents a novel ultrathin g-C₃N₄ nanosheet with hexagonal CuS nanoplates composite under solar light irradiation for H₂ production, to further explore the different CuS-based nanocomposites for the H₂ generation ability compared to the **Chapter 4**.

Chapter 6 evaluates novel carboxylated graphene oxide-CuS-Ag nanocomposite glass coating for organic degradation under solar light, Ag is involved to further enhance the disinfection ability based on the **Chapter 3** nanocomposite GO-COOH-CuS.

Chapter 7 further reports the novel mpg-C₃N₄/TiO₂ nanocomposite photocatalytic membrane reactor for sulfamethoxazole photodegradation by comparison with the **Chapter 6** glass coating method

Chapter 8 summarizes the overall research findings, provides general conclusions and presents several recommendations for the future work.

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

CHAPTER 2. LITERATURE REVIEW

2.1 Traditional water treatment technology

Water treatment is any process that makes water more acceptable for a specific end-use. The end use may be drinking, industrial water supply, irrigation, river flow maintenance, water recreation or many other uses, including being safely returned to the environment. Water treatment removes contaminants and undesirable components, or reduces their concentration so that the water becomes fit for its desired end-use. Treatment for drinking water production involves the removal of contaminants from raw water to produce water that is pure enough for human consumption without any short term or long term risk of any adverse health effect. Substances that are removed during the process of drinking water treatment included suspended solids, bacteria, algae, viruses, fungi, and minerals such as iron and manganese. The processes involved in removing the contaminants include physical processes such as settling and filtration, chemical processes such as disinfection and coagulation and biological processes such as slow sand filtration. Measures taken to ensure water quality not only relate to the treatment of the water, but to its conveyance and distribution after treatment. It is therefore common practice to keep residual disinfectants in the treated water to kill bacteriological contamination during distribution.

What's more, conventional water treatment plants relying on biological and simple physical-chemical treatments such as coagulation and flocculation are inadequate in completely removing the toxic organic pollutants as they do not entirely annihilate them, but only change them to other phases. Hence, more suitable and polished water technology is required to address the aforementioned issues. Semiconductor-mediated heterogeneous photocatalysis technology has gained recognition as an effective treatment method for the removal of emerging organic contaminants (EOCs).

2.2 Semiconductor-mediated heterogeneous photocatalysis technology

2.2.1 Decontamination

Photocatalysis is a process that can cause dissociation or mineralization of the pollutants by photons, accelerated by the presence of a photocatalyst. The contaminants that absorb the incident light are being photo-excited by the photons and further degrade into harmless products. There are two types of photocatalytic processes widely applied in the water treatment technologies for the degradation of the EOCs, namely homogeneous photocatalysis and heterogeneous photocatalysis. Homogeneous photocatalysis is the reaction where both the photocatalyst and the reactants are in the same phase (Herrmann 1999). Homogeneous photocatalysis most commonly refers to the photo-Fenton system, in which hydroxyl ions are released under UV or visible light irradiation. On the other hand, in semiconductor-mediated heterogeneous photocatalysis, the semiconductor photocatalyst and the reactants are in different phases (Herrmann 1999).

As for the photocatalysis mechanism, when light energy (photon energy $h\nu$ is more than the band gap energy of the semiconductor) is radiated on the surface of the semiconductor (SC), electrons are released, leading to the establishment of an electron-hole pair:

The photo-generated electrons are located at the conduction band whereas the holes are located at the valence band. The photo-generated negatively-charged electrons then bind with adsorbed oxidants (usually O_2) to generate superoxide anions, $\cdot O_2^-$, while the photo-generated positively-charged holes take up electrons from the surface hydroxyl groups of the semiconductor or moisture in the air (H_2O) to form hydroxyl radicals, $\cdot OH$. The reactions that take place can be exemplified in the following equations:

The superoxide anions produced then undergo one-electron reduction to form hydrogen peroxide, H_2O_2 . Subsequently, H_2O_2 undergoes an additional one-electron reduction to generate water and additional $\cdot\text{OH}$:

The above-described mechanism of electron-hole generation of the semiconductor-mediated heterogeneous photocatalysis is summarized in Fig. 2.1 below.

Fig. 2.1 Schematic drawing of the photocatalytic process on the photocatalyst. Reaction (a) denotes the reduction of an electron acceptor (usually O_2) by the photo-generated electrons, at the surface of the semiconductor. Reaction (b) denotes the oxidation of an electron donor (H_2O) by the photo-generated holes. Both reactions generate active radicals. Reaction (c) and (d) denote the recombination of the electron-hole pair at the surface, or in the bulk of the semiconductor respectively.

As seen from Fig. 2.1, recombination of the electron-hole pairs can occur at the surface or the bulk of the semiconductor, which will diminish the efficiency of the semiconductor photocatalyst. Hence, reactions (c) and (d) that include electron-hole

pair recombination have to be minimized to yield maximum active radicals from reaction (a) and (b). The formation of $\cdot\text{OH}$ radicals is more preferred over $\cdot\text{O}_2^-$ radicals as they are more versatile and highly reactive. During photocatalysis, these active radicals generated are then able to decompose the organic pollutants such as dye through oxidative reduction, and mineralise them into water and harmless inorganic substances such as carbon dioxide (Mills and Lee 2002, Tseng; et al. 2010):

The semiconductor photocatalyst remains chemically unchanged and can be recovered for subsequent treatment.

2.2.2 Disinfection

Disinfection through solar irradiation had been proven to effectively destroy biological microorganisms and this simple approach, also known as Solar Water Disinfection (SODIS), has been widely applied especially in developing countries (Malato et al. 2007). As SODIS itself is not appropriate for large or channeled volumes of water, the addition of photocatalysts has been explored to aid in the disinfection process (Malato et al. 2007). Photo-sterilisation, also known as photo-disinfection, is another possible function of the semiconductor material promoted in photochemistry (Mills and Lee 2002). With the aid of the semiconductor photocatalyst, microorganisms such as bacterial, fungal spores and viruses could be effectively destroyed by solar irradiation.

The electron-hole pair generated from solar irradiation produces $\cdot\text{OH}$ radicals via the same mechanism as described in Fig. 2.1 earlier. Similarly, these active radicals are capable of damaging and disintegrating the cell wall of the biological microorganisms (Mills and Lee 2002). Likewise, the semiconductor photocatalyst remains chemically unchanged and can be recovered for subsequent treatment.

The cells with impaired or destroyed cell walls are not sustainable and will subsequently die due to the leakage and degradation of cellular components, hence effectively disinfecting the contaminated water (Mills and Lee 2002, Chong et al. 2010). The process of the cell mineralisation could be illustrated in Fig 2.2 below.

Fig. 2.2 Cell mineralization during the solar photocatalytic treatment process (Adapted from(Foster 2011))

The advanced oxidation processes via photocatalysts have many advantages:

- (1) it can remove contaminants with fast reaction rates
- (2) It has the potential to reduce toxicity and possibly complete mineralization of organics
- (3) Reactions in photocatalysis do not produce excess materials like “spent carbon” or chemical sludge
- (4) It is a non-selective process that can take care of wide range of organics
- (5) It can be used to flocculate and disinfect portable water preferably than chlorine because it doesn’t add T.D.S (dissolved solids) and chemicals.

2.3 Photocatalytic membrane technology

Photocatalysts are commonly applied in fine-powder form in water treatment. Aggregation and agglomeration of powdered nanoparticle in aqueous solution is usually a big issue associated with such applications. Incorporating photocatalyst into a supporting media, e.g. membrane, can help immobilize the nanoparticles. Compared with the coating/spraying nanoparticles on the substrates like glass (Modesto-López et al. 2015, Shuyan Yu 2017) and polyester fiber (Han et al. 2013),

using membrane as a supporting media can provide enhanced material recovery rate from the liquid phase. One common method to develop the nanoparticle membrane is to sequential filtration or coating the nanoparticles on the membrane (C.P. Athanasekou 2012, Molinari et al. 2015, Bet-moushoul et al. 2016, Zhao et al. 2016). However, the procedure often result in increased preparation cost and time, and the reduced membrane water permeability (C.P. Athanasekou 2012). It is believed that by fixing photocatalysts within the membrane rather than filtration on the membrane surface, which can efficiently capture the photocatalyst and improve the recovery and recycle of the nanomaterial (Bet-moushoul et al. 2016). Photocatalytic membrane reactor (PMR) has been proven as an effective method for wastewater treatment and water purification, arising from the combined functions of organic degradation, physical filtration and anti-bacterial properties within a single unit (Leong et al. 2014, Molinari et al. 2015).

2.4 Various photocatalysts

2.4.1 Copper sulfide (CuS)

The ever-growing demand for the clean water has stimulated significant research effort for the huge development of advanced water treatment technologies. Semiconductor-mediated heterogeneous photocatalysis is considered as a promising method to remove pathogens and organic pollutants from wastewater (Mills et al. 1993). A great number of materials have been developed and involved, including CuS, CdS and ZnO etc. Among those, copper sulfide (CuS) has been reported as one of the most important semiconductors due to its excellent chemical and physical properties at room temperature with a narrow band gap (2.1eV) (Basu et al. 2010). Their special properties are arising from its varied nonstoichiometric composition, valence states, nanocrystal morphologies, complex structures. CuS, as one of the important semiconductor has potential application as p-type semiconductor, solar energy converter, cathode material, catalyst, optical filter, sensor and nonlinear optical material (Wan et al. 2004, Li et al. 2009, Mao et al. 2009).

In recent time, various morphologies of CuS including nanoparticles, nanoflakes,

nanotubes, microspheres, flower-like structures, nanowires, nanorods, sea-urchin-like structures and nanoribbons have been fabricated using different methods (Ding et al. 2009, Huang et al. 2010, Saranya et al. 2014), which include solventless and solution thermolysis, hydrothermal or solvothermal method, ultrasonic and microwave irradiation, electrodeposition, chemical vapor deposition, and so on (Feng et al. 2007, Yan et al. 2008, Nagarathinam et al. 2009). An ethanolic dispersion of CuS presents a high band gap energy (2.2 eV) which assists visible light photocatalytic mineralization of different EOCs. Such nontoxic, inexpensive, and stable under ambient conditions CuS would be ideal to use in clean technology.

However, there are still several issues limiting its application. One is the low photogenerated charge transfer rate on the photocatalyst surface; the other is the nanoparticles aggregation, which significantly degrades the photocatalytic performance due to the reduced surface area. In addition, the recovery and reuse of nanomaterials in heterogeneous systems remain a steep challenge for practical applications. An effective option for overcoming these drawbacks is to disperse the nanomaterials onto a suitable support such as GO/TiO₂/C₃N₄, which could increase the surface area, inhibit the recombination of photogenerated charges, and allow easy recovery of the nanomaterials.

2.4.2 Titanium dioxide (TiO₂)

TiO₂ is polymorphous and exists in three kinds of crystal structures which are Anatase (tetragonal), Rutile (tetragonal) and Brookite (orthorhombic) (Diebold 2003). Most TiO₂ in anatase form is produced as white powder, whereas other rutile grades are have slight color depending on its physical form. It has already been demonstrated that the size, composition, and wall thickness of TiO₂ could be readily varied in a controllable way to tailor their optical, electrical, thermal, mechanical, magnetic, electro-optical, and catalytic properties over a broad range. Nevertheless, very little has ever been done in an effort to control the shape for these hollow particles. Many improved TiO₂ species such as Degussa P25 TiO₂ and nanoporous anatase TiO₂ mesocrystal have achieved high level of performance in many photocatalytic applications. In our previous work, “nanosphere-like” anatase TiO₂ mesocrystal also be synthesized successfully via a facile method, which showed

excellent photocatalytic performance.(Liu et al. 2014)

Nowadays, TiO_2 is undoubtedly the most widely used photocatalyst because of its biological and chemical stability, nontoxicity, cost effectiveness, and high activity. TiO_2 coupled with other semiconductor materials with the narrow band gap like CuS has been approved to be a suitable method to improve the overall photodegradation performance (Cao et al. 2004).

2.4.3 Carboxylic acid functionalized graphene oxide (GO-COOH)

Although TiO_2 is currently considered as the most important semiconductor photocatalyst due to its non-toxicity and high thermal stability, its photocatalytic properties are limited by its rapid charge-carrier recombination. It only can degrade organic contaminants under UV light, which however accounts for less than 5% solar light (Hashimoto et al. 2005). Graphene overcomes all weaknesses of TiO_2 and has become more suitable support. As a single layer of graphite, graphene has a perfect sp^2 -hybridized two-dimensional carbon structure, enables perfect crystal and microstructure with large surface area (Lee et al. 2008, Geim 2009). Those properties not only contribute to its excellent photocatalytic ability, but also make it to be a suitable support (Dikin et al. 2007). However, the van der Waals forces and high π - π stacking between adjacent layers, facilitate irreversible aggregation of graphene or even restacking to graphite, which greatly impede its application (Kuila et al. 2012). Along with a large number of different approaches that have been developed to address this obstacle, the most reliable and facile technique is the functionalization of graphene. Graphene oxide (GO) is an oxygen-containing graphene derivative with partial breakage of sp^2 - sp^2 bonds into sp^3 - sp^3 bonds for the insertion of some pendent groups like epoxy, carboxylic acid, and hydroxyl (Chen et al. 2011, Liu et al. 2014, Zhang et al. 2014). For example, with further carboxylation, GO-COOH has enhanced hydrophobicity and more carboxyl groups as anchoring sites to bind other nanomaterials such as CuS to the surface of GO.

2.4.4 Carbon Nitride (C_3N_4)

Polymeric graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), as a metal-free *n*-type graphene-like

semiconductor, possesses many promising properties, such as unique optical, electrical, physiochemical and structural properties, which make g-C₃N₄ materials a new class of multifunctional nanocomposites for catalytic, energy and electronic applications (Wen et al. 2017). Especially, it has been reported as an attractive, inexpensive photocatalyst for hydrogen production better than GO from water splitting due to both of its reduction and oxidation levels being located inside the bandgap (Wang et al. 2014). So it is meaningful to further explore the rising star g-C₃N₄-based nanocomposites for the water remediation applications. Depending on the various methods, the g-C₃N₄-based photocatalysts can form different nanoscale morphological structures, such as nanotubes, nanorods, nanospheres, nanosheets and others (Dong et al. 2015). In general, as in the case of the graphite to graphene-based materials, ultrathin two-dimensional (2-D) nanosheets have attracted extensive attention for their exceptional optical, biocompatible and electronic properties with respect to the bulk materials. To date, ultrathin 2D g-C₃N₄ nanosheets have been proved to improve photo-response abilities compared to bulk g-C₃N₄ materials (Zhang et al. 2013, Han et al. 2016), which is mainly attributed to the unique two-dimensional architecture, environmentally benign characteristics, tunable electronic structure, and excellent chemical stability (Dong et al. 2015). The smaller particle size could shorten the distance between the photogenerated electrons and the surface, which suppresses the recombination rate of photo-generated electron-hole pairs.

2.4.5 Silver (Ag)

Recent studies have also verified that the higher specific surface area of Ag nanoparticles (<10 nm) results in a better disinfection performance (Liu et al. 2013). Due to the surface plasmon resonance (SPR) effect, Ag nanoparticles can also absorb visible light strongly, which can be utilized to induce photocatalytic disinfection as well as degradation of organic dyes, including anionic, cationic and neutral dyes (Wang et al. 2008).

The hybrid nanocomposites consisting of graphene/GO/RGO and novel metal nanoparticles provide opportunities for water purification. As reported, the GO-

TiO₂-Ag nanocomposites exhibit higher photodegradation ability (Liu et al. 2013). The unique strategy to design a nanocomposite by using 0 D Ag nanoparticles and 2D GO sheets can enhance the water disinfection and decontamination capabilities under solar irradiation.

CHAPTER 3. EFFECT OF SYNTHESIS METHOD ON THE NANOSTRUCTURE AND SOLAR-DRIVEN PHOTOCATALYTIC PROPERTIES OF TiO₂-CUS COMPOSITES

3.1 Introduction

Energy shortage and environmental pollution are major challenges for sustainable environmental development. As solar energy is a more sustainable energy source compared to others, numerous technologies have been developed based on it (Hoffmann et al. 1995). Recently, the development of photocatalysts for energy production (in the form of hydrogen) and toxic pollutants degradation under solar light has attracted great research attention (Hitoki et al. 2002) as well as their application in disinfection (Zhou et al. 2015).

So far, titanium dioxide (TiO₂) has been demonstrated as an effective photocatalyst in hydrogen generation and organic contaminants degradation under UV light, because it is chemically stable, cheap and harmless (Mills et al. 1993). UV wavelength range light, however, only accounts for less than 5% of the solar light spectrum. Thus, TiO₂ based materials have been further modified using various methods to improve its photocatalytic characteristic under visible light (Linsebigler et al. 1995). One of the methods is to couple TiO₂ with semiconductor materials that have a narrow band gap (Cao et al. 2004). Among all the semiconductor materials, copper sulfide (CuS) has been reported as one of the most effective semiconductors due to its excellent chemical and physical properties with a narrow band gap (2.1 eV) (Basu et al. 2010).

To date, two strategies have been proposed to prepare TiO₂-CuS composites. One is the direct deposition of semiconductor CuS onto the surface of TiO₂ (Ratanatawanate et al. 2008), which is a straightforward method and sensitive to the solvent owing to the weak binding force between them (He 2016). However, this method is simple and cost effective for commercial production (Chen et al. 2016). The second method is *via* a bifunctional linking molecule to bind CuS with the oxide on the surface of TiO₂ nanotubes, which can form a stronger adhesion

between the two materials to attach more CuS on the surface (Ratanatawanate et al. 2011). For instance, L-cysteine ($\text{HSCH}_2\text{CHNH}_2\text{COOH}$) can assist metallic ions or other functional groups to conjugate with semiconductors due to its multifunctional groups ($-\text{SH}$, $-\text{NH}_2$ and $-\text{COO}^-$) (Xiong et al. 2007) (Zhang et al. 2006). Moreover, L-cysteine can also release H_2S under high temperature conditions, where H_2S can act as a sulfur source and reducing agent to induce the formation of CuS nanoparticles (Chen and Zhang 2008).

However, to the best of our knowledge, few researchers have compared these two methods of TiO_2 nanospheres surface modification, for photocatalytic and hydrogen generation performance of TiO_2 -CuS. Therefore, in this study, TiO_2 nanospheres were synthesized as base material due to their superior optical, electrical, mechanical, hydrodynamic properties and more diverse applications over normal TiO_2 nanoparticles (Xu et al. 2008). Both fabrication strategies mentioned above (direct deposition vs. bifunctional linker coupling methods) were employed for copper (II) sulfide (CuS) coupling onto TiO_2 nanospheres. The effects of the different loading methods on the structure of TiO_2 -CuS composites and the influence of CuS content were further investigated. The performances of TiO_2 -CuS composites in the applications of RhB and phenol photodegradation, *E.coli* inactivation and the hydrogen generation under solar and UV light were also evaluated.

3.2 Materials and methods

3.2.1 Materials

Tetrabutyl titanate (TBT), acetic acid (CH_3COOH , 99%), thioacetamide (98%) and L-cysteine were purchased from Sigma Aldrich. Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2$, 99.5%) was purchased from Strem Chemicals. Acetone, ethanol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and Rhodamine B (RhB) were purchased from Merck Ltd (Singapore). *E.coli* K12 ER2925 was purchased from New England Biolab. Deionized (DI) water was produced by a Millipore Milli-Q water purification system.

3.2.2 Preparation of anatase TiO₂ nanospheres

Acetic acid (HAc) capped anatase TiO₂ nanospheres were synthesized by a facile solvothermal method followed calcination(Chen et al. 2013). Briefly, 1.2 mL of TBT was dropwise added into 50 mL HAc solution. Then the solution was mixed and transferred into a Teflon-lined stainless steel autoclave vessel, and maintained at 250°C for 16 h. After naturally cooling down, the precipitation was washed and centrifuged twice with ethanol and twice with DI water. The as-prepared material was calcined at 400°C temperatures at a ramp rate of 1 °C min⁻¹ and kept for 1 h at the final temperature, then cooled naturally to the room temperature.

3.2.3 Fabrication of TiO₂-CuS composites

The bifunctional linker coupling method was modified from a previous report (Ratanatawanate et al. 2011). Briefly, 50 mg TiO₂ and 224 mg (2 mmol) L-cysteine were added into 30 mL DMF solution and adjusted to pH 4 with 0.1 M HCl and ultrasonicated for 30 min. The mixture was transferred into a Teflon-lined stainless steel autoclave vessel and heated at 120°C for 2 hours under a nitrogen atmosphere. After naturally cooling down, 188 mg (1 mmol) Cu(NO₃)₂, 5 mL DMSO and 75 mg (1 mmol) thioacetamide were added into the mixture and stirred at 30°C. Then the as-prepared products were stirred and reacted with 0.5M Na₂S at room temperature to form the final TiO₂-CuS-b products. The products obtained for comparison after 6 h, 14 h, 24 h and 48 h stirring were labelled as TiO₂-CuS-b-1, TiO₂-CuS-b-2), TiO₂-CuS-b, and TiO₂-CuS-b-3, with longer reaction times leading to larger amounts of CuS loaded and lower TiO₂/CuS ratios. In order to remove residual surfactants, the composites were further washed with methanol, and freeze-dried at -50°C for 2 hours. The photodegradation performance of all these composites was evaluated and the one with the best performance (TiO₂-CuS-24h) was denoted as TiO₂-CuS-b.

For the direct deposition, 250 mg of Na₂S as the sulfur source was mixed with 50 mg TiO₂ nanospheres and then dissolved into 20 mL water(Zhang et al. 2014). After stirring for 24 h, the obtained product TiO₂-S was centrifuged and re-

dissolved into water to remove the residual sodium ions. Meanwhile, 94mg (0.5mmol), 188 mg and 376mg $\text{Cu}(\text{NO}_3)_2$ as the copper source were dissolved into water, and then added into the obtained TiO_2 -S solution gradually within 30 min, followed by continuously stirring for another 90 min to produce TiO_2 -CuS-a-1, TiO_2 -CuS-a and TiO_2 -CuS-a-2. Because the CuS can react with TiO_2 directly in short times, the reaction time was not prolonged to increase the loading of CuS; instead different amounts of CuS were added for comparison. The solution was washed and centrifuged with methanol and DI water several times. The final products were obtained after freeze-drying at -50°C for 2h, to produce the one (188mg $\text{Cu}(\text{NO}_3)_2$ added) with the best photocatalytic performance, namely TiO_2 -CuS-a.

3.2.4 Characterizations

X-ray powder diffraction (XRD) patterns were recorded on a D8-Advance Bruker-AXS diffractometer using Cu K_α irradiation to determine the crystallinity and phase. The morphology of the as-synthesized samples was evaluated by field emission scanning electron microscopy (FESEM, JEOL 7600F). Energy dispersive X-ray (EDS) measurement was conducted using the EDAX system (Oxford, 80 mm^2). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken using a JEOL 2010-H TEM. Fourier transform infrared (FTIR) spectra were collected on a Bruker FTIR spectrometer (Nicolet IS10) with solid powder samples. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Kratos Axis Ultra Spectrometer with a 15 kV and 10 mA monochromic Al K_α source at 1486.7 eV. UV-Vis absorption spectra of the 0.1 mg mL^{-1} dispersion solutions were measured using an Evolution 300 spectrophotometer under room temperature. The possible leaching of Cu^{2+} was checked by quantification of the Cu^{2+} concentration in solution using micro plasma atomic emission spectroscopy (MP 4100 AES).

3.2.5 Photocatalytic degradation of RhB dye and phenol

The photocatalytic degradation of RhB dye and phenol were carried out at room

temperature. 50 mg of TiO₂-CuS composite samples were mixed into 50 mL RhB (1 mg L⁻¹) or phenol (200 mg mL⁻¹) in a 120 mL quartz capsule. After stirring for 1 hour in the dark to reach the adsorption equilibrium, the suspensions were exposed to either solar light or UV light from a solar light simulator. The light sources were either a 200W ozone free mercury-xenon lamp for UV light generation or a 300 W ozone free xenon lamp for visible light (Newport Oriel). The distance between the light source and the quartz capsule surface was 15 cm.

Three milliliter mixed liquor was collected for analysis at 5 mins, 10 mins, 20 mins, 30 mins, 40 mins, 50 mins, 60 mins, 70 mins and 90 mins. The RhB degradation results were visualized by UV-Vis spectrometry. The analysis of concentration and intermediates of phenol degradation was conducted by high performance liquid chromatography (HPLC, Agilent 1100) with a reverse-phase column (Agilent, Eclipse XDB-C18, 150 × 4.6 mm). Total organic carbon (TOC) was measured using a TOC analyzer (TOC-L CPH/CPN; Shimadzu, Kyoto, Japan).

3.2.6 Antibacterial test under solar light

Gram-negative bacteria *E.coli* (ATCC 8739) was chosen as a standard microorganism to evaluate the antibacterial ability of the obtained samples. *E. coli* was cultivated in Luria-Bertani broth and incubated for 24 h at 37°C. *E. coli* cells were harvested at exponential growth phase by centrifugation and resuspended in a saline solution (0.9% NaCl) to remove residual macromolecules. The final concentration was around 10⁸ colony forming units (CFU mL⁻¹). All solution and glass apparatuses used in the experiments were autoclaved.

The photocatalytic antibacterial experiment was conducted under the same solar irradiation simulator using a 300 W ozone free xenon lamp for the visible light source (Newport Oriel). Meanwhile, the control tests were conducted in the dark. The experiment was initiated by mixing composites (1 mg mL⁻¹) with *E.coli* saline solution (10⁸ CFU mL⁻¹). At 0, 20, 40, 60, 80 and 100 mins, the mixtures were sampled for cell viability evaluation. Briefly, samples were diluted with a gradient method and applied uniformly on three LB plates as triplicates to count the

inactivation rate. As a comparison, a blank control experiment without any composites was also conducted under the same conditions.

The TiO₂-CuS composites disinfection capability was further verified by LIVE/DEAD BacLight bacterial viability assay (Invitrogen, USA) and visualized with a Leica TCS SP5 laser scanning confocal microscope (Leica Microsystems, Germany). The morphological changes of *E. coli* were observed by scanning electron microscopy (SEM, JEOL, 6340). The *E. coli* and TiO₂-CuS composites mixture was collected with a 0.22 µm glass filter. Cells on the filter were quickly soaked in 2% glutaraldehyde for 2 h, and then soaked and washed 3 times (soaked 20 min for each time) with 0.1 M sodium cacodylate buffer. Cells were attached on a filter and dehydrated in series of 50, 70, 85 and 90% ethanol for 10 mins and stored in 100% ethanol. Before being visualized by SEM, the filter was dried at the critical point.

3.2.7 Hydrogen evolution reaction under solar light

The photocatalytic hydrogen evolution reaction was conducted in a top-irradiation type closed Pyrex reactor (volume: 550 mL) under the same solar irradiation simulator (Newport Oriel). 1 mg mL⁻¹ of the photocatalyst powder was suspended in 100 mL of the triethanolamine water mixture (10 %) by magnetically stirring. The photocatalyst suspension was sparged by nitrogen gas for 20 mins to remove dissolved oxygen. Gas produced via the photocatalytic hydrogen evolution reaction was analyzed using an off-line TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A).

3.2.8 Electrochemical and electron paramagnetic resonance (EPR) measurements

Electrochemical experiments were performed in a three electrode arrangement with a Ag/AgCl (KCl_{sat.}) reference electrode, a platinum foil as the counter electrode and a 0.071 cm² surface area planar glassy carbon working electrode (GCE). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using an ECO Chemie Autolab potentiostat. All

current densities were calculated using the geometrical area of the GCE. Continuous wave X-band EPR experiments were conducted with a Bruker Biospin ELEXSYS-II E 500 spectrometer. The modulation amplitude was set to 1 G and field sweep time was 30 seconds. Photolysis experiments were conducted with a Bruker ER 203 UV irradiation system using a short arc 100 W mercury lamp (LSB610 100W Hg).

3.3 Results and discussion

3.3.1 Fabrication of TiO₂-CuS-a and TiO₂-CuS-b

The difference of two synthesis pathways of TiO₂-CuS-a and TiO₂-CuS-b are illustrated in scheme 3.1. As an amino acid, L-cysteine contains three reactive centers: an amine (-NH₂), a thiol group (-SH), and a carboxylic acid (-COOH), which can assist in anchoring CuS nanoparticles on the surface of TiO₂ nanospheres. For TiO₂-CuS-b, the TiO₂ nanospheres reacted with L-cysteine through carboxylic acid groups. Meanwhile, thiol groups provided binding sites for copper ions (step 1 of scheme 1a). After adding copper nitrate Cu(NO₃)₂ and DMSO (step 2 of scheme 1a), Cu(II) ions showed a high affinity to the thiol groups and S(II) provided by DMSO to form CuS. Color change of the sample from white to brown indicated the successful fabrication of the TiO₂-CuS composite. In the direct deposition process, Na₂S was added in methanol and stirred for one day to reinforce the binding between S(II) and TiO₂ nanospheres (step 1 in scheme 1b). After adding Cu(NO₃)₂, CuS nanoparticles were successfully synthesized and grown on the surface of TiO₂ nanospheres.

Scheme 3.1 Schematic of reaction mechanism of the binding of copper sulfide with TiO_2 nanosphere (MC) via direct deposition (a) or bifunctional linker coupling method (b).

Fig. 3.1 shows the FTIR spectra of all products for each deposition step, including pure TiO_2 nanospheres, $\text{TiO}_2\text{-S}$, $\text{TiO}_2\text{-CuS-a}$, $\text{TiO}_2\text{-L-cysteine}$ and $\text{TiO}_2\text{-CuS-b}$. The absorption band around 1640 cm^{-1} is the characteristic vibration of the hydroxyl ($-\text{OH}$) group (Dutoit et al. 1996), and the broad shoulder from approximately 950 to 800 cm^{-1} results from the characteristic vibrations of the inorganic Ti-O-Ti network (Liu et al. 2008). Furthermore, adsorbed water detectable in the spectrum via the bending mode of H-O-H can be seen below 1000 cm^{-1} (Liu et al. 2013). CuS nanoparticles were formed as evidenced by the adsorption bands around 1348 cm^{-1} of $\text{TiO}_2\text{-S}$ (in the $\text{TiO}_2\text{-CuS-a}$ spectrum). The peak at 1126 cm^{-1} indicates the presence of the S-O stretch, suggesting the CuS binding on the surface of TiO_2 through building the S-O group. From the $\text{TiO}_2\text{-L-cysteine}$ spectrum, groups of $-\text{NH}_3^+$, $-\text{CH}_2$, and $-\text{SH}$ from the L-cysteine can be found in the albeit weak peaks at

3429, 2971 and 2534 cm^{-1} , respectively (Ratanatawanate et al. 2008). The clearly observed peaks at 1371 and 1520 cm^{-1} are assigned to the asymmetric stretching vibration of the carboxylate group (COO^-), which can also be found in the TiO_2 -CuS spectrum (Ratanatawanate et al. 2011). It suggests that the L-cysteine was likely anchored on the surface of the TiO_2 nanosphere via the carboxylate group. The characteristic spectrum of the thiol group ($-\text{SH}$) at 2534 cm^{-1} cannot be observed. After adding copper ions, a binding between the $-\text{SH}$ group and Cu^{2+} ions contributed to form CuS nanoparticles at the surface of TiO_2 nanosphere, as evidenced by the disappearance of the $-\text{SH}$ group in the FTIR spectrum of TiO_2 -CuS-b. FTIR results supported the successful synthesis of TiO_2 -CuS-a and -b composites via the routes in Scheme 3.1.

Fig. 3.1 FTIR spectra of TiO_2 nanosphere, $\text{TiO}_2\text{-S}$, $\text{TiO}_2\text{-CuS-a}$, $\text{TiO}_2\text{-L-cysteine}$ and $\text{TiO}_2\text{-CuS-b}$.

3.3.2 Structural and Morphological Properties

The microscopic images of TiO_2 , $\text{TiO}_2\text{-CuS-a}$ and -b are shown in Fig 3.2. The change of surface morphology after CuS nanoparticles were anchored on the surface of $\text{TiO}_2\text{-CuS-a}$ and -b can be clearly observed. According to the FESEM

images, TiO_2 , $\text{TiO}_2\text{-CuS-a}$ and -b all displayed the nanosphere morphology. The diameter of anatase TiO_2 (MC) nanosphere was around 200-500 nm. Fig 2b and 2f show CuS were undoubtedly loaded onto the TiO_2 surface in the form of nanoflakes with the length (around 800 nm) larger than the diameter of TiO_2 nanospheres. This demonstrates that a “spiky ball” $\text{TiO}_2\text{-CuS-b}$ was obtained and such kind of 3D hierarchical microstructure also can be found in other TiO_2 -based metal sulfide/oxide, for instance, $\text{TiO}_2\text{-CdS}$ with flower-like nanostructure(Mao et al. 2013). Compared with $\text{TiO}_2\text{-CuS-b}$, only small amounts of CuS were anchored on the $\text{TiO}_2\text{-CuS-a}$ in nanoparticle morphology. It is obvious that $\text{TiO}_2\text{-CuS-b}$ may provide a larger surface area that can improve its catalytic properties. Fig 3. 2e and 3.2g display lattice planes of CuS (103) with a lattice spacing of 0.33 nm(Yu et al. 2010) and the presence of TiO_2 nanospheres, which confirmed that CuS was uniformly anchored on the surface of the whole of the TiO_2 nanospheres without aggregation in $\text{TiO}_2\text{-CuS-a}$ and -b . Moreover, there was no significant change observed of the surface morphology of both $\text{TiO}_2\text{-CuS-a}$ and $\text{TiO}_2\text{-CuS-b}$ after the photocatalysis reaction (Fig. 3. 2d&h), which confirmed the good stability of the products.

Fig. 3.2 FESEM and HRTEM images of (a,e) TiO_2 nanosphere, (b,f) $\text{TiO}_2\text{-CuS-b}$, (c,g) $\text{TiO}_2\text{-CuS-a}$, (d,h) FESEM Images of $\text{TiO}_2\text{-CuS-a}$ and $\text{TiO}_2\text{-CuS-b}$ after photocatalysis

The surface area analysis using typical plots of N₂ adsorption-desorption isotherms and pore size distribution curves of all as-prepared products are shown in Fig. 3.3. The samples exhibited isotherms of type IV (BDDT classification) with hysteresis loops of type H3 at relative pressure ranges of 0.7–1.0, indicating the presence of mesoporous structures(Wei et al. 2013). The corresponding pore size distribution of the samples are shown in Fig 3b. The pore size distributions indicated that TiO₂-CuS-b presented a relatively wide distribution. Taking into account the morphology of the nanocomposite observed by HRTEM, the pores should be the inter pores between the CuS nanoflakes. In addition, the BJH method cumulative adsorption surface area of the prepared TiO₂-CuS-b nanoparticles was 37.4 m²/g. In contrast, the adsorption surface area of TiO₂-CuS-a and TiO₂ were 19.8 m²/g and 18.1 m²/g respectively. A larger surface area provides more surface active sites for the adsorption of the reactive molecules, leading to a more efficient photocatalytic process, so we conclude that the TiO₂-CuS-b nanocomposites might have better photocatalytic performance.

Fig. 3.3 (a) Nitrogen adsorption-desorption isotherms and the (b) Corresponding pore size distribution curves of all the as-synthesized products.

In order to identify the crystal phase of TiO₂ nanospheres and TiO₂-CuS-a and -b, XRD patterns were obtained and are shown in Fig. 3.4. The peaks at $2\theta = 25.3^\circ$, 37.9° , 48.3° , 55.3° , 63.1° , 69.2° and 75.1° correspond to the properties of crystallized

anatase TiO₂ (JCPDS No.21-1272) (Gao et al. 2012), whereas in TiO₂-CuS-a and -b, the obvious peaks at around 29.3° and 32.5° were attributed to the (101) and (006) crystal planes of CuS (JCPDS No.06-0464) (Wang et al. 2014). These XRD spectra further verified the formation of TiO₂-CuS composites.

Fig. 3.4 XRD patterns of TiO₂ nanosphere, TiO₂-CuS-a and TiO₂-CuS-b.

From the XPS of each element in the powder samples (Fig. 3.5a, b, c and d), the Ti2p₃ at 459.2 eV, O1s at 530 eV, Cu2p₃ at 931.8eV and S2p₃ at 162eV can be observed clearly, indicating the components of TiO₂-CuS-a and -b were mainly TiO₂ and CuS. Furthermore, the atomic concentrations were obtained from XPS narrow spectra (Table 1). In comparison to TiO₂-CuS-a, TiO₂-CuS-b contained a higher CuS content (13.4% vs. 6.7%). The excess amount of Cu in TiO₂-CuS-a might form Cu(OH)₂, which is supported by the two peaks of O1s in TiO₂-CuS-a indicating the presence of metal-O and O-H. The excess amount of S in TiO₂-CuS-b might be from the -SH functional group in L-cysteine.

Table 3.1. Atomic concentration from XPS narrow spectra

	Ti2p	O1s	Cu2p3	S2p
TiO ₂	27.6	52.6	N.D.	N.D.
TiO ₂ -CuS-a	17.0	36.4	6.7	2.1
TiO ₂ -CuS-b	9.2	19.9	13.4	12.7

Fig. 3.5 XPS high –resolution spectrum of each element and survey spectra of TiO₂, TiO₂-CuS-a and TiO₂-CuS-b.

EDS analysis also further confirmed the result of XPS analysis that TiO₂-CuS-b contained a higher CuS content than TiO₂-CuS-a. In addition, as observed from Fig. 3.6, the elements of Ti, O, Cu and S dominate all TiO₂-CuS composites without obvious impurities.

Fig. 3.6 EDS spectra of (a) TiO₂-CuS-a and (b) TiO₂-CuS-b.

3.3.3 Optical properties of all TiO₂-based nanomaterials

UV-visible diffuse reflectance spectra (DRS) of all obtained products are shown in Fig. 3.7. All samples except pure CuS exhibited a strong absorption band at around 400 nm, due to the presence of the wide band gap anatase TiO₂ (up to 3.3 eV) (Babu et al. 2015). Pure CuS had a clear optical response in the visible region with a peak at around 600 nm ($E_g=2.1$ eV) (Nair et al. 1998). Hence, obtained TiO₂-CuS-a and TiO₂-CuS-b composites had strong absorption in both the UV and visible light due to the presence of copper compounds. In contrast, TiO₂-S and TiO₂-L-cysteine (without copper) provided similar absorption capabilities as pure TiO₂ in the UV region. With copper incorporation, both TiO₂-CuS-a and -b exhibited a quantitative red shift of λ_{onset} compared to pure TiO₂. Moreover, the peaks of CuS in TiO₂-CuS composites had red-shifts compared to pure CuS. More redshift was observed for the -S ligand than for L-cysteine ligand, which may lead to the different electron-donating abilities of ligands (Cheng and Walker 2010).

Fig. 3.7 UV-Vis diffuse reflectance spectra (DRS) of all as-synthesized samples

3.3.4 Disinfection, Photodegradation of organic compounds and hydrogen evolution under solar and UV light

The effect of composite structure on disinfection efficiency

In order to study the effect of different composite structures on the photodegradation efficiency, *E.coli* inactivation experiments by TiO₂-CuS-a and -b were carried out and compared under solar irradiation. TiO₂-CuS-b displayed higher capabilities for photocatalytic sterilization than TiO₂-CuS-a (Fig. 3.8a). 99% *E.coli* cells were inactivated by TiO₂-CuS-b within 60 mins. under solar irradiation and 80 mins without solar light. Yet, around 10% and 30% *E.coli* survived in the TiO₂-CuS-a saline solution until the end of experiment, with and without solar light irradiation, respectively. Fig. 3.8b and c show the FESEM images of *E.coli* cells after photocatalytic inactivation by TiO₂-CuS-b. The cell walls of the *E.coli* were significantly damaged and almost all bacteria were disintegrated.

Fig. 3.8 Antibacterial capabilities of TiO₂-CuS-a and -b with and without solar irradiation (a) *E.coli* viability percentage by time course; SEM images of *E.coli* cells after 0.22 μ m membrane filtration after photocatalytic sterilization under solar light with TiO₂-CuS-b (b) and (c).

In order to verify the reliability of the colony forming count method, the LIVE/DEAD BacLight bacterial viability kit was used to further confirm the antibacterial activity of TiO₂-CuS-a and -b. The bacteria with damaged membranes exhibit red fluorescence and the bacteria with intact cell membranes show green fluorescence after treating with the aforementioned kit. As presented in Fig. 3.9a

and d, nearly all *E.coli* were inactivated and appeared in red fluorescence with or without solar irradiation using TiO₂-CuS-b, which is consistent with the results in Fig. 3.9(1) and (4). In contrast, some *E.coli* still survived and expressed green fluorescence using TiO₂-CuS-a (Fig 9(2) and (5)) regardless of light conditions. Against the control, 80% *E.coli* were removed with or without solar light in 100 mins.

Fig. 3.9 Fluorescence microscopic images and agar plate pictures of bacteria after incubation with or without solar light in saline solution after 100 mins. with different samples (1,a) &(2,b): TiO₂-CuS-b & -a with solar light; (3,d)&(5,e): TiO₂-CuS-b & -a without solar light; (3,c)&(6,f): Blank control with and without solar light.

It is therefore concluded that “spiky ball - like” TiO₂-CuS-b had improved photocatalytic abilities compared to pure “nanosphere-like” TiO₂ and TiO₂-CuS-a because of the higher surface area and the improved charge separation efficiency.

Photodegradation of organic compounds and hydrogen evolution under solar light

In order to study the effect of different composite structures on the photodegradation efficiency, phenol photodegradation and the hydrogen evolution reaction initiated by TiO_2 , $\text{TiO}_2\text{-CuS-a}$ and -b were carried out and compared under solar light. As shown in Fig 3.10a and b, the $\text{TiO}_2\text{-CuS-b}$ displayed higher degradation ability and TOC removal of phenol compared to $\text{TiO}_2\text{-CuS-a}$. The degradation percentages of phenol were 81% and 100% for $\text{TiO}_2\text{-CuS-a}$ and -b respectively and the TOC removal efficiency by $\text{TiO}_2\text{-CuS-a}$ and -b were 49.5% and 59% under 390 mins. Solar light exposure, demonstrating that the loaded CuS nanoflakes enhanced the photocatalytic abilities of TiO_2 under solar light. In order to further investigate the capability of organic matter degradation, the photodegradation of RhB by $\text{TiO}_2\text{-CuS}$ composites was conducted as well (SI). The RhB removal rate by $\text{TiO}_2\text{-CuS-b}$, $\text{TiO}_2\text{-CuS-a}$ under solar irradiation within 90 mins. were 69.2%, 44.8%, respectively, and both were higher than the pure TiO_2 removal rate of 30.7%.

Fig. 3.10 The comparison of percentage (a) photocatalytic degradation and (b) TOC removal (mineralization) of phenol (200 mg L^{-1}) in aqueous suspension (1 mg mL^{-1}) by TiO_2 , $\text{TiO}_2\text{-CuS-a}$ and -b under solar irradiation

Fig. 3.11a shows that the amount of hydrogen generated by bare TiO_2 nanosphere was the lowest under solar light because of the rapid recombination between CB electrons and VB holes. With modification by CuS nanoflakes, the H_2 generation

activity of TiO₂ nanospheres could be improved significantly to 1.06 and 1.53 mmol h⁻¹ g⁻¹ for TiO₂-CuS-a and -b, respectively. Moreover, as shown in Fig 3.11b, during 4 cycles of H₂ evolution experiments on TiO₂-CuS-b, the activity is still maintained without noticeable decrease, demonstrating the good recyclability and stability of the samples.

Fig. 3.11 (a) Stable hydrogen evolution from water by TiO₂-based composites under solar light, (b) 4 cycles of H₂ evolution experiments on TiO₂-CuS-b under solar light.

Photodegradation of organic compounds and hydrogen evolution capabilities under UV light

In order to compare photodegradation abilities of TiO₂, TiO₂-CuS-a & -b under solar light and UV light, experiments of phenol degradation and the hydrogen evolution reaction were also performed under UV light. Similar to solar light, TiO₂-CuS-b showed better photocatalytic ability than TiO₂-CuS-a under UV light. However, as shown in Fig 3.12b, the performance of TiO₂-CuS-b was not better than pure TiO₂, likely due to the coverage of UV-activated reaction sites by CuS loaded on the surface of TiO₂. Pure TiO₂ could make better use of the UV light to excite those reaction sites. Hence, CuS can enhance the degradation ability of TiO₂ under solar light, but it did not assist TiO₂ under UV light. Fig 3.12c shows the

main intermediates of phenol degradation under UV light including maleic acid, oxalic acid and hydroquinone at low concentrations. Toxic intermediates such as catechol (Jawad and Nawi 2011) and benzoquinone were not found, which proved that TiO₂-CuS-b is more eco-friendly.

Fig. 3.12 The comparison of percentage (a) photocatalytic degradation, (b) TOC removal (mineralization) of phenol (200ppm) in aqueous suspension (1mg/mL) by TiO₂, TiO₂-CuS-a & -b under UV irradiation (c) the intermediates in the phenol degradation under UV light.

In contrast, under UV light, the H₂ generation rate of TiO₂-CuS-b composites was 1.76 mmol h⁻¹ g⁻¹ which was lower than TiO₂ (7.55 mmol h⁻¹ g⁻¹) and TiO₂-CuS-a (6.47 mmol h⁻¹ g⁻¹). Also the recyclability and stability of TiO₂-CuS-b was further demonstrated from the 4 cycles of H₂ evolution experiments on TiO₂-CuS-b as shown in Fig. 3.13b. The overall photocatalytic hydrogen evolution performance of all obtained TiO₂-based composites under UV light was better than those under solar light (Fig. 3.11). The reason was discussed in the above section. Furthermore, CuS anchored on TiO₂-CuS-b was more stable than those on TiO₂-CuS-a as shown in the Cu²⁺ leaching measurement (Table 3.2).

Fig. 3.13 (a) Stable hydrogen evolution from water by TiO₂-based composite under UV light, and (b) 4 cycles of H₂ evolution experiments on TiO₂-CuS-b under UV light.

Table 3.2 The concentration of leached Cu²⁺ after degradation

mg L ⁻¹	RhB	Phenol	HER
TiO₂-CuS-a	0.082	0.073	0.098
TiO₂-CuS-b	0.043	0.045	0.052

3.3.5 Photocatalytic mechanism

The anti-recombination abilities of all TiO₂ based nanomaterials were investigated by PL spectroscopy. A broad emission from 345 to 430 nm peaked at $\lambda = 400$ nm under an excitation at 250 nm and a broad emission from 570 to 675 nm peaked at $\lambda = 600$ nm under an excitation at 450 nm were observed (Fig. 3.14). In both excitation wavelengths, TiO₂-CuS-b composites exhibited the most significant low PL emission intensity, which indicates that TiO₂-CuS-b can effectively suppress the e⁻/h⁺ recombination via faster electron transfer and therefore, contribute to better photocatalysis ability.

Fig. 3.14 PL spectra (excitation at (a) 250 nm and (b) 450 nm respectively) of all TiO₂ based composites.

The cyclic voltammetric (CV) profiles of bare glassy carbon electrode (GCE), TiO₂ and TiO₂-CuS-a and -b modified GCE were obtained to analyze the electron transfer process. Fig 3.15a shows there was a small increase in the redox peak currents for GCE-TiO₂-CuS-b compared to bare GCE, GCE-TiO₂ and GCE-TiO₂-CuS-a. This is most likely caused by an increase in the surface area of the electrode due to the porous coated surfaces or a change in the diffusion mode within the porous structure(Chan et al. 2015). However, the CV results in Fig 15a indicated that the anodic (E_p^{ox}) to cathodic (E_p^{red}) peak-to-peak separation was the smallest on the GCE-TiO₂-CuS-b coated electrode suggesting that it had the fastest heterogeneous electron transfer rates and supporting better catalysis capability(How et al. 2014).

The internal resistance and the electron transport process of all TiO₂-based nanomaterials were also studied by using electrochemical impedance spectroscopy (EIS). It can be seen from the Nyquist plots in Fig 3.15b, that the electrochemical reaction and the charge transfer at the GCE contributed to the semicircles spectra. In this study, GCE-TiO₂-CuS-b exhibited the smallest charge transport resistance due to the increase in surface area, thus increasing the potassium ferricyanide adsorption as well as penetration of redox couples into the surface. Correspondingly, bode phase plots with characteristic frequency peaks (1-10⁴ Hz) are shown in Fig. 15c. GCE-TiO₂-CuS-b had the lowest frequency peak which

reflects the long recombination lifetime (τ_r) or electron lifetime (τ_e)(Hsu et al. 2008). In conclusion, TiO₂-CuS-b not only had a lower electron transport resistance but also a longer electron lifetime than other two nanomaterials.

Fig. 3.15 (a) CVs of 50mM potassium ferricyanide in 0.1M phosphate buffered saline at bare GCE, modified GCE with TiO₂ and TiO₂-CuS-a & -b over the potential range from - 1 to 1 V vs. SCE by 10 consecutive CV scans at a scan rate of 0.05 V s⁻¹. (b) Nyquist plots and (c) Bode phase plot of electrochemical impedance spectra measured in a potassium ferricyanide solution.

As a result, TiO₂-CuS-b achieved higher photocatalytic degradation activity, better antibacterial and hydrogen generation abilities than TiO₂-CuS-a and TiO₂ under solar irradiation. In order to better understand the underlying causes, the photocatalytic mechanism was further explored and discussed. DMPO spin-trapping EPR measurements were employed in methanol dispersions for DMPO-O₂^{•-} and aqueous dispersions for DMPO-•OH (Ma et al. 2016)(Fig. 3.16). Irradiation of aqueous solutions containing TiO₂-CuS-b in the presence of DMPO resulted in the characteristic 4 line spectrum with a 1:2:2:1 ratio due to the DMPO-•OH radical. The signal that is present before irradiation was due to additional radicals being produced under ambient light conditions in the several minutes it took the sample to be transferred to the EPR spectrometer. The additional signals were due to the formation of much lesser amounts of other radicals that occurs in aqueous solutions containing DMPO.

For the methanol solutions containing TiO₂-CuS-b and DMPO, irradiation produced the 6 lines signal characteristic of DMPO-O₂^{•-} along with overlapping lines from other radicals (such as DMPO-OCH₃[•]) that are produced via irradiation of methanol solutions containing TiO₂ and DMPO ($CH_3OH + h^+ \rightarrow OCH_3^{\bullet} + H^+$)(Dvoranova et

al. 2014). Much weaker signals were also seen before irradiation due to some reactions in ambient light. Because $O_2^{\bullet-}$ is itself not an oxidant although it can act as a hydrogen atom abstracting agent, therefore, it is possible that other lesser long-lived radicals are also responsible for the degradation reactions. However, the signal of $O_2^{\bullet-}$ is much stronger than that of $OCH_3^{\bullet}$ and $\cdot OH$ even 1 minute after the irradiation source was disconnected, suggesting that $O_2^{\bullet-}$ is the main radical species produced via photocatalysis under solar light in methanol.

Fig. 3.16 EPR spectra obtained for solutions containing the spin-trap DMPO and TiO_2 -CuS-b. Aqueous dispersions formed DMPO- $\cdot OH$ and methanol dispersions formed DMPO- $O_2^{\bullet-}$.

A possible photocatalytic mechanism of the charge excitation and separation processes of TiO_2 -CuS-a and TiO_2 -CuS-b is proposed in Scheme 3.2. Under solar light irradiation, photogenerated electrons can be transferred from conduction band (CB) of CuS to TiO_2 since the CB of TiO_2 is more positive than CuS. Meanwhile, the holes leave the VB of CuS, so that efficient electron-hole pairs can be achieved. Then the generated electrons will react with O_2 or H^+ during organic photodegradation or hydrogen generation processes respectively. In the case of

photodegradation process, the generated electrons react with surface O_2 and convert them to reactive oxygen species (ROSs), specifically the superoxide radical ($O_2^{\cdot-}$) which is the main radical to degrade pollutants (Ma et al. 2016). In the hydrogen generation process, the generated electrons react with H^+ in the presence of a sacrificial agent (in this case triethanolamine), and the H^+ on the surface of the photocatalysts will be converted to hydrogen. For the generated holes at the surface of CuS and TiO_2 , during organic photodegradation process, h^+ will oxidize H_2O/OH^- to form $\cdot OH$, which will degrade the RhB/phenol/bacteria directly. However, during the hydrogen generation process, the h^+ trapped on the surface of CuS are scavenged by triethanolamine (a well-known h^+ scavenger) present in the reaction medium to produce H^+ , which in turn will be reduced by the photo-excited electron to produce hydrogen.

The combination of TiO_2 and metal sulfide aims to prevent the recombination of electrons and holes by prolonging the reaction path and accelerating the electron transfer rate under solar irradiation, resulting in the increase of the amount of generated radicals which contribute to better photocatalytic performance. The CuS flakes anchored on the surface of TiO_2 formed a “spiky ball - like” TiO_2 -CuS-b, which can provide larger surface area to enhance the photocatalytic ability under solar light.

Scheme 3.2 The mechanism illustration of the photo degradation activity for TiO₂-CuS-a and -b composites.

3.4 Conclusion

In this study, semiconductor CuS was fabricated onto TiO₂ with two different strategies to generate TiO₂-CuS-a through direct deposition and TiO₂-CuS-b *via* the aid of the bifunctional linking molecule - L-cysteine respectively. The effect of different fabrication methods on the nanostructure and morphology of TiO₂-CuS composite were systematically studied. Synthesized two different TiO₂-CuS composites were evaluated with different wavelengths of irradiation light in terms of pollutant degradability, disinfection and hydrogen generation capabilities. It is concluded that TiO₂-CuS-b *via* the aid of bifunctional linking molecule - L-cysteine, has a regular “spiky ball - like” structure with high-effective combination with CuS as well as better RhB & phenol degradation performance, inactivation of *E.coli* and hydrogen generation abilities than TiO₂-CuS-a under solar light due to its larger surface area and the improved charge separation efficiency. The mechanism was also investigated systematically by various techniques to prove that reactive oxygen species were produced to degrade the pollutants.

CHAPTER 4. FACILE ROOM-TEMPERATURE SYNTHESIS OF CARBOXYLATED GRAPHENE OXIDE-COPPER SULFIDE NANOCOMPOSITE WITH HIGH PHOTODEGRADATION AND DISINFECTION ACTIVITIES UNDER SOLAR LIGHT IRRADIATION

4.1 Introduction

The ever-growing demand for the clean water has stimulated significant research effort for the huge development of advanced water treatment technologies. Semiconductor-mediated heterogeneous photocatalysis is considered as a promising method to remove pathogens and organic pollutants from wastewater ¹. A great number of materials have been developed and involved, including Cu_{2-x}S ($0 \leq x \leq 1$), CdS, ZnO etc. Among those, copper sulfide (CuS) has been reported as one of the most important semiconductors due to its excellent chemical and physical properties at room temperature ². Various morphologies of CuS including nanopowders, nanotubes, nanorods, nanoribbons and so on have been successfully fabricated via versatile synthetic strategies such as solventless and solution thermolysis, solution-phase reaction, ultrasonic and microwave irradiation, etc ^{3,4}. However, those methods usually require complicated procedures and elevated temperatures, which greatly hinder the process of scale up. Recently, some relatively facile synthesis approaches have been advocated to prepare CuS-based semiconductor photocatalyst. For example, TiO₂-CuS was obtained via a facile route using a sol-gel method by Park et al. ³. Zhang et al. obtained CuS nanopowder by solvothermal method using Na₂S as the sulfur source ⁴. Nevertheless, there are still several issues limiting the application of CuS. To the best of our knowledge, there are few low-energy approaches developed for the synthesis of CuS-based composite photocatalyst, e.g., at room temperature. Moreover, the low photogenerated charge transfer rate on the photocatalyst surface and high aggregation of CuS nanomaterials, which significantly degrade the photocatalytic performance. An effective option for overcoming these drawbacks is to disperse the nanomaterials onto a suitable support, which could increase the surface area, inhibit

the recombination of photogenerated charges, and allow easy recovery of the nanomaterials.

As a single layer of graphite, graphene has a perfect sp^2 -hybridized two-dimensional carbon structure, including perfect crystal and microstructure with large surface area ^{5,6}. Those properties can not only enhance photoactivity of other photocatalysts, but also make it be suitable support ⁷. However, the van der Waals forces and high π - π stacking between adjacent layers, facilitate irreversible aggregation of graphene or even restacking to graphite, which greatly impede its application ⁸. Along with a large number of different approaches that have been developed to address these obstacles, the most reliable and facile technique is the functionalization of graphene. Graphene oxide (GO) is an oxygen-containing graphene derivative with partial breakage of sp^2 - sp^2 bonds into sp^3 - sp^3 bonds for the insertion of some pendent groups like epoxy, carboxylic acid, and hydroxyl ⁹⁻¹¹. For example, with further carboxylation, GO-COOH has enhanced hydrophilicity and more carboxyl groups as anchoring sites to strongly bind other nanomaterials such as CuS to the surface of GO.

In this work, we put forward a facile yet efficient room-temperature synthesis approach for the fabrication of GO-COOH-CuS nanocomposite and explored its general environmental applications. A systematic characterization was carried out for the pristine materials (CuS and GO-COOH) and their composite (GO-COOH-CuS). Laboratory-scale batch experiments were conducted to investigate the photocatalytic degradation of phenol and rhodamine B (RhB), as well as the inactivation of *Escherichia coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*) under solar light irradiation using the as-synthesized materials as the photocatalysts. A plausible charge-transfer mechanism is tentatively proposed for the photocatalysis process. To the best of our knowledge, the multifunctional GO-COOH-CuS nanocomposite is for the first time rapidly synthesized via such a facile and scalable room-temperature method and used for water decontamination and disinfection with excellent performance just during a short operating period under solar irradiation.

4.2 Materials and methods

4.2.1 Materials

Sodium nitrate (NaNO_3 , 99%), potassium permanganate (KMnO_4 , 99%), hydrogen peroxide (H_2O_2 , 35%), concentrated sulfuric acid (H_2SO_4 , 98%), chloroacetic acid ($\text{ClCH}_2\text{CO}_2\text{H}$, 99%), concentrated hydrochloric acid (HCl , 36.5%), and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, 99%) were purchased from Sigma-Aldrich (Singapore). Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2$, 99.5%) was purchased from Strem Chemicals. Natural graphite (SP1) was purchased from the Bay Carbon Company (USA). Ethanol, acetone, dimethyl sulfoxide (DMSO), and rhodamine B (RhB) were purchased from Merck Ltd (Singapore). The deionized (DI) water was produced from Millipore Milli-Q water purification system.

4.2.2 Synthesis of GO-COOH sheets and GO-COOH-CuS nanocomposites

GO sheets were exfoliated from natural graphite according to the modified Hummers' method^{12,13}. GO-COOH was synthesized under strongly basic condition to convert hydroxyl groups to carboxylic acid moieties by activating the GO sample with chloroacetic acid ($\text{ClCH}_2\text{CO}_2\text{H}$)¹³. In a typical process, 1.2 g of chloroacetic acid, 1 g of NaOH and 50 mg of GO were added to 100 mL DI water and then sonicated for 3 h to speed up the elimination of sodium chloride. The resulting GO-COOH solution was neutralized by HNO_3 , and purified with acetone and water for several times.

For the synthesis of GO-COOH-CuS nanocomposite, we herein developed a facile and scalable method to anchor CuS nanoparticles (NPs) on large GO-COOH sheets at room temperature. Briefly, various amounts (1 mL, 5 mL, 10 mL and 20 mL) of 1 mg mL^{-1} GO-COOH solution were mixed with 1 mmol of $\text{Cu}(\text{NO}_3)_2$, 1 mmol of $\text{C}_2\text{H}_5\text{NS}$ and 10 mL of DMSO. DMSO acted as a solvent and co-reactant to furnish the sulfur source in the form of H_2S . The mixture was stirred for 24 h at ambient temperature to ensure CuS NPs anchored on GO-COOH sheets. The products were centrifuged and rinsed with acetone, ethanol and DI water several times to remove the residual. The resulting solid samples were freeze-dried for 2 h under -50°C to obtain the final GO-COOH-CuS catalysts. Here, the samples prepared by addition

of various amounts GO-COOH solutions (1 mL, 5 mL, 10 mL and 20 mL) were named as GO-COOH-CuS-1, GO-COOH-CuS-5, GO-COOH-CuS-10 and GO-COOH-CuS-20, respectively. The synthesis process is illustrated in Fig. 4.1.

Fig. 4.1 Synthetic route of GO-COOH and GO-COOH-CuS nanocomposites.

4.2.3 Characterizations

X-ray powder diffraction (XRD) patterns were taken on a D8-Advance Bruker-AXS diffractometer using Cu K_{α} irradiation to determine the crystallinity phase. Transmission electron microscopy (TEM) images were carried out using a JEOL 2010-H microscope TEM operating at 200 kV. The samples were prepared for the analysis by dropping dilute solutions of samples on 400-mesh carbon-coated copper grids and leading the solvent to dry. Fourier transform infrared spectra (FTIR) were collected on a Bruker FTIR spectroscopy (Nicolet IS10) with solid powder samples. Thermogravimetric analysis (TGA) was recorded using a NETESCH STA 409 PC thermogravimeter. Briefly, 5-6 mg samples were heated from room temperature to 900 °C in dry nitrogen at a rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were taken by using a Kratos Axis Ultra Spectrometer with a 15 kV and 10 mA monochromic Al K_{α} source at 1486.7 eV. The UV-vis diffuse reflectance spectra (DRS) of the 0.1 mg mL⁻¹ dispersion solutions were measured by using an evolution 300 spectrophotometer under room temperature. The photoluminescence (PL) emission spectra were recorded on a fluorescence spectrometer (PerkinElmer). The leaching of Cu²⁺ was checked by quantification of Cu²⁺ concentration in solution using micro plasma atomic emission spectroscopy (MP 4100 AES). The total organic carbon (TOC) was measured using a TOC analyzer (TOC-L CPH/CPN; Shimadzu, Kyoto, Japan). The analysis of intermediates of phenol degradation was conducted by a high performance liquid

chromatography (HPLC, Agilent 1100) with a reverse-phase column (Agilent, Eclipse XDB-C18, 150 × 4.6 mm).

4.2.4 Photocatalytic degradation of phenol and RhB under solar irradiation

In order to investigate the application potential for wastewater treatment, the photocatalytic degradation of phenol and RhB using the as-synthesized nanocomposites were conducted in a laboratory-scale batch photoreactor with 8 quartz capsules. A 500 W Xenon lamp was used as the simulated solar light source. Cool deionized water was circulated through a quartz jacket. And the distance between the light source and the quartz test tubes contained our samples was 15 cm where the measured light intensity was 100 mW cm⁻². Before commencement of irradiation, the reaction suspension containing organic pollutants (40 mg L⁻¹ RhB or 200 mg L⁻¹ phenol) and photocatalysts (1 g L⁻¹) were stirred in the dark for 1 h to achieve equilibrium. Samples of 3 mL solution were withdrawn from the quartz test tubes and centrifuged to collect supernatants. The concentrations of RhB and phenol were analyzed by recording their maximum absorbance on the UV-Vis spectrophotometer at the wavelengths of 550 nm and 270 nm, respectively.

4.2.5 Photocatalytic disinfection under solar irradiation

Gram-negative bacteria *E. coli* (ATCC 8739) and Gram-positive bacteria *B. subtilis* (ATCC 6633) were chosen as standard organisms to evaluate the antibacterial ability of GO-COOH-CuS. Normally, *E. coli* and *B. subtilis* were cultivated in Luria-Bertani nutrient solution followed by incubation at 37 °C and 30 °C respectively for 18 h to get the exponential growth phase. The pure *E. coli* and *B. subtilis* cells were harvested by centrifugation and washed with saline solution (0.9% NaCl) to remove residual macromolecules. Then, the cells were re-suspended in the saline solution to maintain a concentration of ~10⁸ colony forming units (cfu mL⁻¹). All glass apparatuses and solutions used in the experiments were sterilized in autoclave at 121°C for 20 min to ensure sterility.

The photocatalytic disinfection experiments were performed in the photochemical reactor. The nanocomposites (GO-COOH-CuS-1, GO-COOH-CuS-5, GO-COOH-CuS-10 and GO-COOH-CuS-20) were magnetically mixed with 10⁸ cfu mL⁻¹ *E.*

coli or *B. subtilis* saline solution. After irradiation under simulated solar light for 2 h, 100 μL of solution was daubed uniformly and cultivated on the solidified agar nutrient plates. The colony forming units were counted and compared with control plates to calculate ratio of cell viability (C/C_0). As comparison, a contrast experiment under dark condition and a blank control experiment without any nanomaterial were carried out under the same condition. All the experiments were conducted in triplicates.

4.3 Results and discussion

4.3.1 Morphological and structural analysis

TEM is employed to characterize the morphology and microstructure of the graphene-based catalyst, to verify the effective anchoring of CuS NPs onto the large GO-COOH sheets. Fig. 4.2(a) presents that the size of the as-synthesized GO-COOH sheets is around 1-2 μm , which may benefit the recovery of GO-COOH based nanocomposite materials by simple filtration. The edge of GO-COOH sheets is clearly observed in Fig. 4.2(a), (b) and (c), indicating no significant restacking of GO-COOH sheets. It may be due to the insertion of the carboxylic acid functional groups with CuS NPs anchored among layers. Moreover, as shown in Fig. 4.2 (b) and (c), CuS NPs with sizes of 20-30 nm are highly monodispersed on the single GO-COOH sheet without any aggregation and no CuS NPs are observed outside the sheets. This can be attributed to the oxygen-containing groups, which provided uniformly anchoring sites on the both sides of GO-COOH sheets for CuS NPs. Thus the CuS NPs could anchor exactly on GO-COOH sheets and their aggregation was inhibited as well. The clear 0.28 nm lattice spacing of CuS NPs shown in Fig. 4.2 (d) further confirms the effective self-anchoring of CuS NPs on the GO-COOH sheets. By the TEM analysis, it could be deduced that the carboxylic acid functional groups in the synthesis process have triple function: (1) increasing the hydrophilicity of GO sheets to facilitate CuS interaction with GO sheets; (2) reducing the van der Waals bond between carbon layers to promote the delamination of the GO sheets; and (3) providing strong anchoring sites for CuS NPs to inhibit their aggregation¹³.

Fig. 4.2 TEM images of (a) GO-COOH sheet, (b,c,d) GO-COOH-CuS nanocomposite.

Fig. 4.3 shows the XRD patterns of GO-COOH and GO-COOH-CuS. The observed diffraction peak at 2θ of 11.9° in GO-COOH can be attributed to the stacked GO-COOH sheet, which is consistent with the $[001]$ interlayer spacing of $7.43\text{\AA}$ ¹⁴. In contrast, the $[001]$ reflections of GO are not detected in the XRD patterns of all GO-COOH-CuS samples, indicating the regular stacks of GO were destroyed by the effective intercalation of CuS NPs. In addition, the obvious diffraction peaks at 29.76° , 33.85° and 48.30° can be assigned to (102), (103) and (110) facets of cubic CuS (JCPDS No. 01-1281), which further validate the effective anchoring of CuS NPs on the large GO-COOH sheets¹⁵.

Fig. 4.3 XRD patterns of CuS, GO-COOH and GO-COOH-CuS nanocomposites.

XPS is used to analyze the quantity of elements and the surface electronic state of the obtained products. The XPS spectra (Fig. 4.4) display graphitic C 1s, O 1s, Cu and S 2p peaks for GO-COOH-CuS nanocomposites, and the existence of C and O in the GO-COOH. In addition, the high-resolution C 1s spectra (Fig. 4.4b) exhibit three main separated peaks at 283.9 eV, 286.2 eV and 288.4 eV for all samples, which are connected to the graphitic C-C, C-O and COOH bonds, respectively. Fig. 3c and d show the binding energies of Cu $2p_{3/2}$, Cu $2p_{1/2}$ peaks at 932.6 and 952.4 eV and double S $2P_{3/2}$, $2p_{1/2}$ peaks around 162 nm. The XPS results further confirm the carboxylation of GO and the existence of CuS in the composites, which is in good agreement with our subsequent TEM and XRD analyses.

Fig. 4.4 (a) Full XPS spectra of GO-COOH and of GO-COOH-CuS nanocomposites with different mass ratios; (b, c, d) high resolution XPS spectrum of C 1s, Cu 2p, S 2p of GO-COOH-CuS.

4.3.2 Composition and surface properties

The FTIR spectra of GO-COOH and GO-COOH-CuS are shown in Fig. 4.5. The bands at 1721 and 1070 cm^{-1} are ascribed to the C=O and C-O stretching vibrations of carboxylic acid group, respectively¹⁶. Furthermore, the doublet bands at 1627 and 1373 cm^{-1} correspond to the COO- symmetric and asymmetric vibrations complexed with surface Cu centers¹⁷. The doublet bands at 2921 and 2849 cm^{-1} in the GO-COOH-CuS FTIR spectrum are assigned to the C-H stretching vibrations¹⁸. The broad band ranging from 3000 to 3600 cm^{-1} with peak centered at 3423 cm^{-1} is attributed to the O-H stretching vibrations of adsorbed water molecules. The FTIR analysis confirmed the coordination between CuS and carboxylic acid groups in GO-COOH, which is essential and decisive for the controlling growth of CuS on the GO-COOH sheets.

Fig. 4.5 FTIR spectra of GO-COOH and GO-COOH-CuS samples.

TGA was used to evaluate the thermal stability of GO-COOH, CuS and GO-COOH-CuS. In Fig. 4.6, all materials show slight weight losses from 0 to 200 °C, which was due to the evaporation of tightly bounded water or some organic solvent molecules. In the case of GO-COOH, with the further increase of temperature, a sharp weight loss appears around 200 °C. It is resulted from the thermal decomposition of oxygen-containing functional groups ¹⁹. After the temperature exceeds 200 °C, the weight of CO-COOH falls fair steadily. The grafting percentages of CuS on GO-COOH sheets could be estimated from the TGA thermograms. The mass percentage of CuS in the as-prepared composites of GO-COOH-CuS-1, -5, -10, -20 is about 89%, 47%, 24%, and 20%, respectively.

Fig. 4.6 Thermogravimetric analysis of CuS, GO-COOH and GO-COOH-CuS nanocomposites.

4.3.3 Optical properties

Fig. 4.7(a) depicts the UV-vis diffuse reflectance spectra (DRS) of the CuS, GO-COOH and GO-COOH-CuS nanocomposite, as well as their Kubelka-Munk (K-M) transformed reflectance spectrum of CuS (inset). A notable broad absorption in the visible-light and near-infrared (NIR) region is observed from DRS for GO-COOH-CuS compared to GO-COOH, while E_g of CuS is 2.27 eV obtained by the formula $((h\nu)^2 = A(h\nu - E_g))^2$ ²⁰. This suggests that the GO-COOH-CuS presents the enhanced absorbance over pure GO-COOH. The less amount of coupled CuS can effectively extend the absorption of GO-COOH onset to the visible light and NIR region, which is similar to the extended absorption for rGO-TiO₂ composite caused by the formation of C-O-Ti bond²¹.

The effect of GO-COOH on the anti-recombination of e^-/h^+ was investigated by PL spectroscopy²². Fig. 4.7(b) displays the as-synthesized nanomaterials with a broad emission peak at $\lambda = 571$ nm under an excitation at 400 nm. The GO-COOH-CuS nanocomposites exhibit a significantly lower PL emission intensity than pure CuS,

which indicates that GO-COOH is effectively suppressing the e^-/h^+ recombination via faster electron transfer.

Fig. 4.7 (a) UV-vis diffuse reflectance spectra (DRS) of CuS, GO-COOH and GO-COOH-CuS nanocomposites, and Kubelka-Munk transformed reflectance spectra of CuS (inset); (b) PL spectra (excitation at 400 nm) of CuS, GO-COOH and GO-COOH-CuS nanocomposites

4.3.4 Photocatalytic degradation of phenol and RhB

In order to explore their potential application in water treatment, phenol and RhB dye were taken as representative organic compounds to investigate the photodegradation ability of GO-COOH-CuS nanocomposites with various mass ratios (GO-COOH:CuS) under simulated solar light irradiation. Phenol is among the most resistant class of potential pollutant in the wastewater with strong toxicity and excellent solubility. RhB is a basic dye widely used and discharged by the paper printing, paint, textile dyeing and leather industries. Fig. 4.8(a) and Fig. 4.9(a) show the concentration of pollutants as a function of degradation time. Compared to CuS and GO-COOH, GO-COOH-CuS nanocomposites exhibit higher adsorption for both phenol and RhB. Among the different mass ratios, GO-COOH-CuS-5 has the strongest adsorption ability, followed by GO-COOH-CuS-1, GO-COOH-CuS-10 and GO-COOH-CuS-20, as summarized in Table 4.1. The facilitation of the organic pollutants adsorption on nanocomposites may be due to their stronger non-covalent intermolecular forces. For example, the adsorption of phenol by GO-COOH sheets was caused by the interaction of π -conjugated and the ion-dipole interactions

between GO-COOH and phenol due to the presence of similar conjugated aromatic cycles. This can also confirm the phenomenon that adsorption increases with the increasing graphene : CuS ratio, e.g., GO-COOH-CuS-5>GO-COOH-CuS-1. However, it seems that π -conjugated and the ion-dipole interactions are limited for GO-COOH-10 and GO-COOH-20 because of excessive functional groups of GO-COOH, which causes a lower adsorption of phenol and RhB than GO-COOH-CuS-1 and GO-COOH-CuS-5.

As we known, the enhanced adsorption ability of nanomaterials could benefit the subsequent degradation process, which is confirmed in our work as well. In Fig. 4.8a and Fig. 4.9a, the degradation ability of the nanocomposites for either phenol or RhB is coherent with their adsorption phenomenon. And in order to further investigate the long-term stability of synthesized GO-COOH-CuS composite, the photocatalytic degradation of phenol and RhB on GO-COOH-CuS-5 under simulated solar light irradiation was performed over five cycles. As shown in Fig. 4.8b and Fig. 4.9b, no evident change was observed for the photocatalytic activity through the 5 cycles of experiments for both phenol and RhB degradation, indicating good photocatalytic stability of the GO-COOH-CuS composite.

Fig. 4.8 (a) Photocatalytic performance of CuS, GO-COOH and GO-COOH-CuS nanocomposites for phenol under solar light irradiation. (b) Four consecutive cycling curves of phenol photodegradation by GO-COOH-CuS-5.

Fig. 4.9 (a) Photocatalytic performance of CuS, GO-COOH and GO-COOH-CuS nanocomposites for RhB under solar light, (b) five consecutive cycling curves of RhB photodegradation by GO-COOH-CuS-5.

In addition, photocatalytic degradations for organic pollutants are often described in terms of the Langmuir-Hinshelwood model, which can be simplified as pseudo-first order reaction $dC/dt = -kC$, where k refers to the corresponding reaction rate kinetic constant. The photocatalytic degradation kinetic curves shown in Fig. 4.10 apparently follow the pseudo first-order kinetics in the studied concentration range. The calculated k (min^{-1}) constants for all the applied nanomaterials are shown in Fig. 4.9 and the same order is found as degradation ability: GO-COOH-CuS-5 > GO-COOH-CuS-1 > GO-COOH-CuS-10 > GO-COOH-CuS-20 > GO-COOH > CuS (Table 1). Furthermore, the percentage of leached Cu^{2+} after degradation followed the same order as summarized in Table 4.1. All these results indicate that integration of CuS with GO-COOH sheets could enhance the photocatalytic activity, due to the improved light absorption, increased pollutants adsorption and inhibition of charge combination, etc. But the optimal mass ratio is preferred for the best performance of nanocomposites, such as GO-COOH-CuS-5 in this study. This could be explained as following: (1) For the GO-COOH-CuS-5, the well combination of GO-COOH and CuS nanoparticle can motivate more effective charge transfer from conduction band (CB) of CuS to GO-COOH, to achieve low recombination rates of photogenerated electron-hole pairs; (2) the GO-COOH-CuS-

10 and GO-COOH-CuS-20 with small amount of CuS has limited capabilities to absorb solar light, which results in poor photodegradation abilities; and (3) the GO-COOH-CuS-1 with great amount of CuS also shows lower ability than GO-COOH-CuS-5 because the excessive CuS NPs will cover most of the reactive sites on GO-COOH surface and also act as recombination centers, leading to the decreased photocatalytic ability²³.

Fig. 4.10 Pseudo first order photocatalytic degradation of (a) phenol and (b) RhB over the CuS, GO-COOH and GO-COOH-CuS nanocomposites

Table 4.1. Adsorption percentage (%), photo degradation efficiencies (%) and kinetics (min^{-1}) of all as-synthesized samples

	GO-COOH	CuS	GO-COOH-CuS			
			-1	-5	-10	-20
Adsorption (%)						
<i>Phenol</i>	2.3	1.4	6.3	8.5	4.2	3.7
<i>RhB</i>	6.1	5.9	12.2	15.1	12.8	9.3
Photo degradation (%)						
<i>Phenol</i>	16.4	15.7	46.2	61.8	30.2	20.1
<i>TOC removal</i>	15.6	14.7	40.0	55.2	29.3	19.6
<i>RhB</i>	13.8	26.8	72.7	95.4	61.3	41.3
Kinetics (min ⁻¹)						
<i>Phenol</i>	0.0011	0.00095	0.0032	0.0047	0.0019	0.0012
<i>RhB</i>	0.0027	0.0014	0.0013	0.032	0.0095	0.0054
Leached Cu ²⁺ after photodegradation(%)						
<i>Phenol</i>	/	19.5	6.4	5.8	9.5	10.1
<i>RhB</i>	/	15.2	4.5	3.4	7.8	9.3

The total organic content (TOC) analysis was monitored as a function of the rate of mineralization of phenol and its related intermediates. As the results shown in Table 1 and Fig. 4.11 (a), the TOC was decreasing over time, and the GO-COOH-CuS-5 displayed the highest TOC removal ability. Moreover, the main intermediates of phenol degradation were analyzed by HPLC. After 3 h solar irradiation, the main intermediate formed was identified as maleic acid, which is non-toxic and at low concentration. Those toxic intermediates such as catechol and benzoquinone were not found, which may due to their further degradation during 3 h reaction.

Fig. 4.11 (a) TOC concentrations versus time, and (b) HPLC analyses of byproducts of phenol degradation on CuS, GO-COOH and GO-COOH-CuS nanocomposites under 3 h solar light irradiation.

4.3.5 Disinfection performance

The antibacterial activity of GO-COOH and GO-COOH-CuS nanocomposites was evaluated with or without simulated solar light irradiation, using both Gram-negative *E. coli* and Gram-positive *B. subtilis* bacteria as the bacterium models. As the results shown in Fig. 4.12, the nanomaterials could inactivate both bacterial strains in the darkness and showed higher antibacterial activity with CuS anchoring, indicating CuS NPs play an important role in the toxicity. It may due to the release of Cu^{2+} ions. A possible mechanism is that Cu^{2+} can form chelates with biomolecules or dislodge in some metalloproteins which may cause their dysfunction and further cell inactivation²⁴. However, it cannot infer that the more CuS content, the higher toxicity of nanocomposites because the excess CuS may cover the adsorption sites of GO-COOH sheets, leading to the decreased attachment of bacteria on the surface of nanocomposites. In this work, GO-COOH-CuS-5 exhibits the highest toxicity due to its optimal coupling ratio. After 60 min exposure to GO-COOH-CuS-5, nearly 40% *E. coli* and 30% *B. subtilis* were inactivated.

Under solar light irradiation, both bacterial strains exposed to the nanocomposites had a much lower survival rate contrast to that in darkness. The improved disinfection efficiency is attributable to the synergistic effect in photocatalysis

process. GO-COOH sheets adsorb bacteria on the surface, providing more biocontact opportunities for CuS NPs. Aside from the toxicity of the released Cu^{2+} , the photoinduced reactive oxygen species (ROS) by CuS NPs can attack the attached bacteria as well, leading to the enhanced antibacterial activity. Among those nanocomposites, GO-COOH-CuS-5 again shows the highest photocatalytic disinfection efficiency due to its optimal ratio of coupling content. It inactivated 90% *E. coli* and 80% *B. subtilis* after 30 min reaction. With the further increase of contact time to 60 min, the *E. coli* and *B. subtilis* were inactivated nearly by 100%. The higher inactivation efficiency to *B. subtilis* indicates that Gram-positive bacteria were more susceptible to the photodynamic effects than Gram-negative bacteria, which might be due to resistance of the outer membrane in Gram-negative bacteria. An additional outer membrane of Gram-negative bacteria can protect their inner layer from radical or chemical attacking²⁵.

Fig. 4.12 Antibacterial activities of GO-COOH-CuS nanocomposites with and without solar irradiation (a) *E. coli* survival, (b) *B. subtilis* survival, and (c) agar plates pictures of *E. coli* exposed to GO-COOH-CuS-5 under solar light with time (0 min, 10 min, 30 min, 60 min, 90 min and 120 min).

4.3.6 Photocatalytic mechanism

For the enhancement of photocatalytic activity, an efficient charge transfer is crucial²⁶. In the system of GO/PcZn, GO/TiO₂ and rGO/CuS, GO has shown excellent property to be an effective acceptor and transporter, suppressing the recombination of electron-hole pairs and facilitating charge transfer^{21,27,28}. Similarly, a charge transfer might be achieved in our GO-COOH-CuS nanocomposite system, where GO-COOH sheets act as the electron acceptor. Based on the experimental results and analyses, a possible mechanism for the enhanced photocatalytic activity and good stability of synthesized GO-COOH-CuS nanocomposite is proposed in Fig. 4.13. Under solar light irradiation, the electrons could be generated either from excited dye (*RhB**) molecules or CuS NPs, then transfer to GO-COOH. They react with absorbed surface O₂ on GO-COOH sheets to produce reactive oxygen species (ROS) which assist the pollutants degradation. Meanwhile, the photogenerated holes on CuS also could oxidize pollutants. In addition to the charge separation, the photocatalytic activity can be influenced by the adsorption of pollutants, the light absorption and the surface oxygen adsorption as well. The enhanced visible light absorption of GO-COOH-CuS is verified by UV-vis absorption analysis (Fig. 4.6). The high adsorption ability of GO-GOOH sheets for organic pollutants has been confirmed by previous works^{22,29}, as well as in our study (Fig. 7 and Fig. 8). All these improved properties of GO-COOH-CuS result in the higher photocatalytic activity towards our synthesized nano-system.

Fig. 4.13 Schematic illustration of proposed photocatalytic and antibacterial mechanisms of GO-COOH-CuS nanocomposite.

4.4 Conclusions

In summary, with a facile and up scalable synthesis process, multifunctional GO-COOH-CuS nanocomposites were successfully synthesized. The uniform deposition of CuS NPs on GO-COOH sheets contributes to the superior photocatalytic activities of the nanocomposite, not only towards organic pollutants (phenol and RhB) but also waterborne pathogens (*E. coli* and *B. subtilis*). Herein, GO-COOH was demonstrated as an appropriate conductive ligand to support the CuS NPs used in photocatalysis. In addition, as the electron acceptor, GO-COOH improved the lifetime of electron-hole pairs of CuS resulting in a better pathway for electron transport. The GO-COOH-CuS nanocomposite material can overcome the limitations of the pristine GO-COOH and CuS photocatalysts, and combine the merits of the both materials to maximum synergistic effects, including (1) perfect contact between GO-COOH sheets and CuS NPs to minimize the photocorrosion. (2) uniformly distributed CuS NPs onto the GO-COOH surface to improve isolating photogenerated electrons and holes, meanwhile, to enhance the charge transfer. Moreover, the durability study showed that the photocatalytic activity of the GO-

COOH-CuS is stable enough for multiple recycling. This study signifies that GO-COOH-CuS nanocomposite can be a promising photocatalyst in the field of water decontamination and disinfection.

CHAPTER 5. A NOVEL ULTRATHIN G-C₃N₄ NANOSHEET WITH HEXAGONAL CUS NANOPATES COMPOSITE UNDER SOLAR LIGHT IRRADIATION FOR H₂ PRODUCTION

5.1 Introduction

With the increased global concerns in tackling environmental-related issues by sustainable approaches, it is imperative to improve solar energy usage and conversion to build a solar-energy based society. A possible solution would be to utilize semiconductor-mediated photocatalysis. A rapid development of solar-light driven photocatalysis is generally regarded as one of the advanced technologies for environmental remediation, organic synthesis and energy conversion(Chen et al. 2015). Particularly, the hydrogen evolution reaction over semiconductors with sacrificial electron donors utilizing solar light, has been recognized as one of the most promising clean and renewable energy sources with high energy capacity (Mateo et al. 2016).

Polymeric graphitic carbon nitride (g-C₃N₄), as a metal-free *n*-type semiconductor, possesses many promising properties, such as unique optical, electrical, physiochemical and structural properties, which make g-C₃N₄ materials a new class of multifunctional nanocomposites for catalytic, energy and electronic applications(Wen et al. 2017). Especially, it has been reported as an attractive, inexpensive photocatalyst for hydrogen production from water splitting due to both of its reduction and oxidation levels being located inside the bandgap(Wang et al. 2014). Depending on the various methods, the g-C₃N₄-based photocatalysts can form different nanoscale morphological structures, such as nanotubes, nanorods, nanospheres, nanosheets and others(Dong et al. 2015). In general, as in the case of the graphite to graphene-based materials, ultrathin two-dimensional (2-D) nanosheets have attracted extensive attention for their exceptional optical, biocompatible and electronic properties with respect to the bulk materials. To date, ultrathin 2D g-C₃N₄ nanosheets have been proved to improve photo-response abilities compared to bulk g-C₃N₄ materials (Zhang et al. 2013, Han et al. 2016),

which is mainly attributed to the unique two-dimensional architecture, environmentally benign characteristics, tunable electronic structure, and excellent chemical stability(Dong et al. 2015). The smaller particle size could shorten the distance between the photogenerated electrons and the surface, which suppresses the recombination rate of photo-generated electron-hole pairs.

To date, synthesized ultrathin g-C₃N₄ nanosheets via a “green” liquid exfoliation route from bulk g-C₃N₄ in water or in isopropanol (IPA) is the most popular method compared to thermal oxidation etching of bulk g-C₃N₄ in air and chemical exfoliation(Tian et al. 2013, Dong et al. 2015). However, the wide scale application of ultrathin 2D g-C₃N₄ nanosheets have been limited by the following factors, namely, high recombination rates of electron-hole pairs, materials aggregation and poor light absorption efficiency. Hence, it is critical to overcome the limitations to ensure effective photocatalytic applications. Modification of g-C₃N₄ using a narrow band gap semiconductor is a acceptable method. g-C₃N₄-TiO₂, g-C₃N₄-Ag/AgBr, and g-C₃N₄-ZnO have been explored comprehensively for photocatalytic applications(Sun et al. 2012, Xu et al. 2013, Ma et al. 2016).

In this study, we proposed to use copper sulfide (CuS) as the narrow band gap semiconductor to enhance the photocatalytic properties of g-C₃N₄. CuS has been reported as one of the most important narrow band gap *p*-type semiconductor. It has an additional absorption band in the near-infrared region (NIR)(Ratanatawanate et al. 2011) and exhibits low reflectance in the visible and relatively high reflectance in the NIR, which make it a promising candidate for solar energy absorption. To the best of our knowledge, this is the first study to integrate hexagonal CuS nanoplates with g-C₃N₄ nanosheets to fabricate g-C₃N₄-CuS nanocomposite and investigate its hydrogen evolution performance. In this study, ultrathin g-C₃N₄ nanosheets were successfully prepared by a “green” liquid exfoliation route from bulk g-C₃N₄ in isopropanol (IPA). The optical properties, crystal phase, morphology of the different nanostructural g-C₃N₄ and g-C₃N₄-CuS composites were analysed. The hydrogen evolution performance of all all obtained composites under solar irradiation and the H₂ generation mechanism were systematically investigated.

5.2 Methods and materials

5.2.1 Synthesis of bulk g-C₃N₄, ultrathin g-C₃N₄ nanosheet and g-C₃N₄-CuS nanocomposite

Bulk g-C₃N₄ was synthesized by direct heating of melamine (Liao et al. 2014). Briefly, 2 g of melamine powder was incubated for 2 hours at a temperature of 550 °C in a crucible, and naturally cooled down to room temperature. The thermal polymerization of melamine to g-C₃N₄ is shown in Fig. 5.1. The g-C₃N₄ was then dissolved in isopropanol (IPA) to form a 1 mg mL⁻¹ solution. In order to exfoliate the g-C₃N₄ into ultrathin layers, the solution was sonicated (Elmasonic P ultrasonic cleaner) for 24 hours. Ultrathin g-C₃N₄ nanosheets were obtained after centrifugation and freeze-dried.

Fig. 5.1 Thermal Polymerization of melamine to obtained g-C₃N₄

Then 306 mg (1 mmol) and 612 mg (2 mmol) copper ethyl xanthate were mixed with 50 mg obtained g-C₃N₄ nanosheet respectively to produce g-C₃N₄-CuS-1 and g-C₃N₄-CuS-2. The mixture was heated for 1 hour at 180 °C under argon atmosphere, and cooled down to room temperature thereafter. Subsequently, the mixture was washed with acetone to remove excess inorganic materials and with toluene to remove excess organic compounds such as oleylamine.

5.2.2 Material characterization

The morphology of the as-synthesized samples was observed by field emission scanning electron microscopy (FESEM, JEOL 7600F). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken using a JEOL 2010-H TEM. The Brunauer-Emmett-Teller (BET) specific surface area of all-obtained composites were determined from the N₂ adsorption–desorption isotherm at 77 K (Quantachrome Autosorb-1 Analyzer). X-ray powder diffraction (XRD) patterns were recorded on a D8-Advance Bruker-AXS diffractometer using Cu K_α irradiation to determine the crystallinity and phase. Fourier transform infrared (FTIR) spectra were collected on a Bruker FTIR spectrometer (Nicolet IS10) with solid powder samples. UV–Vis absorption spectra of the 0.1 mg mL⁻¹ dispersion solutions were measured using an Evolution 300 spectrophotometer under room temperature.

5.2.3 Hydrogen evolution reaction under solar light irradiation

The photocatalytic hydrogen evolution reaction was conducted in a top-irradiation type closed Pyrex reactor (volume: 550 mL) under a solar irradiation simulator (Newport Oriel) with a 300 W ozone free xenon lamp to provide solar light. 1 mg mL⁻¹ of the photocatalyst powder was suspended in 100 mL of the triethanolamine water mixture (10 %) by stirring. The photocatalyst suspension was sparged by nitrogen gas for 20 mins to remove dissolved oxygen. Gas produced via the photocatalytic hydrogen evolution reaction was analyzed using an off-line TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A).

5.2.4 The photoluminescence (PL) emission spectra and electron paramagnetic resonance (EPR) measurements

The PL emission spectra were recorded on a fluorescence spectrometer (PerkinElmer). Continuous wave X-band EPR experiments were conducted with a Bruker Biospin ELEXSYS-II E 500 spectrometer. The modulation amplitude was set to 1 G and field sweep time was 30 seconds. Photolysis experiments were conducted with a Bruker ER 203 UV irradiation system using a short arc 100 W mercury lamp (LSB610 100W Hg).

5.3 Results and discussion

5.3.1 Structural and optical characterizations of g-C₃N₄-CuS

Fig. 5.2a and b are the SEM and TEM images of the synthesized bulk g-C₃N₄. It is clear that the layers of bulk g-C₃N₄ were not exfoliated at all, and the irregular particles were composed of multi-layers of g-C₃N₄ sheets. Fig. 5.2c and d displayed the ultrathin layers of g-C₃N₄ nanosheets, which provide clear evidence that the bulk g-C₃N₄ was exfoliated to distinguished layers. Lattice planes of CuS (103) with a lattice spacing of 0.32 nm is displayed in Fig. 5.2e, which confirmed that hexagonal CuS nanoplates were synthesized successfully (Yu et al. 2010). Fig. 5.2f demonstrates the CuS nanoplates were dispersed over the surface of the g-C₃N₄ nanosheets and appeared as black dots.

Fig 5.2 (a, b) SEM and TEM images of bulk g-C₃N₄; (c, d) SEM and TEM images of g-C₃N₄ nanosheets; (e) TEM images of hexagonal CuS nanoplates and (f) TEM image of C₃N₄ nanosheet with hexagonal CuS nanoplates composite (g-C₃N₄-CuS-1).

The surface area analysis using typical plots of N₂ adsorption-desorption isotherms and pore size distribution curves of as-prepared products are shown in Fig.3. The products exhibited nitrogen adsorption-desorption isotherms of type IV (BDDT

classification) with H3 hysteresis loops at relative pressure ranges of 0.6–0.9, indicating the presence of mesoporous structures (Wei et al. 2013). The corresponding pore size distribution curves indicate that g-C₃N₄ nanosheets presented a relatively wide distribution. Taking into account the morphology of the nanocomposite observed by HRTEM, the pores should be for the g-C₃N₄ nanosheets intra pores so that the surface area became larger after exfoliation from bulk g-C₃N₄. From the pore size distribution curve shown in the Fig. 5.3, the small mesopore size of g-C₃N₄ is around 3 nm. The specific surface area and pore volume of g-C₃N₄ nanosheets (158.36 m² g⁻¹ and 0.522 cm³ g⁻¹ respectively) are about 7 times higher than those of pure bulk g-C₃N₄ (21.73 m² g⁻¹ and 0.072 cm³ g⁻¹ respectively). A larger surface area provides more surface active sites for the adsorption of the reactive molecules and a more efficient photocatalytic process, and leading to the conclusion that the g-C₃N₄ nanosheet might have better photocatalytic performance than bulk g-C₃N₄. Moreover, when combined with CuS, the g-C₃N₄-CuS might more promote the enhancement of photocatalytic activity compared to pure g-C₃N₄ under solar light irradiation due to its improved charge separation efficiency even though its specific surface area and pore volume (139.45 m² g⁻¹ and 0.491 cm³ g⁻¹ respectively) slightly reduced in comparison to the g-C₃N₄ nanosheet (158.36 m² g⁻¹ and 0.522 cm³ g⁻¹ respectively).

Fig. 5.3 Nitrogen adsorption-desorption isotherms and the Corresponding pore size distribution curves of as-synthesized products (Inset).

To investigate the changes made to the structure of g-C₃N₄ by anchoring of CuS nanoplates, X-ray diffraction analysis was conducted. The XRD patterns of g-C₃N₄-CuS composites at varying CuS concentrations were compared with the patterns displayed by pure g-C₃N₄ and CuS (Fig 5.4). The strongest XRD peaks of both bulk and nanosheet g-C₃N₄ samples locate at 27.1°, confirming an interlayer distance of 0.326nm and being indexed as (002) diffraction plane. For CuS, the diffraction peaks are observed at 29.1°, 32.3°, 48.3°, 52.3° and 58.9°, which can be assigned to (102), (103), (110) (108) and (118) facets of the hexagonal CuS phase (JCPDS No. 06-0464)(Yu et al. 2010, Saranya et al. 2015). The various diffraction peaks of CuS in both g-C₃N₄-CuS-1 and g-C₃N₄-CuS-2 imply the CuS nanoparticles were successfully attached onto the g-C₃N₄ sheets and altered the structure of the composites. The higher diffraction peaks in g-C₃N₄-CuS-2 correspond to the larger amount of CuS nanoparticles attached on it. In addition, the XRD results also

coincide with the SEM and TEM images, further supporting the successful attachment of CuS nanoparticles on g-C₃N₄ sheets.

Fig. 5.4 Comparison of the XRD spectra of pure g-C₃N₄, CuS and g-C₃N₄-CuS hybrids

Fig. 5.5 illustrates a comparison of the FTIR spectra of g-C₃N₄-CuS composites with pure g-C₃N₄. Several bands were observed within the range of 1200-1650 cm⁻¹ in the spectra, with the peaks at 1245, 1317, 1423 and 1629 cm⁻¹ identified. These peaks correspond to the typical stretching vibration modes of C-N (Wang et al. 2009). In addition, another peak at 805 cm⁻¹ was also observed which is attributed to the out-of-plane bending modes of triazine rings (Liao et al. 2014). Fig. 5 also shows the main distinctive peaks of pure g-C₃N₄ appeared in the samples of g-C₃N₄-CuS-1 and g-C₃N₄-CuS-2. These peaks remained unshifted after the introduction of CuS nanoparticles as the peaks remained in line with the peaks from pure g-C₃N₄ (Xu et al. 2013). Therefore, it can be deduced that CuS nanoparticles were deposited on

the g-C₃N₄ surface. This particular observation corresponds to the results of the SEM and TEM imaging.

Fig. 5.5 FTIR spectra of g-C₃N₄, g-C₃N₄-CuS-1 and g-C₃N₄-CuS-2.

According to the DRS spectra of pure g-C₃N₄ and g-C₃N₄-CuS hybrids in Fig. 5.6, g-C₃N₄-CuS-1 exhibited the highest absorption intensity. Using the absorption wavelengths (λ), the corresponding band gap energy (E) can be calculated using the formula, $E=1240/\lambda$. g-C₃N₄-CuS-1 with the shortest band gap (1.94eV) required the least energy to reach the most efficient electron transfer compared to g-C₃N₄-CuS-2 (2.28 eV) and bulk g-C₃N₄ (2.58 eV) and nanosheet g-C₃N₄ (2.70 eV). The band gap of bulk g-C₃N₄ is very close to the theoretical result from previous density-functional-theory (DFT) calculations for infinite g-C₃N₄ sheets (2.6eV)(Yang et al. 2013). Obvious blue shift of the intrinsic absorption edge in the nanosheets g-C₃N₄ was observed compared to the bulk g-C₃N₄. The well-known quantum confinement effect by shifting the conduction and valence band edges in opposite directions attributed to the larger band gap by 0.12 eV of nanosheet g-C₃N₄(Niu et al. 2012).

Fig. 5.6 UV-Vis diffuse reflectance spectra of all obtained g-C₃N₄-based nanomaterials.

5.3.2 Hydrogen generation performance

As can be seen from Fig. 5.7, by exfoliating the bulk g-C₃N₄ to nanosheet g-C₃N₄ using IPA, the average hydrogen evolution rate was improved to 50 $\mu\text{mol h}^{-1}$ from 11.5 $\mu\text{mol h}^{-1}$ (g-C₃N₄ nanosheets *vs.* bulk g-C₃N₄). This value is higher than traditional polymeric C₃N₄ (10.6 $\mu\text{mol h}^{-1}$) reported by Wang et al (Wang et al. 2009), and also higher than other reported results obtained from the highly ordered single layer g-C₃N₄ which was exfoliated by water or NEt₄OH (Wang et al. 2012). Given the surface energy of IPA matches with that of g-C₃N₄, so small IPA molecules are easily able to intercalate into the interlayers of bulk g-C₃N₄. Meanwhile, the dangling hydrogens in the neighboring layers of g-C₃N₄ prefer the polar solvents, which also lead IPA to destroy the weak interaction for effective exfoliation (Han et al. 2016). Furthermore, the low boiling point IPA as the solvent contributed to exfoliate the bulk g-C₃N₄ on a large scale similar to water. In addition,

the blank control experiment clearly confirmed that H₂ was indeed evolved from the photocatalytic process in which the radicals were generated by the g-C₃N₄-CuS system.

It was found that the highest amount of hydrogen was generated by g-C₃N₄-CuS-1 under simulated solar light irradiation. This could be due to the synergistic effect of g-C₃N₄ with CuS that decreased the recombination between CB electrons and VB holes. With modification by CuS nanoflakes, the H₂ generation activity of g-C₃N₄-CuS-1 could be improved significantly to 126.5 $\mu\text{mol h}^{-1}$ which is not only higher than CuS nanoplates (49.8 $\mu\text{mol h}^{-1}$) and g-C₃N₄ (20.5 $\mu\text{mol h}^{-1}$), but also higher than that of g-C₃N₄-CuS-2 nanocomposites (87.9 $\mu\text{mol h}^{-1}$) under the 17 h consecutive irradiation. Furthermore, the hydrogen evolution performance of g-C₃N₄-CuS-1 was also better than those other semiconductor modified g-C₃N₄, such as Pt-g-C₃N₄ (12.5 $\mu\text{mol h}^{-1}$), Pt-1wt% sucrose-g-C₃N₄ (108 $\mu\text{mol h}^{-1}$) (He et al. 2015), and CuFe₂O₄/ g-C₃N₄ (76 $\mu\text{mol h}^{-1}$) (Cheng et al. 2016). This also suggests that the optimal mass ratio is preferred for the better hydrogen generation performance of nanocomposites, e.g. g-C₃N₄-CuS-1 in this study. This can be explained by the efficient combination of g-C₃N₄ and CuS nanoflakes for the g-C₃N₄-CuS-1 can facilitate more effective charge transfer from the conduction band (CB) of CuS to g-C₃N₄, thus achieving low recombination rates of photogenerated electron-hole pairs. While for g-C₃N₄-CuS-2, the excessive CuS may cover most of the reactive sites on g-C₃N₄ surface and also act as recombination centers, leading to the decreased hydrogen generation ability. Further, the stability of the photocatalytic activity of g-C₃N₄-CuS-1 for hydrogen generation under solar light irradiation was performed over 3 cycles as shown in Fig 7b. Because both g-C₃N₄ and CuS were stable in aqueous triethanolamine solution under solar light irradiation, the hydrogen generation rate was maintained without a noticeable decrease (only 7.9% decline in 50 hours with 3 cycles), demonstrating the good recyclability and stability of the samples. The less aggregation of g-C₃N₄ nanosheets after the photocatalysis reaction and 30 days storage were observed by TEM (Fig. S2), also indicating the excellent stability.

Fig. 5.7 (a) Stable hydrogen evolution from water by g-C₃N₄ based composites under solar light irradiation, (b) Repeatable hydrogen generation performance by g-C₃N₄-CuS-1 for hydrogen generation under solar light irradiation.

5.3.3 Photocatalytic mechanism

Electron-hole pairs trapping, migration, and transfer in semiconductor can be confirmed by the PL emission (Guo et al. 2016). A lower PL peak intensity indicates a faster electron-transfer rate and a lower electron-hole recombination rate. Therefore, in this study, PL spectroscopy was employed to investigate the anti-recombination abilities of all g-C₃N₄ based nanomaterials. Fig. 5.8 displays the as-obtained g-C₃N₄-CuS nanomaterials with a broad emission peak at $\lambda = 598$ nm under an excitation of 450 nm. The exact charges densities are not known, but comparing with the bulk or nanosheet g-C₃N₄, the PL intensity of g-C₃N₄-CuS-1 and g-C₃N₄-CuS-2 decreased dramatically, suggesting the CuS nanoflakes anchored on the surface of the g-C₃N₄ could efficiently transfer the electrons generated from g-C₃N₄, which could suppress the electron-hole recombination of the g-C₃N₄, indicating higher charge carrier density and improved electron-transfer rates by CuS deposition, which contribute to better photocatalysis abilities (Xu et al. 2013, Dong et al. 2015).

Fig. 5.8 PL spectra (excitation at 450nm) of different ratio of g-C₃N₄-CuS-1.

Different EPR spectra were obtained from the experiments carried out in water and in methanol with the presence of the DMPO spin trap (Fig. 5.9)(Ma et al. 2016). The EPR spectra of DMPO-trapped radicals in aqueous medium under UV-vis irradiation showed 4 major peaks in a 1:2:2:1 ratio which is characteristic of the DMPO- $\cdot$ OH adduct. Fig. 9a shows very weak DMPO- $\cdot$ OH signals, indicating few $\cdot$ OH radicals produced in g-C₃N₄ and g-C₃N₄-CuS containing solution.

Six major characteristic peaks of approximately equal intensity of the DMPO-O₂ $\cdot^-$ adduct could be detected using EPR spectroscopy in methanol under UV-vis irradiation. As shown in Fig. 5.9b, the DMPO-O₂ $\cdot^-$ weak signals were detected either in pure methanol or in the g-C₃N₄ suspension, which is likely due to some photochemical reactions occurring under ambient light conditions. While in g-C₃N₄-CuS suspension, the DMPO-O₂ $\cdot^-$ signal increased significantly in intensity, suggesting that after fabrication with CuS, the g-C₃N₄-CuS system can generate more O₂ $\cdot^-$ to improve the photocatalytic abilities than the pure g-C₃N₄ system,

which indicates more electrons can be generated and react with O_2 . In order to make the generated electrons react with H^+ rather than with O_2 , a sacrifier (in this case triethanolamine) was added to the reaction system, thus the more generated electrons resulted in higher hydrogen production.

Fig. 5.9 DMPO spin-trapping EPR spectra of as synthesized nanomaterials with (a) aqueous dispersion for DMPO- $\cdot OH$ and (b) methanol dispersion for DMPO- $O_2^{\cdot -}$ after 5 min irradiation.

A possible photocatalytic mechanism for the charge excitation and separation processes of g- C_3N_4 -CuS is proposed in Fig. 5.10. Under solar light excitation, photogenerated electrons can transfer from the conduction band (CB) of g- C_3N_4 to CuS since the CB of g- C_3N_4 is more negative than CuS. Meanwhile, the holes leave the VB of g- C_3N_4 , so that efficient electron-hole pairs can be achieved. Because of the faster electron transfer rate in the g- C_3N_4 -CuS system compared with pure g- C_3N_4 system, it can lower the recombination rate of electron-hole, and prolong the reaction time. Then the generated electrons convert surface O_2 to reactive oxygen species (ROSSs) - oxygen superoxide radicals ($O_2^{\cdot -}$) which is the main radical produced to further generate hydrogen or degrade pollutants. The holes in the surface of CuS also oxidize H_2O/OH to form fewer $\cdot OH$, which make lesser contributions to hydrogen generation.

Fig. 5.10 Schematic diagram of energy levels and electron transfer mechanism of g-C₃N₄-CuS nanocomposites.

5.4 Conclusions

In this study, ultrathin g-C₃N₄ nanosheets were successfully prepared by a “green” liquid exfoliation route from bulk g-C₃N₄ in isopropanol, and exhibited better hydrogen evolution performance than bulk g-C₃N₄ under solar irradiation due to their larger surface area. Furthermore, semiconductor hexagonal CuS nanoplates were fabricated onto g-C₃N₄ nanosheets via a hydrothermal method to produce a synergistic effect, owing to a narrowing band gap. It is concluded that g-C₃N₄ can be highly effectively combined with CuS to produce a nonomaterial with better hydrogen evolution rate than pure g-C₃N₄ nanosheets under solar light irradiation due to its improved charge separation efficiency. Its performance is also superior than other semiconductor modified g-C₃N₄, making it a promising photocatalyst for future hydrogen generation application. The optical properties, crystal phase and morphology of the obtained composites were characterized systematically using various analytical methods. It was concluded that O^{2•-} was the dominant radical produced for hydrogen evolution.

CHAPTER 6. NOVEL CARBOXYLATED GRAPHENE OXIDE-CUS-AG NANOCOMPOSITE GLASS COATING FOR ORGANIC DEGRADATION UNDER SOLAR LIGHT

6.1 Introduction

Recently, semiconductor-mediated heterogeneous photocatalysis has gained recognition as an effective treatment method for the removal of emerging organic contaminants (EOCs) from wastewater. The advantages of such technology include higher reaction rates for pollutant removal, complete mineralisation of the contaminants into harmless substances, e.g. water and carbon dioxide, and most importantly the employment of non-hazardous and economical materials – semiconductors(Hoffmann et al. 1995).

Hexagonal CuS, a new narrow band gap semiconductor, has effective catalytic properties under visible light(Basu et al. 2010). Graphene (G) and its derivatives such as graphene oxide (GO) and reduced graphene oxide (RGO) can enhance the electron transfer rate, hence materials like GO-COOH-CuS, RGO-CuS, and G-ZnS/CuS can all show excellent photocatalytic abilities(Zhou et al. 2013, Zeng et al. 2014, Yu et al. 2015). In addition, in order to improve the disinfection ability of the nanocomposite GO-COOH-CuS, silver nanoparticles were introduced into the fabrication of the nanocomposite due to its reputable antibacterial abilities and biological compatibility. Recent studies have also verified that the higher specific surface area of Ag nanoparticles (<10 nm) results in a better disinfection performance(Liu et al. 2013). Due to the surface plasmon resonance (SPR) effect, Ag nanoparticles can also absorb visible light strongly, which can be utilized to induce photocatalytic disinfection as well as degradation of organic dyes, including anionic, cationic and neutral dyes(Wang et al. 2008).

Photocatalysts are commonly applied in fine-powder form for various environmental applications(Hoffmann et al. 1995, Yu et al. 2017). The problem associated with such applications lies in the propensity of powdered nano-particles to cluster and agglomerate as suspensions in aqueous solution(Jiang et al. 2016),

which may reduce the efficiency of photo-catalytic performance and increase the difficulty in recovery, recycling and isolating these nanoparticles. Coating those fine-powder nanoparticles onto common glass slides is a method to solve this problem (Yao Tong 2013, Modesto-López et al. 2015). Moreover, the coating industry has been seeking new technologies and materials to improve the performance of coatings.

Coating is typically used to improve the surface properties of a substrate, corrosion resistance, wettability and adhesion (Yao Tong 2013). For example, Prasai et al. (2012) have demonstrated that using graphene as a corrosive protective coating can inhibit or control the corrosion rate of metal in a corrosive environment (Prasai et al. 2012). In addition, researchers have also paid attention on how to improve the photocatalytic ability of photocatalysts using coating methods. Wang et al. (2012) have shown that the TiO₂-graphene coated culture dishes had enhanced photocatalytic abilities for gas-phase acetone degradation under UV light irradiation (Wang et al. 2012). Kamegawa et al. (2010) illustrated graphene coated TiO₂ can enhance the decomposition performance of 2-propanol in water (Kamegawa et al. 2010).

This study synthesized a hybrid multifunctional nanocomposite (GO-COOH-CuS-Ag) via a facile method by integrating copper sulfide (CuS) nanoflakes, carboxylic acid functionalised graphene oxide (GO-COOH) sheets, and silver (Ag) nanoparticles, with the aim to enhance their EOCs photodegradation and antibacterial applications under solar light irradiation. It is proposed that the performance and stability of GO-COOH-CuS-Ag can be enhanced with glass coating technology thus facilitate its practical application in water treatment.

6.2 Materials and methods

6.2.1 Materials

Natural graphite (SPI) was purchased from Bay Carbon Company (USA). Sodium nitrate (NaNO₃, 99%), potassium permanganate (KMnO₄, 99%), hydrogen peroxide (H₂O₂, 35%), concentrated sulfuric acid (36.5%), hydrochloric acid (35%), nitric

acid (HNO_3), chloroacetic acid (CH_3COOCl , 99%), sodium hydroxide, copper ethyl xanthate $[(\text{CH}_3\text{CH}_2\text{OCS})_2\text{Cu}]$, silver nitrate (AgNO_3 , 99%), Dipropylene glycol monomethyl ether (DPM, 4.5 wt%, Disperbyk 180), polyvinyl alcohol (PVA, Sigma-Aldrich) and Methylene Blue (MB, 99%) were purchased from Sigma-Aldrich. Toluene, acetone and ethanol (absolute) were purchased from Merck Ltd (Singapore). All the reagents were used as received without further purification.

6.2.2 Synthesis of GO-COOH nanosheets, CuS nanoflakes , and Ag nanoparticles

GO was synthesized in accordance to the modified Hummers' method (Hummers and Offeman 1958). The final GO product was used to synthesize the carboxylic acid functionalised graphene oxide (GO-COOH) using a previous reported method (Yu et al. 2015). Hexagonal CuS nanoflakes were synthesized in solution phase via simple wet chemical method using a hydrothermal reaction (Shen et al. 2008). In a typical process, 306 mg (1 mmol) of copper ethyl xanthate $[(\text{CH}_3\text{CH}_2\text{OCS})_2\text{Cu}]$ was added to 20 mL of oleylamine and the mixture was heated to 250°C in an oil bath and incubated at this temperature for 2 hours with nitrogen supplied as a headspace, and finally cooled down to ambient conditions. 96 mg of CuS nanoflakes (1 mmol) was then obtained. The product was centrifuged and washed twice with ethanol. The precipitate was then re-dissolved and kept in toluene for further use. The synthesis method of Ag nanoparticles was similar to that of CuS (Shen et al. 2008). Oleylamine-capped Ag nanoparticles were synthesized by reducing silver nitrate in toluene, as previously reported (Shen et al. 2008). Briefly, 170 mg (1 mmol) of silver nitrate was added to 4 mL of oleylamine and 50 mL of toluene, and the mixture was heated to 200°C under a constant flow of nitrogen gas as headspace. The mixture was maintained at this temperature for 6 hours and cooled down to ambient conditions. 108 mg of Ag nanoparticles (1 mmol) was then produced. The post treatment and storage methods were the same as CuS.

6.2.3 Synthesis of GO-COOH-CuS-Ag nanocomposite

The synthesis started with sonication of GO-COOH for 30 minutes. After adding Ag nanoparticles and CuS nanoflakes, the mixture was stirred for 24 hours and then

centrifuged and washed twice with acetone and subsequently with ethanol. Finally, the product was kept at 4°C for 2 hours, and freeze-dried. In this synthesis, the amount of GO-COOH and Ag was fixed at 30 mg and 20 mg, respectively. While the amount of the main active photocatalyst, CuS was varied at 0, 15 and 30 mg in order to obtain an optimal ratio according to the materials' photodegradation performance. The composites of GO-COOH-CuS-Ag with different CuS contents were named GO-COOH-CuS-Ag-0, GO-COOH-CuS-Ag-15 and GO-COOH-CuS-Ag-30, respectively.

6.2.4 The nanocomposite GO-COOH-CuS-Ag glass coatings

According to the preliminary photodegradation results, GO-COOH-CuS-Ag-15 had the best photodegradation performance (refer to the results section). Three final glass coating products were therefore fabricated and coated with varying mass (50 mg, 70 mg and 100 mg) of GO-COOH-CuS-Ag-15, namely 50 GCCA-15, 70 GCCA-15 and 100 GCCA-15 respectively. The powdered composites were first added into mixtures of 95% dipropylene glycol monomethyl ether (DPM) with different amounts of 4.5% wt. BYK as shown in Table 6.1. The mixtures were sonicated for 6 hours and then another 2 hours after the addition of alumina-silica gel (Nikolic and Radonjic 1997, Tiwari et al. 2007).

Table 6. 1. Summary of dip-coating compositions

Material/Condition	GO-COOH-CuS-Ag (mg)	BYK (μL)	DPM (mL)	Alumina Silica Gel (mL)
Final glass coating product	50	5		
	70	7	0.5	0.5
	100	10		

The resulting sol-gel mixture was then coated onto glass slides using the dip coating method(Lu et al. 1997). Finally, the coated glass slides were air-dried naturally for 2 days before annealing in the furnace at 110 °C for 6 hours with annealing rate of 3.67 °C/min. Triplicates were prepared for characterization and photo-degradation

experiments.

6.2.5 Characterization

X-ray powder diffraction (XRD) patterns were taken on a D8-Advance Bruker-AXS diffractometer using Cu K α irradiation to determine the crystallinity and phase. The morphology of the as-synthesized samples was evaluated by field emission scanning electron microscopy (FESEM, JEOL 7600F). Energy dispersive X-ray (EDX) measurements were conducted using the EDAX system (Oxford, 80 mm²). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out using a JEOL 2010-H TEM microscope. Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker FTIR spectrometer (Nicolet IS10) with solid powder samples. The UV–vis absorption spectra of the 0.1 mg mL⁻¹ dispersion solution were measured using an Evolution 300 spectrophotometer at room temperature. Leaching of Cu²⁺ and Ag⁺ was checked by quantification of Cu²⁺ and Ag⁺ concentrations in solution using micro plasma atomic emission spectroscopy (MP 4100 AES). Total organic carbon (TOC) was measured using a TOC analyzer (TOC-L CPH/CPN; Shimadzu, Kyoto, Japan). Continuous wave X-band EPR experiments were conducted with a Bruker Biospin ELEXSYS-II 500 spectrometer. The modulation amplitude was set to 1 G and field sweep time was 30 seconds. Photocatalysis experiments were conducted with a Bruker ER 203 UV irradiation system using a short arc 100 W mercury lamp (LSB610 100W Hg).

6.2.6 Photocatalytic degradation of organic pollutants and bacteria disinfection under solar irradiation

In order to find the optimal ratio of CuS among the three nanocomposites (GCCA-0, GCCA-15 and GCCA-30), methylene blue (MB) photodegradation as a pre-screening method was conducted under a solar simulator. Before commencement of irradiation, the reaction suspension containing organic pollutants as 100 mg L⁻¹ of MB and 1 g L⁻¹ photocatalysts were stirred in the dark for 30 minutes to achieve adsorption equilibrium.

The selected GCCA was used to carry out the photo-degradation of 100 mg L⁻¹ of MB dye under simulated solar light from a 300W Xenon lamp. The coated glass slides were arranged and placed inside of the solar simulator. During the allocated time intervals, the concentration of MB was measured with a UV–Vis spectrometer to determine the degradation efficiency.

For the photocatalytic antibacterial experiments, 10⁸ cfu mL⁻¹ *E. coli* was used as the initial cell concentration. Solar light was generated from the same solar simulator. The coated glass slides were submerged in the culture solution for 100 mins under solar light. At 0, 20, 40, 60, 80 and 100 mins, mixtures were sampled and diluted with a gradient method and applied uniformly on three LB plates to measure cell viability of all samples. The colony forming units were counted and compared with control plates to calculate the ratio of cell viability (C/C_0). The antibacterial activity of nanocomposite glass coatings were further verified by a LIVE/DEAD BacLight bacterial viability assay (Invitrogen, USA) and observed by a Leica TCS SP5 laser scanning confocal microscope (Leica Microsystems, Germany). The morphological changes of *E. coli* were investigated by scanning electron microscopy (SEM, JEOL, 6340). All the experiments were conducted in triplicate.

6.3 Results and discussion

6.3.1 Structural and morphological analysis

FESEM and TEM were employed to characterize the microstructure and morphology of the GO-COOH-CuS-Ag nanocomposite. Both FESEM and TEM images proved that GO-COOH sheets, CuS nanoflakes, Ag nanoparticles, as well as GO-COOH-CuS-Ag nanocomposites were successfully fabricated (Fig. 6.1). High-resolution TEM (HRTEM) images were also obtained to examine the structure and degree of crystallinity of the nano-materials. Fig. 6.1a clearly shows the single layer structure of GO-COOH sheets and that its typical size observed was more than 2 μm . The large specific surface area of GO-COOH sheets provided sufficient base for CuS nanoflakes and Ag nanoparticles to attach themselves. Both CuS and Ag were evenly dispersed on the GO-COOH sheets without any obvious aggregation as

evidenced in Fig. 6.1b. This may be attributed to the carboxylic acid functionalised groups on the GO sheets, which not only improved its stability in aqueous solution but also increased its ability to adsorb CuS and Ag nanomaterials. The well dispersed and homogeneously distributed CuS and Ag on the GO-COOH sheets can offer a proximate electron interaction between each component, thereby increasing the transfer rate of the photo-excited electrons from the conduction band of CuS to GO-COOH and Ag.

Fig. 6.1d displays the HRTEM image of a hexagonal CuS nanoflake. The edge length of the CuS nanoflake on the GO-COOH sheets was approximately 15-20 nm. Ag nanoparticles were well separated with similar sizes around 10 nm (Fig 1e). Well-defined lattice fringes of hexagonal CuS nanoflakes and Ag nanoparticles can be seen in Fig. 1d and 1e as well. The lattice spacing of 0.31 nm could correlate with the (102) crystal planes of hexagonal CuS, whereas 0.24 nm lattice spacing corresponds to the (111) crystal planes of Ag (Basu et al. 2010, Liu et al. 2013).

Fig. 6.1 TEM images of (a) GO-COOH sheet, (b) GO-COOH-CuS-Ag nanocomposites, (c) FESEM images of GO-COOH-CuS-Ag nanocomposites at 30,000 magnification, and HRTEM images of (d) single hexagonal plate of CuS, and (e) single Ag nanoparticle.

In addition, XRD determined the crystalline phases of all-obtained products. The XRD patterns of GO-COOH nanosheets, GO-COOH-Ag, GO-COOH-CuS and GO-COOH-CuS-Ag nanocomposites can be found in Fig. 6.2. The curve representing GO-COOH sheets revealed a distinct (001) diffraction peak at $2\theta = 11.9^\circ$, which suggests the increase in interlayer spacings. This should be due to the interlamellar water that was trapped within the spacings of the hydrophilic GO-COOH sheets (Liu et al. 2013). The curve also revealed weak (002) and (100) diffraction peaks of the stacked reduced GO at $2\theta = 28.4^\circ$ and $2\theta = 42.6^\circ$, respectively (Liu et al. 2013). The absence of diffraction peak of graphene at 2θ value of 26.1° further confirmed the successful synthesis of graphene oxide. In conjunction with other reports, the three diffraction peaks all faded after synthesis with Ag and/or CuS nanomaterials, and this was due to the disruption of the regular stacked GO-COOH from the intercalation of Ag and/or CuS (Liu et al. 2013, Liu et al. 2013).

The peaks at 2θ values of 38.1° , 44.3° , 64.5° and 77.5° in the curve of GO-COOH-Ag correspond to (111), (200), (220) and (311) crystallographic planes of face-centered cubic Ag nanoparticles (JCPDS No 07-0783). In addition, peaks at 2θ values of 26.7° , 28.3° and 44.9° from the GO-COOH-CuS curve can be assigned to (102), (103) and (110) reflections of pure hexagonal covellite phase of CuS (JCPDS 00-006-0464)(Nagarathinam et al. 2009). The distinct peaks of both Ag and CuS were present in the curve of the GO-COOH-CuS-Ag nanocomposite, namely (111) and (200) reflections of Ag nanoparticles at 2θ values of 38.1° and 44.3° , as well as (102), (103) and (110) reflections of hexagonal CuS nanoflakes at 2θ values of 26.7° , 28.3° and 44.9° . Successful synthesis of GO-COOH-CuS-Ag nanocomposite with the presence of CuS and Ag was hence confirmed by the XRD patterns.

Fig. 6.2 XRD patterns of GO-COOH nanosheets, GO-COOH-Ag, GO-COOH-CuS and GO-COOH-CuS-Ag nanocomposites.

6.3.2 Composition properties of composites

Fig. 6.3 shows the FTIR spectra of GO-COOH sheets, GO-COOH-Ag, GO-COOH-CuS, and GO-COOH-CuS-Ag nanocomposites. For all four spectra, the broad absorption peak at 3423 cm^{-1} corresponded to hydroxyl group (O-H) stretching

vibrations, and the absorption peaks at 1721 cm^{-1} and 1070 cm^{-1} corresponded to carbonyl group (C=O) and C-O bond stretching vibrations respectively, in the carboxylic acid group (COOH) (Socrates 2004, Larkin 2011). This indicates the presence of the carboxylic acid functionalised groups in GO-COOH that replaced the hydroxyl groups of GO during the reaction with chloroacetic acid. The C-H bonds noted at 2921 and 2849 cm^{-1} are commonly present in organic compounds (Nara et al. 1996). In addition, the doublet bands at 1627 and 1373 cm^{-1} were attributed to the COOH symmetric and antisymmetric stretching vibrations complexed with surface CuS and Ag centers. This further confirms the successful synthesis of GCCA nanocomposites.

Fig. 6.3 FTIR spectra of GO-COOH sheets, GO-COOH-Ag, GO-COOH-CuS, and GO- COOH-CuS-Ag nanocomposites.

Elemental composition of the GO-COOH-CuS-Ag nanocomposites was confirmed by EDX. The elements C, O, S, Cu, and Ag were observed in the GO-COOH-CuS-Ag nanocomposite sample (Fig. 6.4). The homogeneous distribution of these elements appeared at the position where the nanocomposite was identified, hence

affirming that the elemental weightage reported were derived from the nanocomposites. The atomic ratio can be seen clearly, in conjunction to the elements' atomic mass.

Fig. 6.4 (a) SEM images of GO-COOH-CuS-Ag nanocomposites, distribution and intensity of elements of Carbon, Oxygen, Sulfur, Copper and Silver, and (b) EDX Spectrum and elemental weightage of GO-COOH-CuS-Ag nanocomposites

6.3.3 Optical properties of composites

Based on the UV-Vis DRS spectra shown in Fig 6.5, GCCA-15 yielded the highest absorption intensity, followed by GCCA-30 and GCCA-0 in the UV and visible light regions. The curve of GCCA-0 displayed an absorption edge at around 400 nm, whereas the curves of both GCCA-15 and GCCA-30 nanocomposites showed prominent red shift to 462 nm and 440 nm, respectively. This is reasonable due to the bonding effect between GO-COOH and CuS, which enhanced the visible light response. However, for GCCA-30, the reactive sites of GO-COOH were partly blocked by the excess CuS nanoflakes, which reduced its visible light absorption intensity compared to GCCA-15. Hence, GCCA-15 required the least energy to be photoexcited and was expected to be the most efficient in electron transfer from CuS to GO-COOH sheets and Ag nanoparticles.

Fig. 6.5 UV-Vis diffuse reflectance spectra of GO-COOH-Ag (GCCA-0), GO-COOH-CuS-Ag-15 (GCCA-15) and GO-COOH-CuS-Ag-30 (GCCA-30).

The anti-recombination of e^-/h^+ of GO-COOH-CuS-Ag was investigated by PL

spectroscopy. Fig. 6.6 displays the as-synthesized nanomaterials with a broad emission peak at $\lambda = 598$ nm under an excitation at 450 nm. The GCCA-15 nanocomposite exhibited a significantly lower PL emission intensity than others, which indicates that its e^-/h^+ recombination via fast electron transfer was effectively suppressed.

Fig. 6.6 PL spectra (excitation at 450 nm) of different ratios of GO-COOH-CuS-Ag nanocomposites.

6.3.4 Photocatalytic degradation of MB by GCCA nanocomposites

In order to select the nanocomposite with the highest photocatalytic activity for the subsequent coating, the photodegradation of MB by the three GCCA nanocomposites and pure CuS, CuS-Ag nanocomposite glass coatings were investigated, GCCA-15 showed the best MB photodegradation performance among the three nanocomposites, indicating that the most desirable synergistic interaction with the 30 mg GO-COOH and 20 mg Ag requires the optimal CuS loading of 15 mg (Fig. 6.7). This ensures the effective charge transfer from the conduction band

(CB) of CuS to GO-COOH sheets and/or Ag nanoparticles, thus the low recombination rates of photogenerated electron-hole pairs can be achieved. Therefore, GCCA-15 was chosen to fabricate the glass coatings with varied mass in the subsequent study.

Fig. 6.7 Degradation of MB by different ratios of GO-COOH-CuS-Ag nanocomposites under solar light

6.3.5 Morphology of GCCA-15 coated glasses

As can be seen from the Fig. 6.8 which shows GCCA-15 coated glass slides, the color was even, which proved that the nanocomposite was evenly coated on the glass by the aid of alumina-silica gel, BYK and DPM.

Fig. 6.8 Coating pictures for GO-COOH-CuS-Ag-15 coated glasses (sol-gel).

According to SEM images, the thickness of the cross section of glass coatings was 16.4 μm , 22.9 μm and 40.1 μm , respectively for 50 mg, 70 mg and 100 mg of loaded GCCA-15. The regular height increased as the coated nanocomposite increased.

Fig. 6.9 SEM image of the cross section of glass coating (a)50 mg (b)70 mg (c)100 mg.

6.3.6 Photodegradation of MB and disinfection performance of GCCA nanocomposite glass coating

As shown in Fig. 6.10, glass coating prepared with 70 or 100 mg GCCA-15 shows the nearly the same MB photodegradation performance, in which 75.5% MB removal was achieved within 90 minutes under solar light irradiation. The results suggest that the photodegradation performance may not increase with the further increase of coated mass once the effective surface is saturated with sufficient material loads, as only the top layer(s) can be irradiated by solar light. Given the

consideration to both performance and cost among the three loads tested, the optimal mass load was identified as 70 mg nanocomposites per 5 cm² glass.

In order to investigate the long-term stability of glass coatings, the photocatalytic degradation of MB by 70 GCCA-15 was repeatedly performed over five cycles. As shown in Fig. 6.10b, no evident change was observed for the photocatalytic activity through the 5 cycles of experiments for MB degradation, indicating good photocatalytic stability of the glass coatings. In addition, TOC analysis was monitored as a function of the mineralization rate of MB and its related intermediates. As shown in Fig. 6.10c, the TOC decreased over time, and the 70 and 100 mg GCCA-15 glass coatings displayed the highest TOC removal efficiency.

Fig. 6.10 (a) Photocatalytic performance for MB by different amount (50 mg, 70 mg and 100 mg) of GCCA-15 nanocomposite glass coating under solar light, (b) five consecutive cycling curves of MB photodegradation by 70 mg GCCA-15, and (c) TOC concentrations versus time.

Under solar light irradiation, 70 GCCA-15 achieved 99.9% *E. coli* inactivation within 60 mins, whereas 50 or 100 GCCA-15 required at least 90 mins to obtain similar disinfection results (Fig. 6.11). On the other hand, under dark conditions, 70 GCCA-15 achieved 99.9% *E.coli* inactivation within 120 mins, whereas 100 GCCA-15 and 50 GCCA-15 could not achieve similar disinfection results even after 120 mins. Therefore, 70 GCCA-15 was identified as the best nanocomposite glass coating for disinfection.

Fig. 6.11. Antibacterial activities of different amount (50 mg, 70 mg and 100 mg) of GO-COOH-CuS-Ag nanocomposite glass coating with and without solar irradiation.

As presented in Fig. 6.12, nearly all *E. coli* was inactivated (appeared in red fluorescence) after solar irradiation with the presence of 70 GCCA-15, which is consistent with the result in Fig. 6.12b. In contrast, before irradiation, large numbers of *E. coli* survived and displayed in green fluorescence (Fig. 6.12a). Fig. 6.12c shows the FESEM image of *E. coli* cells after photocatalytic inactivation under solar light with 70 GCCA-15. The cell walls of the *E. coli* were seriously damaged and almost all bacteria cell membranes were shrunk.

Fig. 6.12 Fluorescence microscopic images of *E. coli* with the 70 GO-COOH-CuS-Ag-15 coated glass (a) before and (b) after solar light irradiation, (c) FESEM image of *E. coli* cells with 0.22 μm membrane filtration after solar light irradiation with 70 GO-COOH-CuS-Ag-15.

Metal (Cu^{2+} and Ag^+) leaching experiments were performed to further investigate the long-term stability and durability of the glass coatings. The results proved that no Cu^{2+} and Ag^+ were detected in the experiment solutions even after 1-month storage in MB solution (Table 6.2). Further, no crack on the coating was observed, which proved the stability and durability of the glass coating. The coating method has a great potential for designing a continuous flow photoreactors.

Table 6.2. The percentage of leached Cu^{2+} and Ag^+ after degradation

(%)	Cu^{2+}	Ag^+
50 GCCA-15	N.D.	N.D.
70 GCCA-15	N.D.	N.D.
100 GCCA-15	N.D.	N.D.

6.3.7 Photocatalytic mechanism

6.3.7.1. EPR analysis

The above results have affirmed that the as-synthesized novel nanocomposite GO-COOH-CuS-Ag significantly enhanced the photocatalytic degradation under solar irradiation, as well as the antibacterial performance with and without solar irradiation. In order to better understand the underlying causes, the photocatalytic

mechanism was further explored and discussed through EPR analysis.

Different EPR spectra were obtained from experiments carried out in water and in methanol for GCCA-15 in the presence of the DMPO spin trap (Fig. 6.13)(Ma et al. 2016). The ESR spectra of DMPO-trapped radicals in aqueous medium containing GCCA-15 under UV-vis irradiation showed 4 major peaks in a 1:2:2:1 ratio which is characteristic of the DMPO- $\cdot\text{OH}$ adduct. Very weak signals were detected for GCCA-15 in the presence of the DMPO spin trap in water before UV-Vis irradiation. This is likely due to the reaction solution photochemically reacting with ambient light in the several minutes required to transfer the sample to the EPR instrument.

The EPR spectra of DMPO-trapped radicals in methanol containing GCCA-15 under UV-vis irradiation showed 6 major peaks of approximately equal intensity which is the characteristic of the DMPO- $\text{O}_2^{\cdot-}$ adduct. The signal increased in intensity after UV-vis irradiation, although a signal was still evident before irradiation due to the photochemical reactions occurring under ambient light conditions. However, the signal of $\text{O}_2^{\cdot-}$ is much stronger than that of $\cdot\text{OH}$, so the result confirmed that $\text{O}_2^{\cdot-}$ is the main radical species for the photocatalysis under solar light.

Fig. 6.13 DMPO spin-trapping EPR spectra of GCCA-15 with aqueous dispersion for $\text{DMPO}\cdot\text{OH}$ and methanol dispersion for $\text{DMPO}\cdot\text{O}_2^{\cdot-}$.

6.3.7.2 Mechanism for organic matter degradation and bacterial inactivation

The efficiency and the rate of degradation and disinfection by the photocatalyst nanocomposite depends on how efficient the pollutants can be attached to the nanocomposite, how effective the excited electrons can be separated to ensure minimal electron-hole pair recombination, and how effective the generated electrons convert surface O_2 to reactive oxygen species (ROSs) - oxygen superoxide radicals ($\text{O}_2^{\cdot-}$) which is the main radical to degrade pollutants (Zhang et al. 2012).

According to Fig. 6.14, under solar light irradiation, plasmonic photocatalysts GCCA can strongly absorb the visible light because of the surface plasmon resonance of Ag nanoparticles (Xu et al. 2013), so that the electrons could be generated either from excited dye (MB^*) molecules or conduction band of CuS nanoflakes, and transfer to GO-COOH sheets and then to Ag nanoparticles (Awodugba and Ibiyemi 2012, Liu et al. 2013). The effective electron transfer and

the π - π interactions between the aromatic structure with the GO-COOH sheets (Zhang et al. 2012) inhibit the recombination of electron-hole pairs at the excited MB molecules, bacteria and CuS nanoflakes. Therefore, the photocatalytic degradation process is enhanced and the photogenerated electrons are then able to produce the superoxide anions, $\cdot\text{O}_2^-$, and/or the hydroxyl radicals, $\cdot\text{OH}$, that can effectively participate in the photodegradation process to mineralize the MB dye and disinfect the bacteria. In addition, not only the solar light can cause mutation to the DNA of the bacterial cells, weakening and subsequently killing the microbial organisms (Malato et al. 2007, Loo et al. 2015), several studies have also shown that nanocomposites consisting of Ag nanoparticles are effective in bacterial disinfection³¹. By attaching on the GO-COOH sheets, Ag nanoparticles can disintegrate the cell walls of the *E. coli*. The optimal CuS content in GO-COOH-CuS-Ag suggests that an excessive increase in CuS content will result in a less desirable photocatalytic performance. This may be due to pure CuS nanoflakes aggregation, which may cover the active sites on GO-COOH. Furthermore, additional CuS might not be attached on the surface of GO-COOH sheets. These prevent the transfer of electrons, resulting in an increase in electron-hole pair recombination in the excited CuS, dye* molecules and bacteria, hence less active radicals are available to participate in the reduction of organic dye molecules and disinfection of bacteria.

Fig. 6.14 Schematic diagram of energy levels and electron transfer mechanism of GO-COOH-CuS-Ag nanocomposites.

6.4 Conclusions

The application of GO-COOH-CuS-Ag glass coatings for organic compound removal in aqueous environments and for bacteria disinfection was explored in this study. The results clearly demonstrate its high performance potential in photodegradation and photo-disinfection processes with the advantage of simplifying the recovery and reuse in comparison to powdered forms, and reducing problems including the agglomeration of powdered particles that may cause blockages. Consequently, the multifunctional GO-COOH-CuS-Ag nanocomposite coated glass may also offer a solution in organic matter removal in the gas phase such as volatile organic compounds (VOCs) removal and indoor air pollution control.

CHAPTER 7. NOVEL MPG-C₃N₄/TiO₂ NANOCOMPOSITE PHOTOCATALYTIC MEMBRANE REACTOR FOR SULFAMETHOXAZOLE PHOTODEGRADATION

7.1 Introduction

Pharmaceuticals are commonly found in surface water and treated wastewater which bring a new research focus on the fate and degradation pathways of the pharmaceuticals and their impact on the aquatic environment (Trovo et al. 2009). Some of the pharmaceuticals and their degradation by-products are recalcitrant that cannot be further degraded naturally. There is a certain need to reduce and transform these compounds before they end up in drinking water supply system. One of the approaches to reduce the pharmaceutical content is through heterogeneous photocatalysis. It is an emerging and promising process for water treatment, and has been applied to the treatment of different organic pollutants in water and wastewater. Among various advanced oxidation processes (AOPs), photocatalysis is cost effectiveness and has more flexibility in process design (Abellán et al. 2007).

However, photocatalysts are commonly applied in fine-powder form in water treatment, and their aggregation and agglomeration in aqueous solution will lower the effectiveness and efficiency of photocatalysis. Further, the photocatalyst-recovering step from the reaction environment is a pivotal stage in view of large-scale applications. Photocatalytic membrane reactors (PMRs) represent a promising approach to overcome this limitation (Bai et al. 2010, Mohamed et al. 2015, Molinari et al. 2015, Nor et al. 2016, Hir et al. 2017, Molinari et al. 2017). Compared with the coating/spraying nanoparticles on the substrates like glass (Modesto-López et al. 2015, Shuyan Yu 2017) or polyester fiber (Han et al. 2013), immobilizing them within membrane can provide enhanced material recovery rate from the liquid phase. One common method to develop the nanoparticle membrane is to sequentially filter or coat the nanoparticles on the membrane (C.P. Athanasekou 2012, Molinari et al. 2015, Bet-moushoul et al. 2016, Zhao et al.

2016). However, the procedure often result in increased preparation cost and time, and the reduced membrane water permeability (C.P. Athanasekou 2012). It is believed that embedding the nanoparticles within the membrane is a facile way to efficiently capture the photocatalyst and to improve the recyclability of the nanomaterials (C.P. Athanasekou 2012, Bet-moushoul et al. 2016, Mohamed et al. 2016).

Mesoporous graphitic carbon nitride (mpg-C₃N₄) has attracted intensive research interests due to its excellent photocatalytic properties as well as nontoxicity, metal-free nature and narrow band gap (Dong et al. 2015, Zhou et al. 2016) characteristics. It is reported that ultrathin mpg-C₃N₄ nanosheet can provide even more narrow bandgap with sufficient light absorption than the bulk g-C₃N₄ (Min and Lu 2012). However, high recombination rate of generated charge may lead to low photocatalytic performance. Hence, combined mpg-C₃N₄ nanosheet with other excellent semiconductor, such as TiO₂, can overcome this problem. TiO₂ has higher chemical stability, lower cost and non-toxic properties compared to other semiconductors like CuS, ZnO etc. (Hashimoto et al. 2005, Bet-moushoul et al. 2016, Zhou et al. 2016). Some reports have confirmed that combination of TiO₂ with mpg-C₃N₄ nanosheet can not only overcome the issue of high electron-hole pair recombination rate of pure mpg-C₃N₄, but also shift the UV light range application of TiO₂ to a broader visible light range, then reaches a synergistic effect (Bet-moushoul et al. 2016, Zhou et al. 2016). Moreover, TiO₂ is the most commonly used semiconductor in PMRs (Shi et al. 2012, Zhang et al. 2016), which was used to treat wastewater and surface water with the combined functions of organic degradation, physical filtration and anti-bacterial properties in a single unit (Bai et al. 2010, Leong et al. 2014, Mohamed et al. 2015, Molinari et al. 2015, Nor et al. 2016, Hir et al. 2017). Membrane with mpg-C₃N₄ combined with TiO₂ can achieve an enhanced effect which may outperform the pure C₃N₄ membrane, and to the authors' knowledge, it is the first time to study the photocatalytic performance of a mpg-C₃N₄/TiO₂ nanocomposite embedded membrane reactor.

Most of the PMRs combined photocatalysis with pressure driven membrane processes such as nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF)(Mozia 2010, Deveci et al. 2016, Molinari et al. 2017). In this study, a UF membrane was prepared by incorporating mpg-C₃N₄/TiO₂ nanocomposite to polysulfone (PSf) matrix. PSf polymer has high thermal, mechanical and chemical resistance and is a very common material for UF membrane preparation (Leong et al. 2014). A typical antibiotic named sulfamethoxazole (SMX) was used as a model pharmaceutical. It has been reported that heterogeneous photocatalysis and photo-Fenton reactions are fast and effective to transform SMX via direct and indirect reactions (Abellán et al. 2007, Trovo et al. 2009, Trovo et al. 2009, Oh et al. 2016). However, the employment of photocatalytic membrane to degrade SMX has not been studied. This study, for the first time, fabricated a UF membrane embedded with mpg-C₃N₄/TiO₂ nanocomposite, and explored its SMX photodegradation performance under solar light irradiation. The structural and morphological properties of the mpg-C₃N₄/TiO₂ nanocomposite, and the performance of mpg-C₃N₄/TiO₂ membrane in terms of SMX photodegradation were systematically investigated.

7.2 Materials and methods

7.2.1 Source of chemicals

Tetrabutyl titanate (TBT), sodium hydroxide (NaOH), sulfamethoxazole (SMX), acetic acid (CH₃COOH, 99%) chloroacetic acid (ClCH₂CO₂H, 99%) and nitric acid (HCl) were purchased from Sigma-Aldrich. Melamine powder, isopropanol (IPA), acetone and ethanol were purchased from Merck Ltd. (Singapore). The deionized (DI) water was produced from Millipore Milli-Q water purification system.

7.2.2 Synthesis of bulk mpg-C₃N₄ and mpg-C₃N₄ nanosheet

Bulk mpg-C₃N₄ was synthesized by directly heating melamine (Liao et al. 2014). Briefly, 2 g of melamine powder was incubated for 2 h in a 550 °C crucible, and naturally cooled down to room temperature (24 °C). In order to exfoliate the mpg-C₃N₄ into mpg-C₃N₄ nanosheet, the bulk mpg-C₃N₄ was then dispersed in

isopropanol (IPA) to form 1 mg mL⁻¹ solution and sonicated (Elmasonic P ultrasonic cleaner) for 48 h. The mpg-C₃N₄ nanosheet was obtained after centrifugation and freeze-drying.

7.2.3 Preparation of anatase TiO₂ nanospheres

Acetic acid (HAc) capped anatase TiO₂ nanospheres were synthesized by a facile solvothermal method followed by calcinations (Chen et al. 2013). In brief, 1.2 mL of tetrabutyl titanate (TBT) was dripped into 50 mL HAc solution. Then the solution was mixed and transferred into a teflon-lined stainless steel autoclave vessel, and kept at 250 °C for 16 h. After cooling down, the precipitation was washed twice with ethanol and twice with deionized (DI) water. The as-prepared material was calcined at 400 °C at a ramp rate of 1 °C min⁻¹ and kept for 1 h at the final temperature. The final product was obtained after cooling down naturally to room temperature.

7.2.4 Preparation of carboxylated functionalized mpg-C₃N₄ and mpg-C₃N₄/TiO₂ nanocomposite

The obtained mpg-C₃N₄ nanosheet was functionalized with carboxylated functional group. The progress was as follows: 12 g of chloroacetic acid (ClCH₂CO₂H), 10 g of NaOH and 500 mg of mpg-C₃N₄ were added to 1000 mL DI water and then sonicated for 3 h. The resulting mpg-C₃N₄ solution was neutralized by HNO₃, and washed with acetone and afterwards water for 3~4 times. Then the carboxylated functionalized mpg-C₃N₄ was obtained after freeze-dried. After that, 400 mg carboxylated functionalized mpg-C₃N₄ together with 200 mg TiO₂ nanospheres were added in DI water, and sonicated for 1 h. The mixture was heated up to 90 °C for 1 h and cooled naturally to the room temperature. The mpg-C₃N₄/TiO₂ nanocomposite was collected after the sample was freeze-dried.

7.2.5 Preparation of membrane

Polysulfone (PSf, molecular weight of 75–81 kDa, Solvay Advanced Polymers, LLC, GA) were used for preparing the UF membranes. N-methyl-2-pyrrolidone

(NMP, Merck) was used as the solvent for the casting solution. Polyvinyl pyrrolidone (PVP, average molecular weight 1,300,000 Da, Alfa Aesar, MA) was used as an additive in the casting solution. The polysulfone (PSf) UF membrane was formed via phase inversion (Wei et al. 2011). To prepare a casting solution, 17% PSf and 0.5% PVP were dissolved in NMP at 70 °C. The solution was stirred on a magnetic stirrer till it became transparent and homogeneous. After it was cooled down to room temperature, a certain amount of nanoparticles (that were homogeneously suspended in NMP solution) were added to the casting solution and stirred for at least 4 h. The solution was degassed for 24 h prior to use. During membrane casting, the solution was spread onto a dry and clean glass plate using an Elcometer 4340 Motorised Film Applicator (Elcometer Asia Pte Ltd) at a gate height of 175 µm. The glass plate was then smoothly immersed into a coagulant bath (~23 °C tap water) and a PSf membrane was formed after complete coagulation. Four types of UF membranes named PSf-0, PSf-1, PSf-2 and PSf-3 (representing blank control, 0.2% mpg-C₃N₄ embedded, 0.2% mpg-C₃N₄/TiO₂ embedded, and 1% mpg-C₃N₄/TiO₂ embedded, in which the membrane with 0.2% and 1% mpg-C₃N₄/TiO₂ embedded was made to compare the effect with different ratio of photocatalyst loading) were prepared by varying the type and content of photocatalysts as shown in Table 7.1.

Table 7.1. Membranes prepared with different photocatalysts loadings.

Membrane	Nanoparticle	Nanoparticle concentration with respect to polymer concentration (%)
PSf-0 ^a	-	-
PSf-1	mpg-C ₃ N ₄	0.2
PSf-2	mpg-C ₃ N ₄ /TiO ₂	0.2
PSf-3	mpg-C ₃ N ₄ /TiO ₂	1

Note: ^aPSf-0 contains no nanoparticle.

7.2.6 Characterization of photocatalysts and membrane

7.2.6.1 Characterization of photocatalysts

The X-ray powder diffraction (XRD) patterns of nanoparticles TiO_2 , mpg- C_3N_4 and mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ were recorded on a D8-Advance Bruker-AXS diffractometer using $\text{Cu K}\alpha$ irradiation to determine the crystallinity and phase. Their morphology was characterized using transmission electron microscopy (TEM) and high-resolution TEM (JEOL 2010-H TEM). The elemental content in mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ nanocomposite was characterized using energy dispersive X-ray spectroscopy (EDS, JEOL 7600F). The specific surface areas of the nanoparticles were determined from the N_2 adsorption–desorption isotherm at 77 K (Quantachrome Autosorb-1 Analyzer). X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Kratos Axis Ultra Spectrometer with a 15 kV and 10 mA monochromic $\text{Al K}\alpha$ source at 1486.7 eV. The Brunauer-Emmett-Teller (BET) specific surface area of all-obtained composites were determined from the N_2 adsorption–desorption isotherm at 77 K (Quantachrome Autosorb-1 Analyzer).

7.2.6.2 Membrane characterization

The surface and cross sectional morphologies of the as-synthesized membranes were characterized by field emission scanning electron microscopy (FESEM, JEOL 7600F) and surface elements analysis were characterized by energy dispersive X-ray spectroscopy (EDX, JEOL 7600F). The membrane samples were fractured in liquid nitrogen, dried in vacuum at room temperature for 24 h, and then coated with a thin layer of platinum. The membrane water permeability and molecular weight cut-off (MWCO) were tested in a cross-flow membrane cell with an active area of 42 cm^2 . To measure pure water permeability, DI water was filtered at an applied pressure of 1 bar at 24°C . To determine the MWCO, permeate sample and feed sample were collected during the filtration of a 2000 mg mL^{-1} dextran solution (molecular weight of 6,000-500,000 Da), and the samples were analyzed using gel permeation chromatography (GPC, Polymer Laboratories-GPC 50 Plus system). The tensile strength of the membranes was measured using a Zwick 0.5 kN Universal Testing Machine (test standard ASTM D 882) (Tian et al. 2015). Prior to the test, membrane samples were carefully cut into 5 cm long dumbbell shaped strips with the narrowest width of 4 mm at the center. The distance between the two tensile grips was 25 mm. The water contact angle of membrane was measured using

goniometer equipment (Data Physics Instruments GmbH) with sessile drop method (Wang et al. 2016).

7.2.7 PMR set-up and operation

The photocatalytic degradation of 10 mg L^{-1} SMX was carried out in the photocatalytic membrane reactor (PMR) at room temperature. As shown in Fig. 7.1, the SMX solution in the feed tank was continuously circulated and passed through a dead-end membrane cell (active area of 8.5 cm^2). The flow rate was $\sim 13 \text{ mL min}^{-1}$ (i.e., membrane flux of $918 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) throughout the 30-h run. Prior to the photodegradation experiment, the PMR was operated for 2 h in the dark to reach adsorption equilibrium. The reactor was then exposed to solar light from a solar light simulator. The light source was a 300 W ozone free xenon lamp (Newport Oriel). The feed water was sampled at pre-determined time interval for SMX concentration analysis.

Fig. 7.1. Schematic of PMR setup with a dead-end UF system with an active membrane area of 8.5 cm^2 for photocatalytic degradation. The feed water contained 10 mg L^{-1} SMX at the start of the run.

7.2.8 SMX concentration analysis

The collected water samples were filtered with $0.45 \text{ }\mu\text{m}$ cellulose acetate syringe membrane filter and analyzed using an ultra-fast liquid chromatography (UFLC) equipped with a Agilent Proshell 120 EC-C 18 column ($4.1 \times 100 \text{ mm}$, $2.7 \text{ }\mu\text{m}$) and an SPD-M20A diode array detector (Shimadzu LC-20AD, Japan). The mobile phases consisted of water (A) and 10 mM ammonium acetate in methanol with 0.1% formic acid (B). The flow rate and injection volume were 0.8 mL min^{-1} and $5 \text{ }\mu\text{L}$,

respectively. The detector wavelength was set at 270 nm. The retention time of SMX was about 7.5 min.

Intermediates of SMX degradation were analyzed using an Agilent 1290 infinity high-performance liquid chromatography (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). The separation of different intermediates was achieved by using a 100 mm $\times$ 2.1 mm Kinetex 2.6 μ m C18 column. The flow rate was set at 0.2 mL min⁻¹ and the injection volume was 5 μ L. The mobile phases consisted of water (A) and 10 mM ammonium acetate in methanol with 0.1% formic acid (B). The liquid chromatography – double mass spectrometry (LC-MS/MS) system was operated in MS2 scan mode and in ESI mode using Jet stream positive ionization. The ionization source was operated at the conditions of 8 L min⁻¹ nebulizer gas and 11 L min⁻¹ sheath gas at a temperature of 325 °C, 30 psi nebulizer pressure and capillary voltage of 3500 V. The mass range between m/z 30 and m/z 600 was scanned to obtain full scan mass spectra.

7.3 Results and discussion

7.3.1 Characteristics of mpg-C₃N₄

The morphology and microstructure of the as-prepared samples are shown in the TEM images in Fig 7.2. Fig 7.2a shows that the mpg-C₃N₄ nanosheet has layered structure with diameter of around 500 nm. Abundant nanopores (semi-transparent features) in the size range of 20-40 nm can be also observed. Recent studies have reported that the nanopores are the key active sites for enhancing the catalytic activity and stability compared to the common bulk catalysts (Min and Lu 2012, Su et al. 2014). TiO₂ nanospheres with a diameter of 200-400 nm can be observed clearly in Fig 7.2b. The size of TiO₂ nanospheres is smaller than that of mpg-C₃N₄, leading to the easy attachment to the mesoporous surface of mpg-C₃N₄ (Fig 2c) (Ma et al. 2014). In addition, in order to identify the crystal phase of TiO₂ nanospheres, mpg-C₃N₄ and mpg-C₃N₄/TiO₂, the XRD patterns are presented in Fig. 7.3. The peaks at $2\theta = 25.3^\circ, 37.9^\circ, 48.3^\circ, 55.3^\circ, 63.1^\circ, 69.2^\circ$ and 75.1° correspond to the properties of crystallized anatase TiO₂ (JCPDS No.21-1272) (Zhang et al. 2016).

For mpg-C₃N₄ and mpg-C₃N₄/TiO₂, the observed peaks at around 12.9° and 27.4° are attributed to the (100) and (002) crystal planes of mpg-C₃N₄, confirming the interlayer distance of 0.681 nm and 0.326 nm (Ma et al. 2014). These XRD spectra of mpg-C₃N₄/TiO₂ contain both information of mpg-C₃N₄ and TiO₂, again indicating the successful formation of the nanocomposite.

Fig. 7.2. TEM images of (a) mpg-C₃N₄, (b) TiO₂ nanospheres and (c) mpg-C₃N₄/TiO₂.

Fig. 7.3. XRD patterns of TiO₂ nanospheres, mpg-C₃N₄ and mpg-C₃N₄/TiO₂.

The elemental analysis and surface electronic state of mpg-C₃N₄/TiO₂ nanocomposite were confirmed by the EDX and XPS. The EDX elemental analysis results of the mpg-C₃N₄/TiO₂ nanocomposite are presented in Fig. 7.4. The elemental image of Ti confirms that TiO₂ nanospheres were deposited on the surface of mpg-C₃N₄ successfully. In addition, the elements C, N, Ti and O are

dominated in the mpg-C₃N₄/TiO₂ composition, without other obvious impurities in this nanocomposite. Fig. 7.5 presents the XPS surface electronic state results of mpg-C₃N₄/TiO₂ nanocomposite. The high-resolution spectra of C 1s at 284.5 eV and N 1s at 398.5 eV observed in Fig. 7.5(d-e) are assigned to the sp² C=N bond in the s-triazine ring (Ma et al. 2014). The peaks at 459.7 eV and 465.5 eV of the Ti 2p spectra prove that Ti has a valence of four. And the two main O 1s peaked at 530.2 eV and 532.2 eV can be ascribed to lattice O²⁻ and O²⁻ ions/hydroxyl group (Reli et al. 2016). Furthermore, The Ti 2p at 459.2 eV and O 1s at 530 eV (Fig. 7.5(b-c)) can be attributed to the O-Ti-O bond (Yu et al. 2017). The contributions of the peaks at 284.2 eV, 287.1 eV and 290.0 eV of C 1s are attributed to the sp² C atom bonded to N to form C-(N)₃, C-N-C or C-C bonds, which can attach to -NH₂ functional group or to an aromatic carbon atom (Lu et al. 2017). Correspondingly, the main peak at 400.3 eV in the N 1s is attributed to N atoms that are bound to three C atoms (Song et al. 2016). The mpg-C₃N₄/TiO₂ nanocomposite sample exhibits C 1s and N 1s signals with a C/N surface atomic ratio of 0.7, which is very close to the ideal C₃N₄ nanosheet composition (C/N 0.65) (Niu et al. 2012, Jo and Natarajan 2015), indicating that the chemical composition in the mpg-C₃N₄ were retained after being transformed into mpg-C₃N₄/TiO₂ (Chen et al. 2016, Mohamed et al. 2017) and the mpg-C₃N₄/TiO₂ nanocomposite were successfully synthesized and in good agreement with SEM and XRD results.

Fig. 7.4. (a) SEM images of the mpg-C₃N₄/TiO₂ and (b-f) EDX elemental analysis spectrum with the same scale bar.

Fig. 7.5. XPS result of (a) mpg-C₃N₄/TiO₂ nanocomposite and the high-resolution spectra of (b) Ti 2p, (c) O 1s, (d) C 1s and (e) N 1s.

The pore size distribution and surface area of mpg-C₃N₄/TiO₂ nanocomposite were analyzed using N₂ adsorption-desorption isotherms and the results are shown in Fig. 7.6. The nanocomposite exhibited nitrogen adsorption-desorption isotherms of type IV (BDDT classification) with hysteresis loops of type H3 at relative pressure of

0.6–0.9, indicating the presence of mesoporous structures (Wei et al. 2013). The corresponding pore size distribution curves (inset) show a relatively wide pore size distribution in the mpg-C₃N₄ nanosheets and TiO₂ nanospheres presented. The specific surface area of mpg-C₃N₄/TiO₂ nanocomposite is 135.77 m² g⁻¹, which is in between the size of mpg-C₃N₄ (83.83 m² g⁻¹) and TiO₂ (146.98 m² g⁻¹), the larger specific surface area of mpg-C₃N₄/TiO₂ nanocomposite than pure mpg-C₃N₄ would provide more reactive sites for photodegradation.

Fig. 7.6. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of as-synthesized products (inset).

7.3.2 Properties of membrane

The SEM images of membrane PSf-0 (blank control) and PSf-3 (1% mpg-C₃N₄/TiO₂) are compared in Fig. 7.7. There is no significant morphological difference was observed by comparing the surfaces and cross sections of the PSf-0 (Fig. 7.7a-b) and the PSf-3 membranes (Fig. 7.7c-d). And the mechanical properties of membranes changed upon the embedment of nanoparticles (Fig. 7.8). The membrane tensile modulus generally increased while the ultimate elongation of the membrane was reduced by almost half for the membranes PSf-1, PSf-2 and PSf-3, revealing that nanoparticles at small amount could still largely affect the tensile property of the membranes. However, all the four membranes demonstrated similar

tensile strength at break. The results indicate that the incorporation of TiO₂ or mpg-C₃N₄/TiO₂ stiffened the membrane material. This observation is common for low density polymer incorporated materials (Strapasson et al. 2005, Cao et al. 2015)-Fig. 7.9a shows that PSf-0 had a contact angle of 70.8°, and PSf-1 and PSf-2 had slightly decreased contact angles (67.7° and 65.6°, respectively), presumably due to the hydrophilic property of mpg-C₃N₄ and mpg-C₃N₄-TiO₂ (Xu et al. 2016, Zhao et al. 2016). With further increase in the nanocomposite loading, the membrane PSf-3 (1% mpg-C₃N₄/TiO₂) showed a much lower contact angle of 58.1°, indicating the significance of embedded mpg-C₃N₄/TiO₂ in increasing membrane hydrophilicity. The MWCO of the four membranes PSf-0, PSf-1, PSf-2, and PSf-3 were found to be ~118 kDa, 90 kDa, 88 kDa and 80 kDa, respectively (Fig. 7.9b). The MWCO of membranes decreased upon the incorporation of nanocomposites, which indicated the narrower membrane pore size. Correspondingly, the membrane water permeability decreased from 628.6 L m⁻² h⁻¹ bar⁻¹ for the blank control membrane (PSf-0) to 504.6, 525.4, and 551.2 L m⁻² h⁻¹ bar⁻¹ for the PSf-1, PSf-2 and PSf-3 membranes, which was also owing to the narrowing membrane pore size leading to the decreased water permeability. Therefore, the embedment of the nanocomposites had an effect of narrowing the membrane pore size. However, PSf-3 had slightly higher permeability, which may be attributed to the markedly increased hydrophilicity (Fig. 7.9a). Similar phenomenon has been reported in other studies (Fang et al. 2014, Lin et al. 2017).

Fig. 7.7. SEM images showing (a-b) the cross sections and surfaces of PSf-0, and PSf-3 membrane (c-d) before solar light irradiation and (e-f) after solar light

Fig. 7.8. Mechanical properties of PSf-0, PSf-1, PSf-2, PSf-3 membranes. (a) Tensile modulus, (b) tensile strength at break, and (c) elongation at break (%); Mechanical properties of PSf-3 membrane before and after filtration run. (d) Tensile modulus, (e) tensile strength at break, and (f) elongation at break (%).

Fig. 7.9. (a) The contact angle, (b) MWCO and (c) pure water permeability of the membranes prepared in the study.

7.3.3 Photodegradation performance evaluation

SMX photodegradation performance of different membranes under solar light is shown in Fig. 7.10. The SMX removal efficiency of the membrane PSf-3 (with 1% mpg-C₃N₄/TiO₂ loading) was the highest over the 30 h consecutive irradiation, i.e., 69% of SMX was degraded at the end of the run. The total SMX removal for membranes PSf-0, PSf-1 and PSf-2 was 14%, 33% and 49%, respectively. The “activity” demonstrated by the blank membrane PSf-0 was likely caused by the membrane adsorption or self-photodegradation of SMX under solar light (C.P. Athanasekou 2012). The observation revealed that higher loading of photocatalysts to the membrane led to better SMX removal efficiency even though the water permeability was lower than blank membrane, presumably due to the hydrophilic property of mpg-C₃N₄ and mpg-C₃N₄-TiO₂ and the larger amount of radicals generated with enhancing photocatalysis performance. The nanocomposite mpg-C₃N₄/TiO₂ had better photodegradation performance than the pure mpg-C₃N₄, which was reflected by comparing membrane PSf-2 and PSf-1 with same amount of photocatalyst loading. The pollutants degradation activity of mpg-C₃N₄ was improved after it was modified with TiO₂ which overcome the high electron-hole recombination rate of mpg-C₃N₄. During the 30 h irradiation period, the potential detachment of photocatalyst was studied using UV-Vis spectrum and ICP-MS, and the result showed no photocatalyst can be found in the liquid phase at all, in addition, the rates of photodegradation reaction of each membrane were relatively constant, suggesting that all the membranes maintained stable photodegradation performance, which not only attributed to the stable photodegradation ability of mpg-C₃N₄/TiO₂, but also owing to the high thermal, mechanical and chemical resistance of PSf polymer, and the stable water permeability of the membrane. The overall SMX photodegradation time of PMRs in the current study was longer than those aqueous suspension photocatalyst systems, due to the lower nanocomposite concentration contained in the membranes, and the weaker light transmittance of the membrane material. However, this is common for PMR systems as shown by the TiO₂-based UF membranes (Abellán et al. 2007, Oh et al. 2016, Molinari et al.

2017). Nevertheless, the photocatalysts embedded membranes do not face the challenge of particle recycling.

Fig. 7.10. SMX degradation performance of photocatalytic membranes under solar light irradiation.

7.3.4 SMX degradation mechanism and pathways

A possible photodegradation mechanism is proposed and shown in Fig. 7.11. The membrane with more nanocomposites loading showed the better photodegradation performance, and this is because the PSf polymer mixed with mpg-C₃N₄/TiO₂ had high thermal, mechanical and chemical resistance that can strongly support mpg-C₃N₄/TiO₂ to generate radicals to degrade the pollutants (Mohamed et al. 2016). Under solar light irradiation, a charge transfer can be achieved in the mpg-C₃N₄/TiO₂ system, as reported by other researchers (Ma et al. 2016, Reli et al. 2016), the conduction band (CB) of mpg-C₃N₄ is -1.3 eV, which is more negative than the CB of TiO₂ (-0.5 eV), and the valence band (VB) of mpg-C₃N₄ (1.4 eV) is less positive than that of TiO₂ (2.7 eV). An immediate electron transfer from the CB of mpg-C₃N₄ to TiO₂ can lead to the immediate photocurrent generation. Meanwhile, the photogenerated holes can be transported immediately from the low VB of TiO₂ to mpg-C₃N₄. The enhanced electron transfer rate can repress effectively charge recombination. Then the generated electrons can react with absorbed surface O₂ to produce reactive oxygen species (ROS) which assists the pollutants degradation (Yu et al. 2015). Meanwhile, the photogenerated holes and

ROS can oxidize $\text{H}_2\text{O}/\text{OH}$ to form hydroxyl radicals, which could further degrade the SMX under solar light. The enhanced effect of mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ system results in a higher photocatalytic activity owing to the larger specific surface area, enhanced electron transfer rate and lower charge recombination rate (Oh et al. 2016, Shuyan Yu 2017).

Fig. 7.11. Schematic illustration of proposed SMX photodegradation mechanism of mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ nanocomposite PMR system.

In order to elucidate the intermediates presented during the photodegradation, the feed water samples collected at the end of the run were analyzed using LC-MS/MS, 7 intermediates were identified and the reaction scheme was proposed and displayed in Fig. 7.12. The molecular formula of original SMX is $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$ with a molecular weight (MW) of 254. The MWs of the other 7 intermediates were 397, 269, 287, 243, 215, 197 and 172, respectively. The compound of the highest MW (397) may correspond to the formula of $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_6\text{S}_2$, which could be a product from the dimerization of SMX. The best-fit formula for MW 269 was $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_4\text{S}$, which is the addition of a hydroxyl radical to the SMX itself (Trovo et al. 2009). The degradation of SMX was initialized by the attack of hydroxyl radicals on the isoxazole ring. This was confirmed by the presence of the compound with MW of 287 $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_5\text{S}$, as a result of the attack to the double bond on the

isoxazola ring. Similar result was also reported by a prior study, where the same compound was generated by TiO_2 photocatalysis (Hu et al. 2007). The compound identified at 243 MW was likely generated by opening of isoxazole ring, and fitted by the formula and structure of $\text{C}_8\text{H}_9\text{N}_3\text{O}_4\text{S}$ (Hu et al. 2007). Further losing one carbonyl group may result in the generation of the compound 215 ($\text{C}_7\text{H}_9\text{N}_3\text{O}_3\text{S}$) (Trovo et al. 2009). Afterwards, the loss of H_2O could generate the intermediate of MW of 197 ($\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S}$) (Nasuhoglu et al. 2011). The compound with lowest MW 172 detected in the current study may correspond to the formula of $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$ with the structure showing in Fig. 7.12. Nevertheless, a few prior studies also reported that these molecules can be subsequently oxidized into small compounds, such as oxalic acid, acetic acid, formic acid and carboxylic acid, and eventually to CO_2 and H_2O (Abellán et al. 2007, Hu et al. 2007, Trovo et al. 2009). The membrane didn't affect the SMX degradation intermediates and pathway, which indicates the polymer is safe to immobilize the photocatalysts.

Fig. 7.12. Proposed photocatalytic degradation pathway of SMX.

7.3.5 Membrane properties evaluation after photodegradation

After membrane filtration was carried out for 30 h in the PMR, the appearance and the morphology of the membrane PSf-3 did not change (Fig. 7.13 and Fig. 7.7e-f), which indicates the structure stability of the membrane after photocatalysis. The flexibility was also well maintained, as no obvious cracks or creases were observed by folding up the membrane for 100 times (Fig. 7.13). The membrane water permeability was almost constant during the 30 h filtration. However, changes in mechanical property were observed after filtration with light radiation. As shown in

Fig. 7.8(d-f), the membrane after PMR process without sunlight shows reduced tensile strength and increased maximum strength and elongation. These changes could be attributed to the exposure to the hydraulic pressure and water fluxes (without light radiation), which led to slightly more compact membrane. When the membrane was exposed to both pressure/flux and light, both the tensile strength and elongation significantly decreased. The weakening of tensile property due to light exposure is generally expected for polymer materials. The chemical bonds were probably broken by the UV irradiation and hydroxyl radicals (Mozia 2010, Yang et al. 2011). Nevertheless, the low-pressure UF application does not require membranes with very high tensile strength. Even if the membrane tensile strength decreases during the PMR run, the membrane water flux and decomposition ability was not affected. Considering the real industrial applications, the long-term stability of the membranes shall be tested in the future study.

Fig. 7.13. The corresponding photographs showing the flexibility of the membrane (a) before and (b) after solar irradiation.

7.4. Conclusions

A novel mpg- C_3N_4 /TiO₂ nanocomposite was successfully synthesized and embedded into a UF membrane for the photodegradation of pharmaceuticals in water. The membrane demonstrated excellent photodecomposition ability for removing SMX from feed water under solar light irradiation. The membrane PSf-3 with the highest mpg- C_3N_4 /TiO₂ loading (1% with respect to polymer concentration)

showed the highest water permeability and the best photodegradation efficiency. In addition, with same amount of nanoparticle loading, the mpg-C₃N₄/TiO₂ loaded membrane exhibited better photodegradation performance than the pure mpg-C₃N₄ loaded membrane. The LC-MS/MS results showed that the SMX molecule was degraded into smaller compounds and 7 intermediates of different molecular weights were identified, which indicates the membrane didn't affect the SMX photodegradation and it is a good method to immobilize and support the photocatalysts. Results also showed that the exposure of membrane to both pressure and light did not affect the membrane flux performance during the 30 h filtration. The membrane integrity and flexibility was well maintained despite some loss in the tensile strength, which still suggests its potential as UF membrane for PMR applications.

CHAPTER 8. CONCLUSIONS AND RECOMMENDATIONS

8.1 Overall conclusions

In recent years, semiconductor-mediated heterogeneous photocatalysis has become ubiquitous in wastewater treatment, and the choice of semiconductor is essential. A great number of materials have been developed and involved, including TiO_2 , g- C_3N_4 , GO, CuS and Ag etc, which are some of the most efficient semiconductors due to its excellent chemical and physical properties. In this study, nanocomposite were explored to enhance electron transfer rate of pure semiconductor, so that TiO_2 -CuS, GO-COOH-CuS, g- C_3N_4 -CuS, GO-COOH-CuS-Ag, mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ were fabricated respectively via different synthesis method, to investigate their water remediation applications. In addition, in order to overcome the aggregation and agglomeration of powdered nanoparticle in aqueous solution, GO-COOH-CuS-Ag was coated onto the glass and mpg- $\text{C}_3\text{N}_4/\text{TiO}_2$ was immobilized into a PSf membrane to explore their water remediation applications. They all showed excellent photodegradation abilities.

First of all, two different strategies were used to generate TiO_2 -CuS-a through direct deposition and TiO_2 -CuS-b *via* the aid of the bifunctional linking molecule - L-cysteine respectively. The effect of different fabrication methods on the nanostructure and morphology of TiO_2 -CuS composite were systematically studied. Synthesized two different TiO_2 -CuS composites were evaluated with different wavelengths of irradiation light in terms of pollutant degradability, disinfection and hydrogen generation capabilities. It is concluded that TiO_2 -CuS-b *via* the aid of bifunctional linking molecule - L-cysteine, has a regular “spiky ball - like” structure with high-effective combination with CuS as well as better RhB & phenol degradation performance, inactivation of E.coli and hydrogen generation abilities than TiO_2 -CuS-a under solar light due to its larger surface area and the improved charge separation efficiency. The mechanism was also investigated systematically by various techniques to prove that reactive oxygen species were produced which

degraded the pollutants.

In order to harness the visible light more efficiently compared to TiO_2 -based nanocomposite, with a facile and up scalable synthesis process, multifunctional GO-COOH-CuS nanocomposites were successfully synthesized. The uniform deposition of CuS NPs on GO-COOH sheets contributes to the superior photocatalytic activities of the nanocomposite, not only towards organic pollutants (phenol and RhB) but also waterborne pathogens (*E. coli* and *B. subtilis*). Herein, GO-COOH was demonstrated as an appropriate conductive ligand to support the CuS NPs used in photocatalysis. In addition, as the electron acceptor, GO-COOH improved the lifetime of electron-hole pairs of CuS resulting in a better pathway for electron transport. The GO-COOH-CuS nanocomposite material can overcome the limitations of the pristine GO-COOH and CuS photocatalysts, and combine the merits of the both materials to maximum synergistic effects, including (1) perfect contact between GO-COOH sheets and CuS NPs to minimize the photocorrosion. (2) uniformly distributed CuS NPs onto the GO-COOH surface to improve isolating photogenerated electrons and holes, meanwhile, to enhance the charge transfer. Moreover, the durability study showed that the photocatalytic activity of the GO-COOH-CuS is stable enough for multiple recycling. This study signifies that GO-COOH-CuS nanocomposite can be a promising photocatalyst in the field of water decontamination and disinfection.

In order to further explore the H_2 generation ability of graphene-like based nanocomposite, semiconductor hexagonal CuS nanoplates were fabricated onto g- C_3N_4 nanosheets via a hydrothermal method to produce a synergistic effect, owing to a narrowing band gap. In this study, ultrathin g- C_3N_4 nanosheets were successfully prepared by a “green” liquid exfoliation route from bulk g- C_3N_4 in isopropanol, and exhibited better hydrogen evolution performance than bulk g- C_3N_4 under solar irradiation due to their larger surface area. It is concluded that g- C_3N_4 can be highly effectively combined with CuS to produce a nanomaterial with better hydrogen evolution rate than pure g- C_3N_4 nanosheets under solar light irradiation due to its improved charge separation efficiency. Its performance is also superior than other semiconductor modified g- C_3N_4 , making it a promising photocatalyst for

future hydrogen generation application. The optical properties, crystal phase and morphology of the obtained composites were characterized systematically using various analytical methods. It was concluded that $O^{2\bullet-}$ was the dominant radical produced for hydrogen evolution.

In addition, in order to overcome the problem from the agglomeration of powdered particles in water, the photodegradation performance of glass coating and membrane methods to immobilize the nanoparticles were explored. For glass coating immobilization method, The application of GO-COOH-CuS-Ag glass coatings for organic compound removal in aqueous environments and for bacteria disinfection was explored in this study. The results clearly demonstrate its high performance potential in photodegradation and photo-disinfection processes with the advantage of simplifying the recovery and reuse in comparison to powdered forms, and reducing problems including the agglomeration of powdered particles that may cause blockages. Consequently, the multifunctional GO-COOH-CuS-Ag nanocomposite coated glass may also offer a solution in organic matter removal in the gas phase such as volatile organic compounds (VOCs) removal and indoor air pollution control.

For membrane immobilization method, a novel mpg- C_3N_4 /TiO₂ nanocomposite was successfully prepared and shown excellent structural, morphological and optical properties. Then it was immobilized into a PSf membrane for the set up of a mpg- C_3N_4 /TiO₂ hybrid PMR. It is the first time to manufacture a dead end UF membrane with embedded nanocomposite to explore its SMX photodegradation performance under solar light irradiation. The increased hydrophilicity of nanocomposite embedded membranes accounted for promoting the water flux of membranes, and the enhanced effect of mpg- C_3N_4 with TiO₂ could be the main reasons for the improved photodegradation performance. The big SMX molecule can be degraded into small molecule compounds, and eventually oxidized to CO₂ and H₂O. Meanwhile, the SMX degradation mechanism and pathway were systematically investigated, totally 7 small molecule intermediates were identified. Results also shown that the exposure to both pressure and light did not vary the membrane flux performance during the 30 h filtration and solar irradiation, the membrane remained

high stability, integrity and flexibility after, which makes it a promising material to be used in real water treatment industry.

8.2 Recommendations for future research

To further extend the potential practical applications of various nanocomposite photocatalysts in the hybrid UF PMR systems for the water reclamation, several recommendations for the future study have been proposed.

1. Novel photocatalysts

- Novel synthesis techniques should be developed to prepare novel photocatalysts with potentially further enhanced solar light photocatalytic activity and up-scalability for mass production.
- The performances of the novel solar light responsive photocatalysts can be examined in the simulated real waters with a wide range of recalcitrant organic pollutants in solution with different pH and various aqueous matrix species, which can indicate their feasibility for practical application for treating real water/wastewaters. In addition, real sunlight and real water/wastewaters can also be utilized to evaluate their practical solar photocatalysis application.
- Prior to the practical solar photocatalysis application of those nanocomposite photocatalysts, some potential challenges should be considered, such as cost-effectiveness, up-scalability, photocatalyst deactivation and the need for pretreatment of the water/wastewaters.

2. Photocatalytic membrane reactors (PMRs)

- The configuration of photoreactor can be further investigated with different light intensities, light sources and light positions (including real sunlight). The fabrication of the hybrid PMR systems can be further improved through varying the relative position of the light source, photoreactor and membrane module.
- Membranes with different properties (pore size, hydrophilicity and

hydrophobicity, etc) and different configurations (flat sheet/hollow fiber) in different membrane modules can be evaluated. The long-term membrane stability should be monitored (e.g. FTIR spectra and contact angle measurements, etc).

- Similarly, the removal efficiency of a wide range of recalcitrant organic pollutants can be examined in the PMR systems, along with the effects of solution pH and various aqueous matrix species. When considering a large-scale application of PMR systems, the inherent drawbacks associated with application of photocatalysis for treating real water/wastewaters (e.g. photocatalyst deactivation and the need for pretreatment of feedwater) should be addressed.
- The experiments of this work were performed in lab at “bench scale”. The future studies could be carried out at “pilot scale” to evaluate the performance in practical. In addition, the capital and operating costs have to be considered in comparison with the currently available treatment options.
- This novel membrane could be applied for other applications, such as photocatalytic hydrogen production and solar cells.

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